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A Critical Review of Electronic Effects in Enediamido and α-Diimino Complexes of the Group 4 Metals

Carlo Mealli,*[a] Andrea Ienco,[a] Andrew D. Phillips,[a] and Agustín Galindo*[b]

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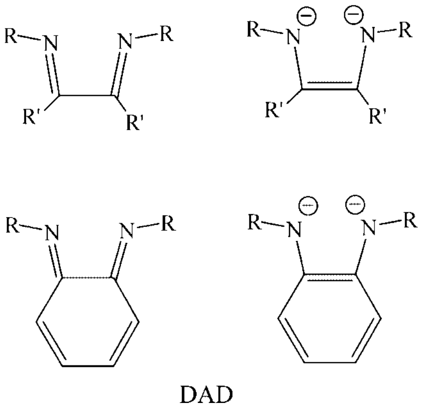
The α-diimino chelating ligand 1,4-diaza-1,3-butadiene, or its dianionic enediamido form (generically defined as DAD), forms a variety of complexes with group 4 transition metals either with or without other co-ligands. The known species are either pseudo-octahedral [L_4M(DAD)] or tetracoordinate [L_2M(DAD)] with a lower degree of metal saturation in the latter case. Additionally, there are a number of known CpML$_n$ species and homoleptic complexes with the formula [M(DAD)$_3$] or [M(DAD)$_2$]. The M-DAD metallacycle is generally either planar or folded at the N···N vector, the latter arrangement being observed when the number of co-ligands is reduced and hence there is insufficient saturation at the metal. The conformation also depends on the relative electron population of DAD, which is a *noninnocent* ligand and exists as a continuum between the neutral and dianionic resonance forms. Herein some theoretical concepts, that have previously been developed to describe the bonding capabilities of DAD toward different triads of transition metals, are extended to complexes of the group 4 metals. New electronic aspects of the [M(DAD)$_3$] complexes are described together with a completely new analysis of the [M(DAD)$_2$] complexes. These exhibit the planar/bent conformational dichotomy, which may have an electronic and/or steric origin as it is affected by the type of substituent at the nitrogen atoms. A reasonable justification of the observed conformational preferences is found from a combination of density functional and QTAIM analyses. The latter clearly demonstrates that a peculiar intramolecular hydrogen bonding can contribute to the stabilization of planar-type structures.

1. Introduction

This article analyzes the bonding capabilities of ligands based on the 1,4-diaza-1,3-butadiene or *o*-diiminobenzene skeleton (generally abbreviated as DAD) towards a transition metal of group 4. The electron population in these molecules varies depending on the nature of the coordinated metal atom.[1] Thus, the chelate is considered a neutral α-diimino species when bound to late transition metals as occurs, for example, in the nickel(II) and palladium(II) complexes, which are capable of converting ethylene into high molecular weight polymers with low polydispersity.[2] More commonly, the ligand behaves as an enediamido dianion with early transition metals. The corresponding complexes have been proposed as a more versatile alternative to metallocene catalysts for polymerization reactions.[3]

With a few exceptions, the coordination of DAD in the enediamido form is characterized by a nonplanar arrangement of the five-membered metallacycle (an N–N folded envelope). We have already dedicated a number of theoretical studies to interpreting the general bonding capabilities of these ligands with metal atoms of groups 5,[4] 6,[5] and 8.[6] Herein, the dichotomy between the diimino and enediamido forms (see Scheme 1), which is a classic example of *noninnocent* behavior,[7] is discussed on the basis of the electronic and structural characteristics of the ML$_n$ metal fragment (M = Ti, Zr, Hf).



Scheme 1. Diimino vs. enediamido resonance forms in ligands derived from the 1,4-diaza-1,3-butadiene or *o*-diiminobenzene skeletons (DAD).

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[a] ICCOM, CNR,
Via Madonna del piano, 50019 Sesto Fiorentino, Firenze, Italy
E-mail: mealli@iccom.cnr.it
[b] Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo. 553, 41701 Sevilla, Spain
E-mail: galindo@us.es

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A search of the Cambridge Crystallographic Database[8] for mononuclear[9,10] complexes of a group 4 metal with at least one DAD ligand yields examples that exhibit both resonance forms depending on the nature of the supporting ML_n fragment, which are of the type MX_2, CpMX, Cp_2M, MX_2L_2, and MX_4 (L = two-electron-donor ligand, X = halide, Cp = cyclopentadienido anion). The set of ancillary ligands may occasionally include other DAD chelates, and homoleptic complexes of formulae $[M(DAD)_2]$ or $[M(DAD)_3]$ are observed in some cases. A few transition metals exhibit examples of both types,[11] although interconversion between the species has only been found to occur in the case of group 4 metals. This unique behavior requires a reasonable interpretation of the electronic structure and ligand-metal bonding as the mentioned dichotomy of the M(DAD) metallacycle (folded or planar) applies to homoleptic complexes as well.

