

Nature of the metal–carbon contacts in ene-diamido d⁰ metal complexes

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Folding of ene-diamido chelates in d⁰ metal complexes is generally attributed to a saturating π interaction of the metal with the central C=C linkage. A MO analysis of selected models (DFT and EHMO levels) shows that the latter interaction is negligible (negative M–C overlap populations). Moreover, a detailed analysis of the orbital interactions highlights a two-electron flow from filled p _{π} orbitals of the nitrogen atoms toward the metal consequent to ligand folding. Conversely, it is evident that the C=C π -electron cloud is only barely affected by the contacts with the metal atom.

Group 4 Cp₂MX₂ derivatives have wide applications in catalysis and they have been extensively studied.¹ For example, to test new reactivity and/or catalytic activity, Cp rings have been stepwise substituted for other ancillary ligands,² including amido groups.³ Still, the fragments MCp(NR₂) and M(NR₂)₂ (where M is a Group 4,⁴ Group 5⁵ or Group 6⁶ metal) are considered metallocene-like and present interesting reactivities. Some of us have reported MO studies on the bonding capabilities of ene-diamido ligands in bridging two metals⁷ and, previously, related 1,2-catecholates were also investigated.⁸ Here, we focus our attention on metallocene-like d⁰ complexes that contain a chelate ene-diamido ligand.^{†9}

A search in the Cambridge database¹⁰ shows that the ligand is bent toward the metal.^{†11} Invariably, the nitrogen atoms remain planar (the bond angles sum up to 360°) and the actual folding occurs through the concerted torsion of the NR groupings about the C–N bonds (ca. 25–35°). In this manner, the amount of π conjugation in the chelate is reduced with a higher localization of the intermediate C=C linkage. Importantly, the shortened M–C distances raise the question as to whether they correspond to actual bonding. In the literature (with the exception of some discussions by Boncella,^{6b,12} Rheingold and Ernst,¹³ Petersen,¹⁴ Dieck¹⁵ and their coworkers) it is almost taken for granted that the cause of bending is π co-ordination of the C=C bond to the metal (see Scheme 1). In other terms, the classic description (σ^2 , π) adopted for the η^4 bonding of butadiene to early transition

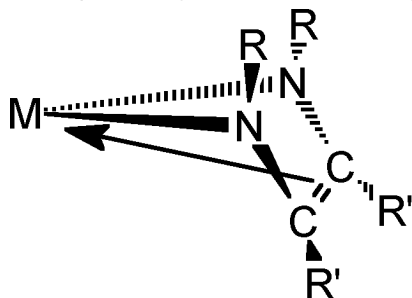
metals¹⁶ is extended to the ene-diamido and other comparable ligands with two additional electrons in the π system.

To understand better the bent co-ordination, MO calculations at different levels of theory (DFT^{§17} and EHMO^{¶18}) were performed for model compounds of selected d⁰ complexes of the Group 4–6 metals. In particular, we have considered the species TiCl₂[*o*-(ⁱPr₃SiN)₂C₆H₄]¹⁹ **1**, M(OAr)₂[(R'N)₂C₂R₂] (M = Ti, Zr),²⁰ Cp'₂Zr[(R'N)₂C₂R₂],²¹ Cp'MCl₂[(R'N)₂C₂R₂] (M = Ta,^{5a–e,22} Nb²³) and W(NPh)₂X₂[*o*-(Me₃SiN)₂C₆H₄] (X = Cl¹² **2**, and alkyl groups^{6a–b}), all containing a bent ene-diamido ligand. Previously, MO calculations of complexes containing the planar 1,4-diazabutadiene ligand²⁴ and the metallacyclotetraazapentadiene moiety²⁵ have been reported, while related complexes with folded dithiolene ligands have been studied with EHMO methods.²⁶

