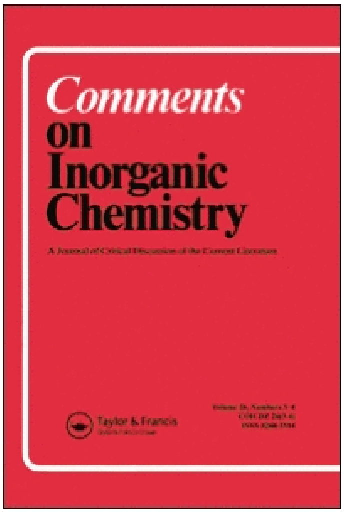

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Structural and Electronic Features of o-*Phenylenediamido Complexes of Group 6 Metals in Different Oxidation States*

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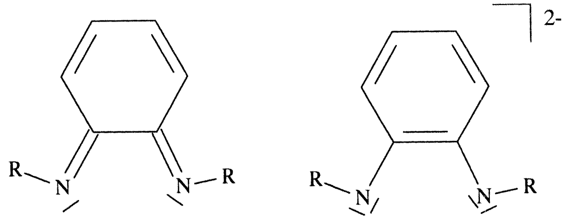
*Reported complexes of general formula L_4M(phenylenediamido-*o*), where M is a metal of group 6 in various oxidation states (VI, IV, II and 0), are analyzed. The possible structural deviations from the most symmetric pseudo-octahedral structure (the one with the chelate in the equatorial plane) are evaluated, case by case, in view of their electronic origin. The analysis is based on systematic DFT calculations and their qualitative MO interpretation based on perturbation theory concepts.*

Keywords: diamido/diimino chelates, group 6 metals, DFT calculations

INTRODUCTION

Nitrogen donor ligands are exploited in organometallic chemistry and homogeneous catalysis.[1] In recent years, amido transition metal chemistry has grown enormously[2] and the usage of polydentate amido ligands is now well established to create specific reaction's sites.[3] In particular, bidentate diamido ligands, for instance *o*-phenylenediamido (*diim*), have been employed by several authors as an effective ancillary ligand.[4–7] The latter also has the special feature of being *not innocent* as the dichotomy ene-diamido/diimino in metal complexes is still often an intriguing issue (Scheme 1).

The neutral/anionic state of the ligand depends on the electron affinity of the coordinated metal ion but also on the structural mode adopted by the

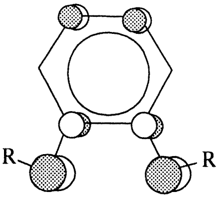


SCHEME 1

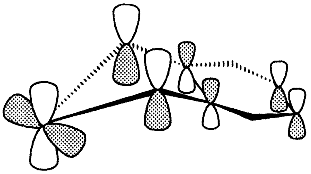
latter and its coligands. Several experimental procedures have been proposed in order to discriminate between the ene-diamido and diimino characters. These include the analysis of the structural parameters,[8] XPS,[9] resonance Raman,[10] and other techniques.[11] Additionally, theoretical studies are considered a very useful approach.

Some of us critically reviewed the bonding capabilities of the ligand when bridging between two metal atoms.[12] Direct comparisons with the analogous 1,2-dioxolene, diphosphidolene and dithiolene were made and it was underlined that the maximum donor power (10 electrons) can be achieved when one of these chelates rides across the M–M bond while bent toward one of the two metals. This mode is found in the complex $[(CO)_2(PPh_3)_2(\mu\text{-dppm})(\mu\text{-}diim)Ru_2](PF_6)_2$[13] and in analogous dithiolene.[14] In monomeric complexes, *diim* can donate up to three electron pairs. This occurs with highly electron deficient metals—namely, d^0 species of Ti(IV), Zr(IV), Ta(V), Nb(V), Mo(VI) and W(VI)—and, in contrast to a common idea, the donations are not all of the canonical σ type. In fact, we have shown[15–17] that the observed folding of the MNC=CN metallacycle at the N–N vector is not promoted by the donation of the C=C π-bond (connecting the N atoms) into an empty σ hybrid of the metal. Rather, the folding (accompanied by some reorientation of the external nitrogen substituents) redirects the lobes of the nitrogen p_π orbitals. In particular, those contributing to the HOMO of the dianion (Scheme 2 highlights a significant C–N π^* antibonding character in the latter) can now overlap with the lateral lobes of an x^2-y^2 *d* orbital type (Scheme 3).