In reviewing the general electronic features of all the group 4 complexes, we focus on the homoleptic species in particular. Given the interest raised by some of the examined species, new ad hoc quantum-chemical calculations have been performed and are presented here for the first time. For this reason, Supporting Information is also available.

2. General Considerations Regarding the Structural and Electronic Aspects of the α-Diimino and Enediamido Forms

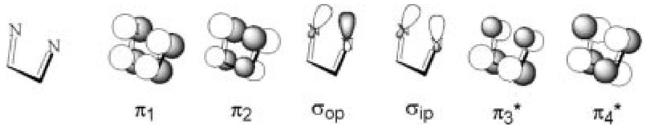
The electronic aspects of the 1,4-diaza-1,3-butadiene ligand have been discussed previously in terms of a qualitative assessment of the relevant molecular orbitals [MOs; the various combinations of atomic orbitals (AOs) are represented in Scheme 2].[12] These include two filled nitrogen σ lone pairs (in-phase σ_{ip} and out-of-phase σ_{op} combinations) and four π levels. Only two of the latter are filled (π_1, π_2) when DAD has the α-diimino form, whereas π_3* is also populated (ligand's HOMO) when DAD behaves as an enediamido dianion.

Carlo Mealli received his doctoral degree in chemistry from the Università di Firenze in 1969. After postdoctoral work with Prof. E. C. Lingafelter at the University of Washington (Seattle), he joined the CNR Institute of Florence directed by Prof. L. Sacconi, where he reached the position of Research Director in 1991. As visiting scientist, he has worked in famous laboratories around the world, including that of the Nobel Laureate Prof. R. Hoffmann (Cornell University). His research interests currently involve the relationship between 3D structures and chemical aspects (including reactivity) of transition metal complexes through computational analysis. For the latter, he has developed, together with D. M. Proserpio and A. Ienco the worldwide used package CACAO. He is the author of more than 200 publications in the field of inorganic/organometallic chemistry.

Andrea Ienco was born in Florence, Italy. He received his chemistry degree from the Università di Firenze in 1993. He then worked in Roald Hoffmann's group at Cornell University. He presently has a research position in Florence at the Istituto di Chimica dei Composti Organometallici of the CNR. His main scientific interest is the application of computational methods in organometallic and transition metal systems.

Agustín Galindo was born in 1960 in Seville, Spain, where he received both his graduate and doctoral (1986, under the direction of Prof. Ernesto Carmona) degrees. After postdoctoral work with Prof. René Mathieu and Prof. Jean-Pierre Majoral (Toulouse), he returned to the Universidad de Sevilla, where he reached the position of Lecturer (1989) and finally that of Professor of Inorganic Chemistry (2001). His research interests are related to transition metal chemistry and the application of coordination/organometallic complexes in homogeneous catalysis (recently extended to nonconventional media).

Andrew D. Phillips completed his B.Sc at the University of Toronto, before proceeding to Dalhousie University, Halifax, where he completed his Ph.D. with Dr. Neil Burford in low-coordinate phosphorus-nitrogen chemistry. Continuing his passion for the synthesis of main-group complexes, a two-year postdoctoral study was completed with Dr. Philip P. Power at U.C. Davis, with whom he is a co-author of over 22 publications. His interest in organometallics and computational chemistry was aroused by research performed at the CNR in Firenze with Drs. Maurizio Peruzzini and Carlo Mealli. At present he is partaking in an independent research project funded by the European Commission's Marie Curie Fellowship program at the Ecole Polytechnique Fédérale de Lasuanne, in collaboration with Dr. Paul J. Dyson. His primary interests include the development of catalytic processes using complexes with sterically demanding ligands.



Scheme 2. Relevant MOs of the 1,4-diaza-1,3-butadiene ligand.

The complexes reported in the Cambridge Crystallographic Database can be separated into two distinct groups in which the M(DAD) metallacycle is either planar or bent depending on the value of the torsion angle M–N–N–C. If the latter is less than 170° the system is considered bent. We have previously addressed the electronic factors which determine the structural arrangement of enediamido ligands in complexes such as [$TiCl_2$(DAD)] and [W(NR)Cl_2(DAD)].[13] In particular, we pointed out that a dianionic character is acquired on bending (oxidized metal center) and the ligand becomes the donor of three rather than two electron pairs. At variance with other interpretations, which attribute the extra donation to the localized C=C π bond in the dianionic DAD,[14] we proposed that the electron pair involved is a filled combination of the nitrogen pπ orbitals that are acting as σ donors.[15] The present study confirms this point of view and discusses other factors that govern the electron distribution and shape of the metallacycle.