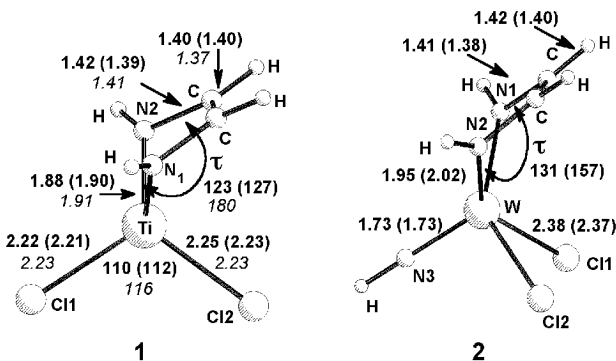
Full geometry optimizations were performed for the model compounds **1** and **2**, both having C_s symmetry. For convenience, Scheme 2 reports a selection of experimental and calculated (in parentheses) geometrical parameters. Moreover for **1**, the values in italics refer to the geometry of a transition state (one negative frequency) characterized by a planar MN₂C₂ ring. Invariably, the bisector of the N–M–N angle coincides with the symmetry axis of the metal fragment [C₂ for Cl₂Ti in **1** and pseudo-C₃ for W(NR)Cl₂ in **2**].

As seen, the DFT calculations provide bent geometries for the chelate ligand. For species **2** in particular, the folding (τ) is on the opposite side with respect to the single NR ligand. Another conformer, with the chelate orientated toward the latter group, lies only 6.4 kcal mol⁻¹ higher in energy. The probable transition state, with an overall planar MN₂C₂ ring, could not be detected, probably on account of a rather flat energy surface. For the same reason, the computed folding of the ligand about the N–N vector is less pronounced than the experimental one (compare the τ values of 157 and 131° in Scheme 2) while the general structural agreement is satisfactory. Conversely, the transition state between the equivalent bent conformers was fully characterized for **1** and lies 12.5 kcal mol⁻¹ above two symmetrical minima. Since our models are significantly less hindered than the experimental species, it may be safely stated that steric factors are definitely of little relevance for the bending of the chelate.

A qualitative MO analysis helps to elucidate the major bonding components between the diamido and metal fragments in both models **1** and **2**. Since the basic MO arguments are similar, we will concentrate mainly on the former case. Because of the filled p _{π} orbitals of the chloride ligands (6 electron donors), a TiCl₂ fragment can be considered as metallocene-like. Here, the d⁰ metal is characterized by three low-lying frontier orbitals, one of b₁ and two of a₁ symmetries.²⁷ While the former has d _{π} nature (in the plane

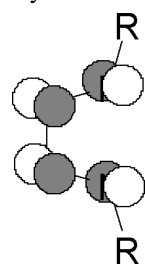


Scheme 1



Scheme 2

orthogonal to TiCl_2), the a_1 ones are z^2 and $x^2 - y^2$ -like orbitals, respectively (z coincides with the C_2 axis of TiCl_2). The basic MO structure of an isolated ene-diamido ligand has been described recently.⁷ Its bonding capabilities arise from the two nitrogen σ lone pairs (in-phase and out-of-phase combinations) and the three filled π MOs. Following the observed torsions of the NR groups about C–N linkages, the σ lone pairs remain well oriented for donation into the d_{π} and z^2 metal orbitals. Most critical, however, is the HOMO of the ligand (see Scheme 3), which is still distributed between the C and N atoms but which has p_{π} components that are no longer parallel. This HOMO is very close in energy to the $x^2 - y^2$ metal orbital and interact strongly with it. The resulting bonding combination, which is also the HOMO of the complex, is shown in Fig. 1 (notice how the drawings generated from DFT and EHMO calculations are consistent). Evidently, the reoriented nitrogen p_{π} lobes overlap significantly with the lobes of $x^2 - y^2$ on each side of the TiCl_2 plane** hence the Ti–N bonds are reinforced. It is significant that in the planar TS structure, where the latter interaction is missing, the Ti–N latter bonds are slightly longer (see Scheme 2) and the corresponding overlap populations are smaller (0.195 vs. 0.213). As another point, the carbon p_{π} orbitals of the ene-diamido ligand are only indirectly involved in bonding; they are still part of the ligand HOMO but do not overlap with the metal lobes. A careful analysis of the fragment orbital interactions does not provide any evidence for drifting of the C=C π -electron cloud toward the metal. In fact, the low-lying MO of the ligand, which is mainly responsible for C=C bonding, is totally unaffected upon formation of the