As an extension of our studies on the bonding capabilities of ene-diamido/diimino ligands, we now analyze known six-coordinated complexes of group 6 metals that have general formula $L_4M(\textit{diim})$. A search in the Cambridge Structural Database[18] (vers. 5.23) produced eight species that may be grouped in terms of different *d* orbital electron count. The hits are: $Cl_2(PMe_3)(NPh)W[C_6H_4(NSiMe_3)_2\text{-}o]$, **1**,[19] $Cl_2(PMe_3)(NPh)Mo[C_6H_4(NSiMe_3)_2\text{-}o]$, **2**,[20] $Me_2(PMe_3)(NPh)W[C_6H_4(NSiMe_3)_2\text{-}o]$, **3**,[19] $(\eta^2\text{-}C_2H_4)(PMe_3)_2(NPh)W[C_6H_4(NSiMe_3)_2\text{-}o]$, **4**,[21] $(PMe_3)_3(NPh)Mo[C_6H_4(NSiMe_3)(NH)\text{-}o]$, **5**,[22] $(CO)(pyridine)_2(NPh)W[C_6H_4(NSiMe_3)_2\text{-}o]$, **6**,[23] $Cl_2(PMe_2Ph)_2Cr[C_6H_4(NH)_2\text{-}o]$, **7**,[24] and $(CO)_2(PPh_3)_2Mo[C_6H_4(NH)_2\text{-}o]$, **8**.[25]



SCHEME 2



SCHEME 3

By considering dianionic both *o*-phenylenediamido and the imido ligand (if present), the oxidation number of the metal changes by quanta along the series, namely, VI in **1–3**; IV in **4–7**, and II in **8**. No structural example is available for the oxidation state 0 in spite of the fact that octahedral coordination is expected to be most stable for a d^6 metal. This could be the case of complex **8** if the chelate was considered uncharged. On the other hand, there is an example of a two electron richer system (i.e., $[(CO)_4W(C_6H_4S_2\text{-}o)]^{2-}$, **9**[26]) where an actual dianionic chelate and a W(0) metal coexist. In contrast, the *o*-phenylenediamido dianion stabilizes the five-coordinated complex $[\{(CO)_3W(C_6H_4(NH)_2\text{-}o)\}]^{2-}$, **10**, where one carbonyl ligand is lost from the coordination sphere.[27] The authors, who originally reported the chemistry of **9** and **10**, did also perform HF optimizations and B3LYP single points in order to quantify the relative stabilities of the six and five coordinated adducts with the various chelates.[27] We will address this point in some detail also in the light of our specific calculations.

The aim of this article is to rationalize the structural trends for various models of compounds **1–10** in the light of DFT calculations,[28] and of their interpretation based on a qualitative MO approach.[29] The ene-diamido/diimino dichotomy of the chelate will be analyzed in terms of the relative nature and energetics of the metal and ligand orbitals able to interact with each other. In this context, it is worth mentioning that a number of d^6 pseudo-octahedral complexes of the type L_4M(*diim*) are known for metals of group 8 in the oxidation state II. In the latter, the L_4 grouping is formed by either monodentate or polydentate coligands. By considering, as for the group 6 metals, only discrete coligands, we retrieved from the CCDC databank[18]4 only a few structures of either Fe^{2+} ion[30] or Ru^{2+} complexes.[31–34] In these cases, the uncharged chelate (diimino) seems imposed by the nature of the group 8 metal itself, or rather, by the relative lower energy of its d orbitals. However, this is only partially true as illustrated by a detailed experimental and theoretical work.[35] Thus, in the uncharged, five-coordinated complex $(PPh_3)_3Ru[C_6H_4(NH)_2$-*o*],[36] the Ru(II) metal is associated again with a diamido ligand due to the substantial higher energy of the L_3Ru d_π orbital as compared to that of the L_4Ru analogue (t_{2g} level).

COMPUTATIONAL DETAILS

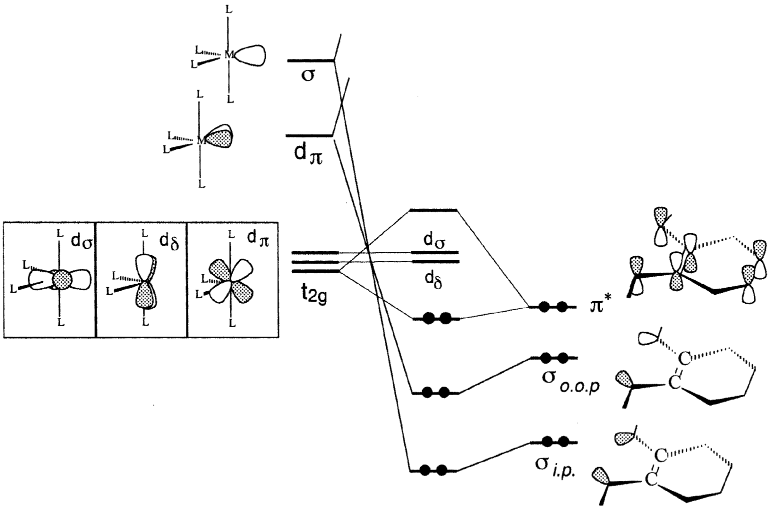
All of the structures reported herein were optimized at the hybrid density functional theory (DFT) using the Becke's three-parameter hybrid exchange-correlation functional[37] containing the non-local gradient correction of Lee, Yang and Parr[38] (B3LYP) within the Gaussian98 program.[39] All optimized structures were confirmed as minima by calculation of numerical vibrational frequencies. A collection of Cartesian coordinates and total energies for all of the optimized molecules are available from the authors upon request. Basis set for the metal atoms utilized the effective core potentials of Hay and Wadt[40] with the associated double-ζ valence basis functions. The basis set used for the remaining atomic species was the 6–31G (d, p) for all atoms.