As mentioned above, a planar metallacycle implies an extended π-type delocalization of the metal's electrons over the entire skeleton of the chelate. Thus, one electron pair available at the d^4 metal is involved in back-donation to DAD without necessarily implying a complete electron transfer from the metal to DAD (oxidative addition). In contrast, a dianionic enediamido formulation of the ligand seems more appropriate when the ring is folded. A key factor for discriminating between the neutral or dianionic forms of the chelate is the population of the π^*_3 MO (see Scheme 2). Since this is a combination of both C=C π-bonding and C–N π*-antibonding character, a larger electron transfer from the metal atom (up to the point of oxidative addition) is manifested by the elongation of the C–N bonds and shortening of the intermediate C=C bond. This point has been extensively discussed by Wieghardt in several papers devoted to complexes of the late transition metals with *o*-diiminobenzene (alternatively behaving as *o*-diiminobenzosemiquinonato) and other related ligands.[16] This author concluded that the discrimination between the diimino or enediamido forms cannot be based solely on the geometric parameters, especially when the crystallographic data are not of the highest quality.

Finally, the recent discovery of planar metallacycles in [Zr{$(Me_3SiN)_2C_6H_4$}$_2$][17] has shown that the bent/planar dichotomy is also present in homoleptic [$M(DAD)_2$] complexes. This point requires special consideration and has been treated by a combination of MO calculations and electron density analysis.

3. [$M(DAD)_3$] Complexes

Our examination of the electron-richer complexes, in which the group 4 metal is hexacoordinate, starts with the homoleptic [$M(DAD)_3$] species. These will be later correlated with the general pseudo-octahedral complexes. Table 1 summarizes the known [$M(DAD)_3$] complexes along with their CCDC refcode.[8] All the M(DAD) metallacycles are planar.

Table 1. Structurally characterized homoleptic [$M(DAD)_3$] complexes.

Composition (M, DAD)	CCDC refcode
Ti, *i*PrNC(H)C(Ph)N*i*Pr	WIMROZ[18]
Zr, *p*-TolNC(Ph)C(Ph)N-*p*-Tol	YOBYAP[19]
Hf, *p*-TolNC(Ph)C(Ph)N-*p*-Tol	YOBYET[19]

A density functional analysis of an equivalent group 5 metal complex, namely the redox species [M(*i*PrNC(H)=C(H)N*i*Pr)$_3$]$^{0,+1}$ (M = Nb, Ta), is available.[20] Based on the MO architecture, it has been suggested that conversion between the two redox complexes is ligand-based. We have examined analogous group 4 complexes and have optimized the model [Ti{MeNC(H)=C(H)NMe}$_3$] (**1**; Figure 1).

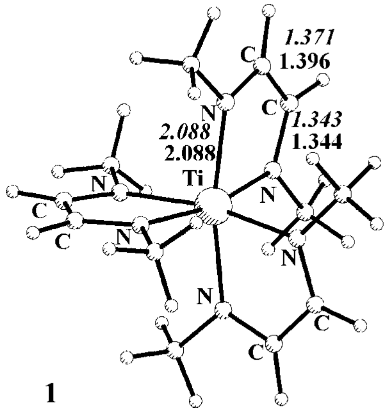
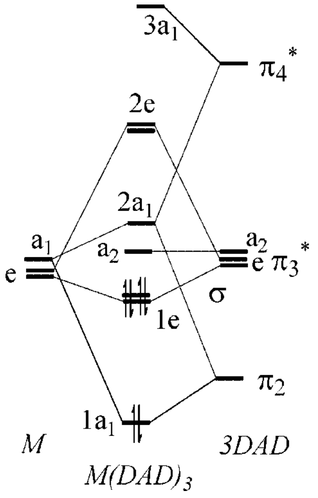


Figure 1. Optimized structure of the model [Ti{MeNC(H)=C(H)NMe}$_3$] (**1**). The experimental geometric parameters of WIMROZ are given in italics.

The structure has essential D_3 symmetry and the agreement with the experimental parameters of [Ti{*i*PrNC(H)=C(H)N*i*Pr}$_3$] (WIMROZ) is satisfactory since the metallacycles are planar and only the C=C double bond is slightly overestimated (by about 0.02 Å).