Scheme 3

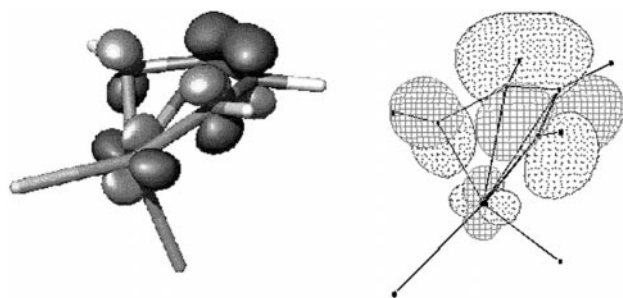
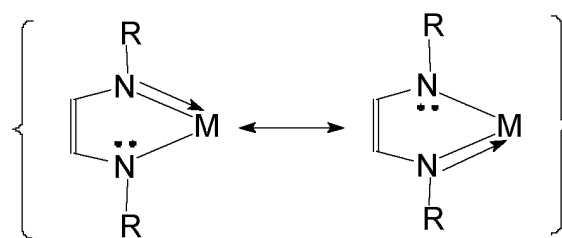


Fig. 1 HOMO of model 1 {based on the structure of $\text{TiCl}_2[\text{o}-(\text{Pr}_3\text{Si})_2\text{C}_6\text{H}_4]$ as it results from (a) DFT and (b) EHMO calculations.

complex. Numerically, a certain electron repulsion is confirmed by the values of the M–C overlap population, which are slightly negative at any computational level. On the contrary, positive M–C overlap population values characterize the σ^2 , π bonding of butadiene to early transition metals.²⁸

Lauher and Hoffmann²⁹ pointed out long ago that the preferential upright orientation of single amido coligands in d^0 Cp_2M complexes is due to important donation of the filled p_{π} orbital into two adjacent lobes of the $x^2 - y^2$ -type orbital. Analogously, the ene-diamido chelate engages all of the $x^2 - y^2$ lobes in the present case. Since such a two-electron donation from nitrogen contributes most to metal saturation, the contribution of the C=C π cloud is negligible.

In conclusion, the present analysis of the bonding of the ene-diamido ligand agrees with a σ^2 , π description where the π component is also largely contributed by the nitrogen atoms. Thus, the valence bond picture of Scheme 1 is inadequate. A better formal description is that of Scheme 4, where the M–N bonds are of order 1.5 and where the C=C linkage of the chelate is localized and largely preserved.



Scheme 4

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Notes and references

† Other nomenclature used for this “non-innocent” type of ligand, which can be considered as the reduced form of diimine ligands, is that derived from the 1,4-diaza-1,3-butadiene moiety. See, for example, ref. 9.

‡ Planar diamido ligands supported by additional coordination are encountered in ref. 11(a–c). Also, a Ti complex containing a planar 1,8-diamidonaphthalene ligand was reported in ref. 11(d). For d^0 complexes containing classical planar diimine ligands see ref. 11(e, f).

§ *Ab initio* calculations were performed using the Gaussian-94 program. Molecular geometries and harmonic vibrational frequencies have been determined using the density functional approach (DFT). In these calculations we have used Becke’s 1988 exchange functional with the correlation functional of Perdew (BP86). The standard double-zeta basis set (LANL2DZ) and effective core potential (ECP) was used for the metal atom. For the other atoms, Dunning’s basis set, augmented with one d polarization function for the non-hydrogen atoms, was used.

¶ All the EHMO calculations were of the extended Hückel type using a weighted-modified Wolfsberger–Helmholz formula. The EH parameters were taken from CACAO. The bond distances and angles used in the calculations have been taken directly from the X-ray results through the new routines of the CACAO program (ref. 18).

|| In the *ab initio* calculations for models 1 and 2, with the aim to speed the calculations, the *o*-phenylene group ($o\text{-C}_6\text{H}_4$) that links the two N atoms of the diamido ligand was simplified to a $-\text{CH}=\text{CH}-$ carbon chain. Also, the organic groups on the nitrogen atoms (trialkylsilyl substituents of amido and phenyl group of imido) were replaced by hydrogen atoms for simplicity.

** Although characterized by a different ancillary L_3M fragment, compound **2** has a HOMO very similar to that in Fig. 1 with $x^2 - y^2$ orbital involved. The latter can be described as a member of the “ t_{2g} ” set typical of L_3M fragments (ref. 27). Notice that the other two t_{2g} members, with d_x character, are already much destabilized by the p_x orbitals of the imido ligand (hence the formulation of $W=NR$ as a triple bond).

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