Perturbation theory arguments were also developed with the help of EHMO calculations[41] (after verifying their consistency with the higher level results) and the usage of a handy graphic interface (CACAO package[29]).

RESULTS AND DISCUSSION

In order to frame the electronic structure in the various L_4M(*diim*) complexes (M=Cr, Mo, W), we point out the most important orbital interactions between the fragments L_4M and $C_6H_4(NH)_2$-*o* that assemble together in the most symmetric arrangement (C_{2v} symmetry with the chelate in the equatorial plane). The diagram in Scheme 4 is quite general as it adapts to a variable number of metal electrons. We start with a metal in the d^0 configuration, so that all of the electron pairs used for metal-chelate bonding belong to the latter unit.

At the left side, the typical frontier levels of the L_4M fragment consist of two higher hybrids of σ and d_π type able to receive electron donation from the *in-phase* and *out of phase* combinations of nitrogen σ lone pairs (lowest FMOs at the right side of the diagram). Additionally, the metal carries a set of three t_{2g} orbitals that can be variously populated. In a first approximation, the latter orbitals are considered unperturbed by the π acceptor or π donor bonding capabilities of the four L coligands. Close in energy to the t_{2g} levels, the chelate features a frontier π^* level (Scheme 2) that is able to interact with the d_π metal orbital (Scheme 4). The relative energy position is crucial for



SCHEME 4

determining the direction of the electron flow and, consequently, both the metal's oxidation state and the charge of the chelate. Importantly, the d orbitals of group 6 metals are, by their nature, relatively high in energy and, in any case, lie above the chelate's π^* MO that is considered populated. Thus, the active C–N π antibonding favors the elongation of the C–N distances with a consequently larger π^*–t_{2g} gap (diamido ligand formulation).

Significant distortional trends may be expected for a non-complete or asymmetric population of the t_{2g} levels not engaged in the d_π–π^* interaction. On the other hand, for a d^6 metal (oxidation state 0), the π bonding metal-chelate interaction transforms into a four electron repulsion. In this case, the system may find it convenient to restore a 2-electron/2-center π interaction, by dismissing one of the ancillary terminal ligands (see below for a more detailed discussion on the complexes of types **9** and **10**).

Having the above general picture in mind, we next examine the specific electronic and structural trends for the $L_4M[C_6H_4(NR)_2$-*o*] species **1**–**9**. Allowance is made in the calculations for the C_{2v} model to relax to lower symmetries. Also, the nature of the various coligands is evaluated case by case and the possible stabilization of open shell systems is taken into account.

d^0 Complexes

A simplified model of the complex $Cl_2(NPh)(PMe_3)W[C_6H_4(NSiMe_3)_2$-*o*], **1**,[19] as optimized by DFT calculations in C_s symmetry, is presented in Figure 1. Single H atoms replace all of the methyl and phenyl substituents at

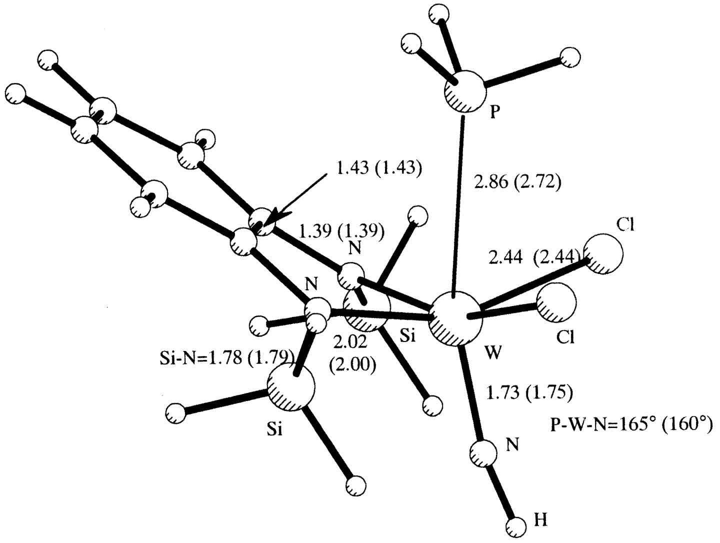
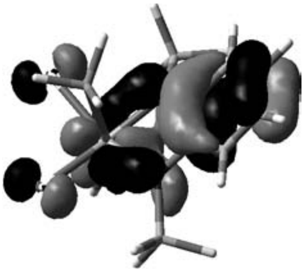