The MO picture is similar to that proposed for the analogous group 5 system. Amongst the important MOs of the DAD ligands (see Scheme 2) we can highlight the in-phase (σ_{ip}) and out-of-phase (σ_{op}) combinations of the nitrogen lone pairs, which donate a total of 12 electrons to the metal. Other interactions involve the π-orbitals of the ligands, some symmetry combinations (D_3 point group) of which are shown on the right-hand side of Scheme 3. Of these, the combinations of π_1 and π_2 orbitals (see Scheme 2) are all populated but are only partially involved in metal interactions (see below). The most critical relationships concern the π_3* orbitals, which determine the *noninnocent* character of the ligands. Given the pseudo-octahedral geometry of the complex, the classical metal "t_{2g}" levels (presented as the a_1 and e levels on the left-hand side of Scheme 3) are close in energy to the π_3* combinations of the ligands (a_2 and e), hence a strong interaction occurs between the two degenerate e sets. The combined 1e MO (the degenerate HOMO depicted in Figure 2) is stabilized due to its bonding character.



Scheme 3. Simplified MO diagram for $[M(DAD)_3]$ complexes.

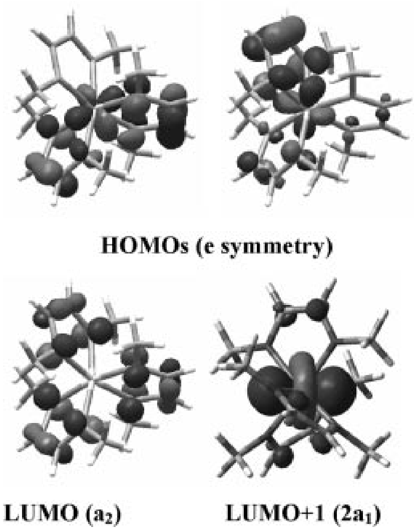


Figure 2. Important frontier MOs associated with model complex **1**.

Given the small energy gap between the interacting levels, it is difficult to discriminate the actual amount of metal- or ligand-based character associated with the four frontier electrons in the 1e level. However, even if a complete metal-to-ligand charge transfer has occurred (oxidative addition), only a maximum of two out of the three ligands could be considered completely dianionic. This is inconsistent with the equivalence of all the ligands constrained by the threefold symmetry. Also, in view of the planarity of the metallacycles, it seems reasonable that the metal is synergetically engaged in back-donation of four electrons into the three DAD ligands.

The two lowest and unpopulated levels (LUMOs in Figure 2) are a combination of pure π_3* ligand-based orbitals (a_2) and a metal "t_{2g}" orbital with some M–L antibonding character ($2a_1$). As shown in Scheme 3, the $2a_1$ level arises from a weak dative interaction between a combination of lower and filled C=N π_2 bonding levels. There is also a stabilizing effect connected with the higher $3a_1$ level (based on a π_4* combination), which justifies why there is no nitrogen contribution in $2a_1$ (see Scheme 2). In any case, the participation of the DAD π_2 MOs in metal donation allows the d^4 metal center to reach a formal 18 electron count. Curiously, it should be noted that the electron richer d^5 complex also has 18 electrons since experimental and computational studies for the neutral [Ta(*i*Pr$_2$-DAD)$_3$] complex confirm that the SOMO has exclusively ligand-based character.[20] This is consistent with the EPR spectra. Moreover, a significantly larger energy gain is computed for singly populating a_2 instead of a_1, while the C–C bond and C–N distances are comparatively shorter and longer, respectively, in the neutral species than in the monocation.[20] In spite of the ligand-based redox chemistry, it might be improper to formulate a prevailing dianionic character of the ligands as this would imply intra-ligand repulsion. Although the additional electron in [Ta(*i*Pr$_2$-DAD)$_3$] is assigned to the ligand, there is no evidence of Ta–N bond elongation. This in an indirect confirmation that the electrons in 1e are mainly metallic in character.

The other two known structures of homoleptic $[M(DAD)_3]$ complexes, namely [M{[*p*-TolNC(Ph)]$_2$}$_3$] (YOBYAP and YOBYET for M = Zr and Hf, respectively),[19] are remarkable for having one metallacycle that is different from the other two. In YOBYET,[19] for instance, the two Hf–N distances for one chelate are significantly shorter than the other four (average values of 2.150(12) vs. 2.216(15) Å] and the C–C distance in the unique metallacycle is correspondingly shorter [1.34(2) vs. 1.405(19) Å]. Since this effect is common to two structures, it cannot be attributed to the poor quality of the crystal data. In principle, a break of the threefold symmetry could be due to an electronic effect of the Jahn–Teller type, since there four electrons are available for three metal–ligand π interactions and the HOMO–LUMO gap is relatively small (see Scheme 3). A DFT optimization of the simple model [Zr{MeNC(H)=C(H)NMe}$_3$], which is similar to the Ti species **1**, shows no electronic bias toward a broken threefold symmetry. A careful examination of the intramolecular contacts in the Zr and Hf structures indicates that the bulky phenyl and tolyl substituents at any core atom of DAD determine the steric hindrance. Rather than a symmetrical weakening of all the M–N distances, the system allows one ligand to be more strongly bound than the other two. A Walsh diagram, constructed at the Extended Hückel Molecular Orbital (EHMO) level,[21] for the simultaneous lengthening of two out of three metal–ligand interactions (the ideal D_3 symmetry of the complete model is lowered to C_2) shows that this distortion produces a large energy gain of about 30 kcal mol^{-1}. Evidently, some four-electron repulsions between the H atoms of the aromatic rings are progressively relieved. Remarkably, the energy minimum found at this low computational level almost corresponds to the experimental structure. Further metal–ligand weakening steeply raises the energy.

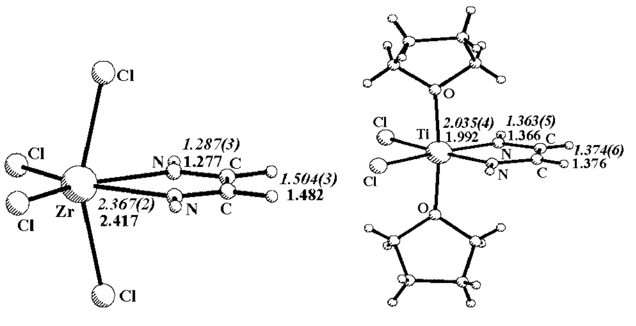
4. Pseudo-Octahedral Complexes with ML_4 Fragments

In order to gain further insight on the electronic peculiarities of the homoleptic $[M(DAD)_3]$ species, it is useful to draw a comparison with pseudo-octahedral DAD complexes supported by an ML_4 fragment (L = two-electron-donor ligand or a halide X). Table 2 lists the structurally characterized examples. In particular, the complexes $[ZrCl_4\{RNC(Ph)=C(Ph)NR\}]$ (**2**; YOBXUI,[19] R = *p*-MeO-C_6H_4), $[TiCl_2(thf)_2\{CyNC(H)=C(H)NCy\}]$ (**3**; PEBCOQ[22]), and $[ZrCl_2(tmeda)\{o\text{-}(Me_3SiN)_2C_6H_4\}]$ (**4**; GUHYEN,[23] tmeda = $Me_2NCH_2CH_2NMe_2$) have been examined. Complex **4** uniquely features a somewhat folded metallacycle.

Table 2. Structurally characterized pseudo-octahedral complexes with ML_4 fragments.

Ancillary fragment	Composition	CCDC refcode
ML_4	[Zr(DAD)(macrocycle)]	NOVNUH[24]
		POCKAT[25]
		POCKUN[25]
ML_2X_2	$[TiCl_2(DAD)(thf)_2]$	PEBQOC[22]
	$[ZrCl_2(DAD)(tmeda)]$, *bent*	GUHYEN[23]
	$[Zr(guanidinate)_2(DAD)]$	PUXTEH[26]
$M(NR)X_2L$	$[TiCl_2(DAD)(NAr)(py)]$	VEBYIK[27]
MX_4	$[ZrCl_4(DAD)]$	YOBXUI[19]

First of all, we satisfactorily optimized models of complexes **2** and **3** with the unsubstituted DAD ligand (see Figure 3). The Ti–N distances and Cl–Ti–Cl angle are underestimated and overestimated with respect to the experimental structure of PEBCOQ[22] by about 0.04 Å and 13°, respectively, in **3**. This is most likely due to important C–H···Cl intramolecular interactions involving the cyclohexyl substituents that are present in the experimental complex but neglected in the calculations.