FIGURE 1 Optimized structure of $Cl_2(NH)(PH_3)W[C_6H_4(NSiH_3)_2\text{-}o]$, a model of the experimentally determined complex $Cl_2(NPh)(PMe_3)W[C_6H_4(NSiMe_3)_2\text{-}o]$, **1**. The structural parameters in parentheses are those available from Reference 19.

the ligands. The model is also used as a prototype for the comparable complexes **2** and **3**.

The agreement between calculated and experimental structures can be considered satisfactory with the only exception of the W-P bond that is somewhat longer than the experimental value (2.86 Å *vs.* 2.72 Å). In any case, the long separation is suggestive of a weak metal-phospine linkage that is likely attributable to the well known *trans* influence of imido ligand triply bonded to the metal (*vide infra*).[42] Eventually, the phosphine may be lost with no major consequence as demonstrated by the stability of the five coordinated species $Cl_2(NPh)W[C_6H_4(NSiMe_3)_2\text{-}o]$[43] and $Me_2(NPh)W\text{-}[C_6H_4(NSiMe_3)_2\text{-}o]$.[19] The latter complex typology has been the subject of a previous theoretical study performed by us.[15] The present calculations reproduce well the non-perfect linearity of the imido ligand (compare the experimental W–N–C angle of 164° in **1** with the 168° value for the W–N–H angle of the model). Also, the tilting of the diamido chelate is consistently reproduced as shown by the 151° and 154° values of the experimental and computed dihedral angles at the N···N vectors, respectively.

At this point, we can illustrate the distortional trends and the nature of the orbital interactions between the various ligands and the d^0 metal. First, the presence of the six electron donor imido dianion alters the general features of the diagram in Scheme 4. Now, the d_π and d_δ t_{2g} orbitals are destabilized



SCHEME 5

by the strong donations of the two orthogonal and filled p_π orbitals of NR. Thus the first LUMO of the L_4M fragment is the d_σ orbital that is the closest in energy to the diamido C–N π^* level (chelate's HOMO). The HOMO of the complex is the corresponding bonding combination between the latter FMOs, whose features have been previously pointed out by us.[15] Its drawing produced with DFT coefficients (see Scheme 5) is fully consistent with the simplified picture of Scheme 3.

The ca. 25°–30° tilting of the chelate off the equatorial plane and toward the phosphine ligand, accompanied by the significant pinning of the silyl substituents in the opposite direction, allows good overlap between nitrogen p_π and the metal x^2-y^2 orbitals. An important role in determining such an unusual interaction must also be played by the silyl substituents and the polarized N–Si linkages that enhance the donor capabilities of the nitrogen atoms. Silyl substituents were also present in even more unsaturated d^0 species, such as $Cl_2Ti[C_6H_4(NSi^iPr_3)_2$-*o*$]$[44] and $Cl_2(NPh)W[C_6H_4$-$(NSiMe_3)_2$-*o*$]$.[43] In contrast, the 18-electron configuration is formally achieved by the species **1–3** as nine different 2-electron donations may be counted. Among the latter, that provided by the phosphine ligand is certainly the least energetic in view of the long W–P separation. The cleavage of such a bond is barely endothermic (only 4 kcal mol^{-1}) as calculated by the separate optimizations of the 16 electron complex $Cl_2(NH)W[C_6H_4(NSiH_3)_2$-*o* and of the isolated PH_3 ligand. It must be additionally considered that, in the actual system, W–P dissociation can be further favored by the steric hindrance as the diamido chelate is bent on the side of the bulky phosphine ligand.

d^2 Complexes

The d^2 configuration is attributable to the complexes **4**–**7**, although **7** has unique electronic features (*vide infra*). Calculations have been carried out on simplified models of the compounds **4** and **7**, respectively. Compounds **4** and **6** have two *trans* axial σ donors (phosphines or pyridines, respectively)

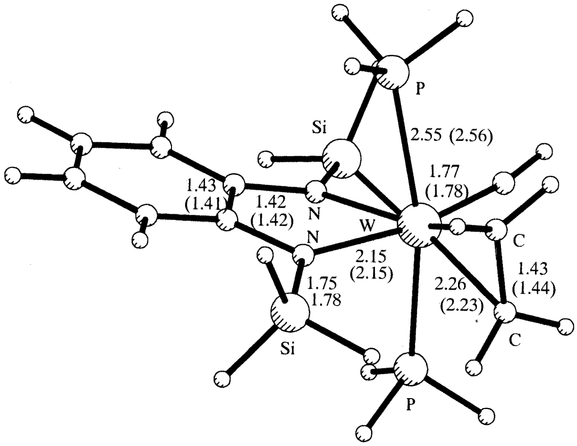


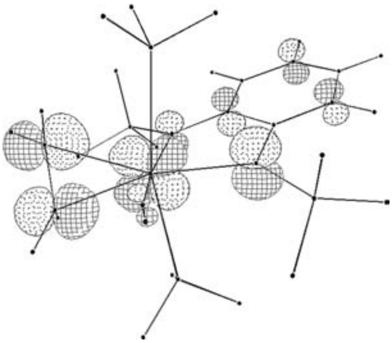
FIGURE 2 Structural parameters for the optimized structure (η^2-C_2H_4)(PH_3)$_2$(NH)-W[C_6H_4($NSiH_3$)$_2$-*o*]. The corresponding experimental values observed in the structure of (η^2-C_2H_4)(PMe_3)$_2$(NPh)W[C_6H_4($NSiMe_3$)$_2$-*o*], **4**, are given in parentheses. Only one value is given for the equivalent chemical bonds as they are quite similar.

and one imido π-donor ligand in the equatorial plane. *Cis* to the latter, lies a π acceptor molecule, namely an upright ethylene in **4** or a carbon monoxide in **6**. This situation is also found in other d^2 complexes of group 6 metals that are easily obtained by substitution of one phosphine with a π acceptor ligand.[45] Simple MO arguments have been used to justify such an arrangement.[46]

The optimized model of **4**, presented in Figure 2, reproduces well the experimental parameters. Only the computed tilting of the diamido chelate on the equatorial plane is somewhat less pronounced than in the experimental structure (compare the dihedral angles of 165° and 157°, respectively).

The pseudo-octahedral complexes **4** and **6** are diamagnetic so that it is interesting to determine which t_{2g} orbital hosts the unique pair of *d* electrons. With respect to the general Scheme 4, two *cis* equatorial positions are occupied by the imido ligand and by a strong π acceptor group (ethylene or CO). The coordination of the latter must have an important backdonation component that involves the only electron pair available to the metal. In view of the upright orientation of the olefin, the latter should be a linear combination of the d_π or d_δ orbitals depicted in the boxes of Scheme 4. This is confirmed by the drawing of the HOMO (Scheme 6) that, for the sake of clarity, is generated from EHMO coefficients but is fully consistent with the analogous DFT drawing.

While the olefin π^* level strongly stabilizes the HOMO, the imido p_π orbitals destabilize significantly the remaining two t_{2g} levels. One of them is the d_σ level that, in the d^0 case, received electron density from the chelate's



SCHEME 6

HOMO (see Scheme 5). In view of the still substantial tilting of the diamido ligand, it cannot be stated that the latter donation is completely vanished in these d^2 complexes. However, this is of secondary importance with respect to the strong donation that a p_π orbital of the imido group does now exert into d_σ. Under these circumstances, the π^* level of the chelate has prevailing non-bonding character or it can even exert some four electron repulsion with the filled metal d_π orbital involved in the backdonation to the olefin. These combined features are clearly evident in the HOMO of the complex, depicted in Scheme 6. On the other hand, the decreased importance of the donation from the chelate's HOMO into an empty d_σ orbital is clearly indicated by the significant elongation of the W–N bonds from 2.02 to 2.15 in going from the complexes **1–3** to **4–6** and their corresponding models. On the contrary, the length of the W–N_{imido} linkage is almost unchanged, as it features three different bonding components in any case.

The electronic structure of the other known d^2 species, namely the complex $Cl_2(PMe_2Ph)_2Cr[C_6H_4(NH)_2\text{-}o]$, **7**, is completely different. In the quasi-octahedral symmetry and in the absence of a multielectron donor such as NR^{2-}, a diamagnetic d^2 complex could be subject to Jahn-Teller instability.[47] Conversely, the experimental structure of **7** has almost C_{2v} symmetry. Since no experimental information is provided about the magnetism of this species (the authors only mention that the compound is EPR silent[24]), we have attempted a first optimization of a C_{2v} model in the singlet ground state. The frequency calculations reveal that this is a transition state between two equivalent C_2 stationary points. The latter show a 21° inclination of the chelate with respect to equatorial Cl_2Cr plane (the experimental tilt is only 3°). Also, the C_2 geometry is calculated to be about 5 kcal mol^{-1} more stable than that of C_{2v}.