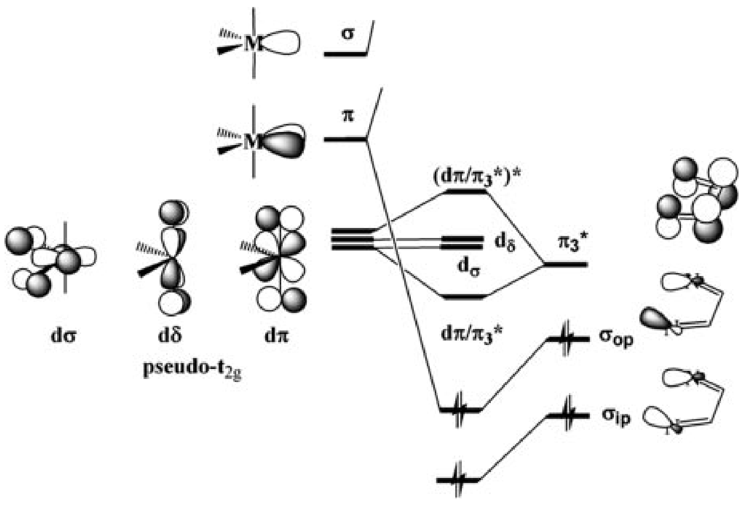


2 **3**

Figure 3. Optimized structures of the model complexes **2** and **3**.

Given the common pseudo-octahedral geometry of complexes **1**, **2**, and **3** and the variety of formal oxidation states (0, IV, and II, respectively), the metallacycle(s) must have a different electronic nature even though they are all planar. For instance, four Cl co-ligands in **2** (d^0 configuration) exclude both the enediamido character of DAD and the metal back-donation. Such a limiting situation is well expressed by the longer C–C (1.482 Å) and shorter C–N (av. 1.278 Å) distances, which suggest that the α-diimino ligand ideally features a single C–C bond and two double C=N bonds. The lack of back-donation should also be reflected by long Zr–N bonds in **2**, which are not directly comparable with the Ti–N distances of 1.992 and 2.088 Å in **3** and **1**, respectively. The latter significant difference is probably due to full engagement of the unique electron pair in **3** (d^2 configuration) in back-donation to one DAD ligand, whereas the two electron pairs (d^4 configuration) in **1** are shared by three DAD ligands.

The diagram for the interaction between the metal fragment and DAD (see Scheme 4) is general for complexes containing four π-donor co-ligands (e.g., halides) and is essentially similar to that proposed by us previously to interpret the features of octahedral *o*-phenylendiamido complexes of group 6 metals.[5] Taking into account these latter



Scheme 4. Simplified MO diagram for $[L_4M(DAD)]$ complexes.

complexes, the population of the four highest frontier MOs in this scheme can vary between 0 and 6 electrons.

Donations of the ligand σ_{op} and σ_{ip} lone-pair combinations into the appropriate σ and dπ hybrid orbitals of the metal are the most effective and general. In **3**, there is a π-type interaction (see the bonding HOMO $d\pi/\pi_3^*$ in Figure 4), while the two remaining "t_{2g}" orbitals (dσ and dδ) are apparently unsaturated. This is not completely true, since electron density is provided by the filled pπ orbitals of the halide co-ligands. This point is highlighted by the drawings of the ML_4 frontier orbitals on the left-hand side of Scheme 4.

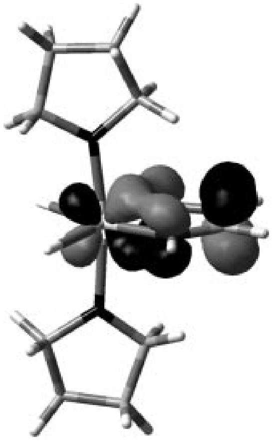


Figure 4. 3D isosurfaces corresponding to the computed HOMO of complex **3**.

Switching the Cl and thf ligands between the equatorial and axial positions in **3** should reduce the saturation of the dσ level because of the weaker π donor capabilities of thf. Conversely, dδ is less affected because it continues to receive the electron density donated from the low-lying π_2 orbital of DAD (see Scheme 2), which complements to the better donation from the Cl ligands. These trends were verified by optimizing three possible isomers, namely *trans*-thf,*cis*-chloride, *trans*-chloride,*cis*-thf and *trans*-chloride/thf,*cis*-chloride/thf. The latter two species are significantly less stable than the observed structure by +14.3 and +13.3 kcal mol^{-1}, respectively (see Supporting Information). A similar problem is found for the formally d^2 complex $[ZrCl_2(tmeda)\{o\text{-}(Me_3SiN)_2C_6H_4\}]$[28] (**4**), which uniquely features a folded Zr(DAD) metallacycle (42° rotation about the N···N vector). In this case, the most stable conformer with the two chloride ligands in the equatorial plane is prevented from forming by the presence of the ethylenediamine chelate, which has no π-donor capabilities. Optimization of the simplest model $[ZrCl_2(eda)(DAD)]$ (eda = $H_2NCH_2CH_2NH_2$) did not reproduce any bending of the metallacycle (see Supporting Information). A better result is obtained for the model **4a** with SiH_3 substituents at the nitrogen atoms of DAD, since this ligand exhibits a limited folding of 20°. The other geometric parameters are also in better agreement with the experimental ones (see Figure 5, a). The HOMO of the species in question (Figure 5, b) clearly shows that the π_3^* level of DAD exerts a σ-type interaction with one lobe of a d orbital rather than the classic $d\pi/\pi_3^*$ one. This was also our original interpretation of the chelate's bending in highly electron-deficient species such as $[TiCl_2(DAD)]$,[13] for which a dianionic character of the chelate must be assumed.

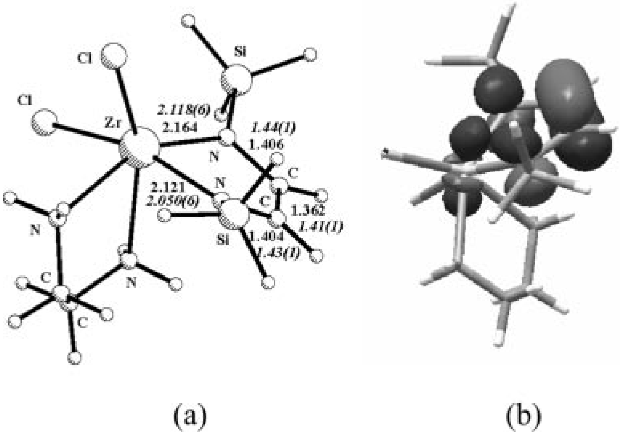


Figure 5. (a) Optimized structure of the model $[ZrCl_2(H_3Si\text{-}DAD)(eda)]$ (**4a**). (b) 3D isosurfaces corresponding to the computed HOMO of **4a**.

Folding of the metallacycle is as large as 54° in the optimized structure of an isomer of **4a** with two axial Cl ligands and the equatorial eda chelating, although the total energy is only 1.0 kcal mol^{-1} higher. In this case, the larger unsaturation of the metal dσ orbital may again be partially compensated by an interaction with the nitrogen pπ lobes of the π_3^* level as σ donors.

In summary, the examined pseudo-octahedral complexes have four frontier levels that are relatively close in energy (see Schemes 3 and 4) and can host up to four electrons (or five in the group 5 derivative). In the homoleptic systems, all the t_2-based orbitals (a_1 + e) are sufficiently saturated by electron donation from suitable combinations of the three DAD ligands. In halide complexes, the electron deficiency at the metal is compensated by the π-donor capabilities of the co-ligands. However, if the co-ligands do not have sufficient donor power or are not properly arranged, insufficient destabilization of a t_{2g} orbital may cause a second-order Jahn–Teller effect. This is likely the cause for the bending of the metallacycle and the shift of the electrons toward DAD, with a consequent improvement of its donor capabilities.

5. Compounds Containing the Fragments $CpML_n$ and Cp_2M

Cyclopentadienido rings can also stabilize an M(DAD) metallacycle. A complex of the type [CpLM(DAD)] can be considered pseudo-octahedral, similarly to the species examined in the previous sections. In some cases, however, the number of co-ligands is higher. In fact, metal fragments of the type $CpML_2$, $CpML_3$ (L = two-electron donor or halide), and Cp_2M can also support DAD coordination. Table 3 summarizes all the species containing at least one

Cp ligand that have been characterized by X-ray diffraction methods. The DAD ligand is generally folded in the latter, with a few exceptions, and hence is dianionic and the oxidation state of the group 4 metal is +4 (d^0 configuration). As underlined before, DAD behaves as the equivalent of a six-electron donor by exploiting a filled combination of the N pπ orbitals for the third σ-type donation.

Table 3. Structurally characterized mononuclear complexes formed by the fragments $CpML_n$ or Cp_2M and one DAD ligand.

Fragment $CpML_n$ type	Simplified formula[a]	CCDC refcode
d^0-CpMX	[Cp′Ti(DAD)Cl]	KISZOB[30] WEVVUO[31] WEVWAV[31] YADBEL[32] YADBIP[32]
	[CpTi(DAD)(NR_2)]	WORGIT[33] YAJCIV[34]
	[Cp′Zr(DAD)(NR_2)]	NETZAN[35] NETZER[35]
	[Cp*Ti(DAD)(CN)]	FAFMIJ[36]
CpMR	[Cp*Ti(DAD)(CH_3)]	ICEGUS[37]
	[CpTi(DAD)(CH_2Ph)]	QULSAR[38]
$CpML_2$	[Cp′Zr(DAD)(allyl)]	POWVEC[39]
	[CpZr(DAD)(acetylacetoneiminato)]	QULRIY[38]
	[Cp*Hf(DAD)Cl(L)] (L = imino group)	YADYEH[40]
	[Cp′Zr(DAD)(NR_2)(NHR_2)]	WOJLAI[29]
$CpML_2X$	[Cp′Zr(DAD)Cl(NHR_2)$_2$]	WOJLEM[29]
CpM	[Cp*Ti(DAD)]$^+$[MeB(C_6F_5)$_3$]$^-$	TEGTAB[41]
Cp_2M type		
Cp_2M	[Cp_2Ti(DAD)]	FUQCID[42] JOFCIQ[43]
	[Cp′$_2$Zr(DAD)]	FATBAD[44] HISWIP[45] JOYXIE[46] SINCAT[47] VIZWEG[48] VIZWIK[48] BAMQUC[49]
	[Cp_2Hf(DAD)]	QULRUK[38]