Since the chelate lies in the equatorial plane and the d_π metal orbital is most likely destabilized, the two available d electrons should be hosted by the degenerate d_σ and d_δ orbitals (Scheme 4). Accordingly, a triplet spin state is reasonably assumed. Indeed, when the latter is imposed to the C_{2v} model of **7**,

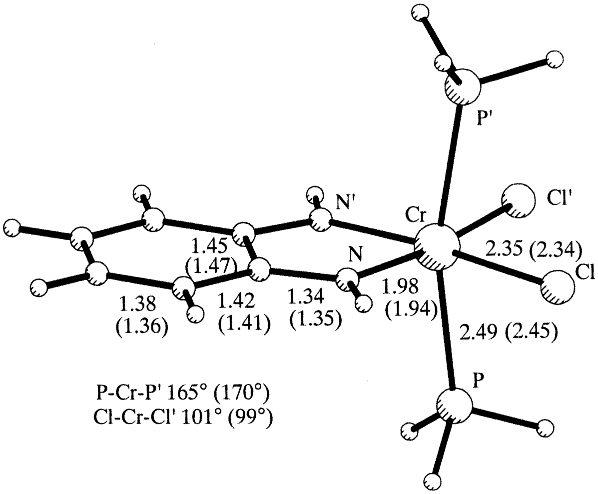


FIGURE 3 Optimized structure of the model $Cl_2(PH_3)_2Cr[C_6H_4(NH)_2$-*o*], a model of the experimentally determined complex $Cl_2(PMe_2Ph)_2Cr[C_6H_4(NH)_2$-*o*], **7**. The structural parameters in parentheses are those available from Reference 24.

the optimized structure is a true stationary point. Figure 3 compares the computed and experimental geometries and a satisfactory agreement is found.

The fact that **7** is EPR silent is not necessarily in contrast with the triplet ground state. In fact, it is known that d^2 high spin systems can be subject to relaxation and high field splittings.[48] On the other hand, the inconsistency of **7** with the singlet ground state is also provided by the ca. 42 kcal mol^{-1} destabilization with respect to the triplet. The gap further increases to ca. −51 kcal mol^{-1} upon a correction or spin contamination.[49]

d^4 Complexes

The availability of four extra electrons with respect to the situation depicted in Scheme 4 should allow full population of the d_σ and d_δ metal orbitals. However, a small HOMO-LUMO gap determines a source of instability, hence structural deformation from the regular octahedron may be predicted. The distortions associated with the incompleteness of the $(t_{2g})^4$ configuration can be interpreted in terms of Jahn-Teller arguments.[47] This subject has been tackled, in detail by Kubacek and Hoffmann.[52] For compounds of the typology $L_2L'_2L''_2M$, it has been shown that the overall electronic structure is subject to the subtle interplay of the σ and π properties of the pairs of the ligands L, L′ and L″ and to the deformational trends within each L_2M subunit. Obviously, in the available complex $(CO)_2(PPh_3)_2$-

Mo[$C_6H_4(NH)_2$-*o*], **8**, an additional complication is due to the presence of the highly delocalized π MO of the chelate that falls more or less in the same energy region as the t_{2g} levels.

The experimental structure of **8** is somewhat surprising, not only because its conformation deviates significantly from the pseudo-octahedron, but also because of the asymmetry in the pairs of M–C(O) and M–N coordination bonds that are supposed to be chemically equivalent. In fact, the chelate is rotated 33° off the equatorial Mo$(CO)_2$ plane and also the two phosphines are not precisely *trans* to each other [P–Mo–P angle = 140.8(2)°]. In addition, the two M–N bonds differ by 0.13 Å and the two Mo–C(O) bonds by as much as 0.21 Å with standard deviations of 0.02–0.03 Å.

In order to evaluate whether the electronic effects could have such a dramatic impact on the geometry, we performed specific DFT calculations on a model of **8** where all of the phenyl rings are replaced with H atoms. It has been found that the C_2 structure, reported in Figure 4, is an actual stationary point, while a C_{2v} model with the chelate coplanar with the Mo$(CO)_2$ unit corresponds to a transition state. Remarkably, the latter is minimally destabilized with respect to the ground state structure ($<1\,\mathrm{kcal\,mol^{-1}}$).

In the optimized C_2 model, the dihedral angle between the chelate and the Mo$(CO)_2$ plane is 20°, i.e., one-third less than in the experiment. Obviously, the imposed C_2 symmetry is inconsistent with any difference within the pairs of bonds Mo–C(O) and M–N. However, a subsequent calculation performed in C_1 symmetry yields essentially the same C_2 structure with no practical distinction between the chemically equivalent bonds. Thus, it is reasonable to conclude that the unexpected geometric features found in the experiment[25]

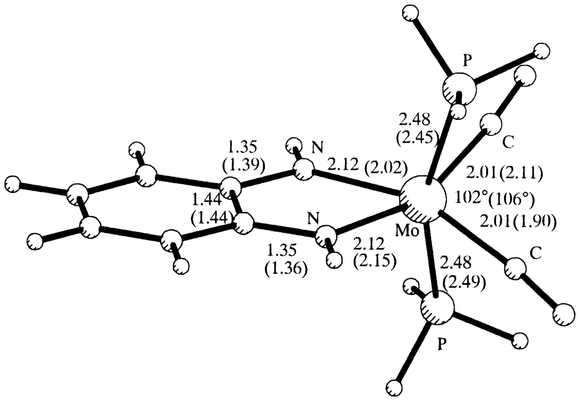
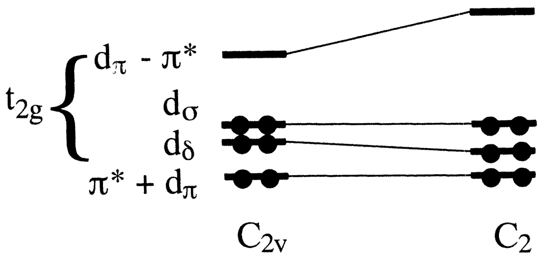


FIGURE 4 The optimized C_2 model of the complex $(CO)_2(PPh_3)_2$Mo[$C_6H_4(NH)_2$-*o*], **8**, where the phenyl rings are substituted for H atoms. The numbers in parentheses are the structural parameters reported in Reference 25.



SCHEME 7

are due to systematic errors affecting the X-ray data or, possibly, to the scarce number of observations available for the refinement.

Also, the calculations confirm that Jahn-Teller forces are operative for d^4 complexes of this type due to the empty t_{2g} orbital that remains at relatively low energy regardless of the antibonding interaction with the HOMO of the chelate. In fact, by looking at the energies of the Kohn-Sham orbitals, we notice an increase of about 0.2 eV of the HOMO-LUMO gap upon the descent to C_2 symmetry. The correlation between the four frontier MOs is depicted in Scheme 7. In particular, the LUMO that has the highest π^* character at the C_{2v} structure gets more destabilized by the mixing of an opportune combination of σ components at the chelate when they get off the nodal plane of the d_π orbital.

d^6 Complexes

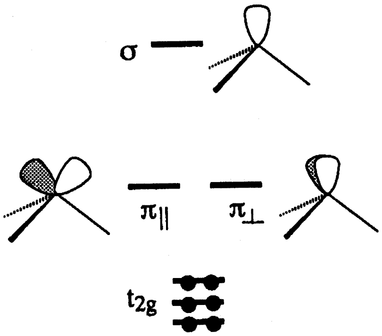
As mentioned in the Introduction, dianionic complexes of formula $[(CO)_4W\text{-}(C_6H_4S_2\text{-}o)]^{2-}$ have been reported, while the corresponding *o*-phenylenediamido species appear more stable with one missing CO coligand.[26,27]

Before addressing this topic, we wish to remark that several L_4M(diimine) complexes ($M = d^6$ ion of group 8 metals)[30–34] are isolectronic with the d^4 complex **8**, outlined in the previous section. At variance with the latter, the Fe^{2+} or Ru^{2+} species have an almost regular octahedral geometry with C_{2v} symmetry. Since the oxidation state IV can be hardly attributable to Fe or Ru metals, it is more likely that non-innocent chelate is effectively uncharged (diimino) in these cases. A qualitative understanding of the different electronic distribution can be attained by considering that the energy of *d* orbitals is generally lower for group 8 than for group 6 metal atoms. Thus, the relative energy order of the fragment orbitals, presented in Scheme 4, is reversed when a group 8 metal ion is involved, with the π^* MO of the chelate lying above the t_{2g} set. In perturbation theory terms, the electron pair that populates the bonding combination $\pi^* + d_\pi$ is preferentially assigned to metal (d^6) with the chelate's π^* level receiving some backdonation.[35] Given the C–N π^* antibonding character of the latter, the scarce electron population accounts for C–N distances that are about 0.1 Å shorter in the group 8 complexes than in any of the complexes **1**–**8** (consider the valence bond structure at the left side of Scheme 1). In turn, the shorter C–N linkages magnify the π^* character of the chelate's LUMO and a larger energy gap with respect to the t_{2g} orbitals is determined. Importantly, since the whole t_{2g} set is filled, no distortional trend is observed in the Fe and Ru complexes that maintain a fairly regular pseudo-octahedral geometry.

Finally, we address the known disulfido, **9**, and the unknown diamido six-coordinated complexes of group 6 metals in an attempt to extend our conceptual framework to these dianionic d^6 species. A series of structural optimizations at the HF level and subsequent B3LYP single points were performed by Darensbourg et al. for the species $(CO)_nW[C_6H_4(X)(Y)\text{-}o]^{2-}$ ($n = 3, 4$; $X = O, S, NH$; $Y = O, S, NH$).[26] Their purpose was to compare the relative stabilities of six- and five-coordinated species. In all cases, it was found that the six-coordinated complex is more stable than the separate components (i.e., the five-coordinated derivative and one free CO ligand). However, the separation of the diamido system is found to be less endothermic than that of the disulfido one. This provides at least an indication of why the former type of six-coordinated complexes remain unobserved.

Our DFT optimizations, for adding or subtracting one CO ligand from the diamido or disulfido species **10** and **9**, are in agreement with the previous numerical results.[26] For instance, we find that the six-coordinated species **9** is about 16 kcal mol^{-1} endothermic with respect to the loss of one CO ligand. Moreover, the following qualitative MO aspects may be highlighted. By referring again to Scheme 4, a sufficient number of electrons is available in $(CO)_4W[C_6H_4(NH)_2\text{-}o]^{2-}$ to fully populate all of the frontier MOs. Obviously, the population of both the bonding and antibonding combinations between d_π and the C–N π^* level of diamido is a source of four electron repulsion that contrasts, but does not destroy, the stability of these systems. Rather than reducing the strength of the metal-chelate bonding, the system may release one CO ligand, thus fully restoring the capability of the diamido ligand to donate three electron pairs. In fact, the d^6-L_3M fragment features, beside the fully populated t_{2g} set, three empty hybrids, two of orthogonal of d_π type and a higher σ one (see Scheme 8).[53] Irrespective of the reciprocal orientation of the chelate and of the L_3M pyramid, one σ and one d_π hybrid accept the σ lone pairs at the N atoms (see the right side of Scheme 4). The remaining d_π empty hybrid is suited to overlap with the HOMO of the chelate significantly better than the pure d_π orbital of the L_4M fragment.

The three strong interactions may not compensate the total energy lost on releasing the CO ligand. Recall, in fact, that any W–C(O) bond has three major components, namely one σ donation and two π backdonations. In conclusion, the dichotomy between five- and six-coordinated dianionic species is governed by very subtle energetic factors that may compensate each other. Also, we should not forget the importance of the entropic factors that, given



SCHEME 8

the electronic stability of the separated components, should in principle favor the system with a higher number of separated objects.

CONCLUSIONS

In this article we have examined an interesting series of group 6 complexes containing one *o*-phenylenediamido chelate and four discrete ligands. Although equally formulated as L_4M(*diim*), the considered complexes present a great variety of electronic situations as the metal oxidation state varies between VI and 0. These are accompanied by more or less pronounced structural rearrangements. DFT calculations and a simple qualitative MO picture have been used to rationalize many of the experimentally observed features in these systems. New light is shed on the bonding capabilities of the *diim* ligand that, often used in catalysis, adapts easily to both the uncharged and the anionic states. An extension of these studies to similar complexes of other transition metal triads is programmed.

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49. The calculation of the triplet state produced a value of 2.75 for the total spin operator S^2 vs. the expected value of 2.00. This problem lies in the usage of a single determinant when treating unrestricted wave functions.[50] On the other hand, it is known that the DFT method is less prone to spin contamination because electron correlation is partially included in the single determinant.[51] In our case, a quintet state is not unreasonable because of the compactness of four frontier MOs containing a total of four electrons (according to Scheme 4, two electrons are assigned to the ligand and two to the metal). Moreover, there is a clear-cut indication that the S^2 value after spin annihilation of the quintet state can become as little as 2.05. Thus, we made a new optimization of the model in the quintet spin state in order to correct the total energy of the triplet state with the formula reported in another study of Cr(II) complexes with semiquinone ligands.[50] Interestingly, it is found that, for the quintet, the partial population of the highest antibonding MO determines a significant elongation of the Cr-N, Cr-Cl and Cr-P bonds by about 0.20 Å, 0.09 Å, and 0.06 Å, respectively. This may partially account for the overestimation of the bonds observed in the optimized triplet structure affected by spin contamination (see Figure 3).
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