[a] Cp* = $C_5Me_5^-$, Cp = $C_5H_5^-$, Cp′ = substituted cyclopentadienido ligand.

Two of the complexes in Table 3 are exceptional in that they contain a planar M(DAD) metallacycle. Their simplified formulae are [Cp′Zr(NR_2)(NHR_2)(DAD)] and [Cp′ZrCl(NHR_2)$_2$(DAD)] (see Figure 6) and refer to the species WOJLAI and WOJLEM,[29] respectively. The supporting metal fragments in the latter are electron rich because of the large number of co-ligands. In fact, both complexes can be assigned 18 electrons by assuming a formally uncharged DAD ligand (d^2 metal configuration). The fragments $CpML_2$ (in WOJLAI) and $CpML_3$ (in WOJLEM) can be considered isoelectronic by assuming that the amido ligand is able to donate as many as two electron pairs to the metal.

Also, it cannot be excluded that the planar coordination of DAD is not directly correlated with an uncharged α-diimino character but is a consequence of a geometric constraint in this case. In fact, the Cp′ and DAD units in both complexes are linked to each other by a Si(CH_3)$_2$ bridge between one N atom and one Cp′ carbon atom. Such a connectivity can reduce the flexibility of DAD and therefore its capability for bending. Moreover, the octacoordinate complex (the geometry can be roughly described as a capped four-legged piano stool, see Figure 6) is highly hindered and the metal may not be able to receive an extra lone pair on the side opposite to the Cp′ ring. Interestingly, the complex [CpHfL(Cl)(DAD)] (refcode YADYEH[40]), which is also of the type [$CpML_2$(DAD)], adopts a four-legged, uncapped piano-stool coordination and shows an evident, although not large, folding of the metallacycle (about 20°). The DAD ligand is also not isolated in this case but is directly connected to other co-ligands.

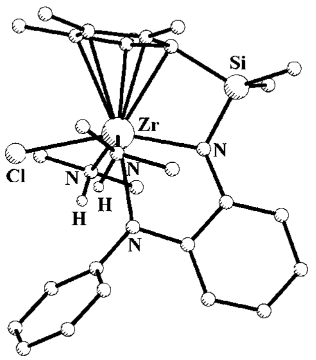


Figure 6. Experimental structure of [Cp′Zr(DAD)Cl(NHR_2)$_2$] (refcode WOJLEM).

The relation between the rigidity and electronic structure of these complexes might deserve an ad hoc theoretical study. In general, the concept of isolobality is helpful for drawing useful relations between the Cp derivatives in question and other [L_nM(DAD)] complexes. MO diagrams similar to those in Schemes 3 and 4 can also be constructed for the Cp_2M and CpL_nM complexes of DAD. The easiest parallelism applies to the orbital interactions in the [L_4M(DAD)] and [CpMCl(DAD)] models, and these qualitative arguments can also be extended to more complex systems. Some of the points concerning the electronic structures of selected Cp metal complexes of DAD have been addressed by some of us in a previous theoretical paper.[50] Here, we simply note that DFT calculations with a QTAIM analysis[51] fully confirmed that, upon bending of DAD, the donation of a third electron pair to the metal occurs through the nitrogen pπ orbitals and not through the C=C π bond of the dianionic enediamido ligand, as often stressed by other authors.[14]

6. Electron-Deficient [X_2M(DAD)] Complexes and Related Homoleptic [M(DAD)$_2$] Species

The DAD ligand, together with only two co-ligands, is found to stabilize pseudo-tetrahedral coordination at a group 4 metal. The upper part of Table 4 lists the known structures of type [L_2M(DAD)], where the metallacycle is invariably folded. For this reason DAD is considered dianionic. In turn, the metal has a d^0 configuration and the

Table 4. Structurally characterized mononuclear complexes of the types [$MX_2(DAD)$] and [$M(DAD)_2$].

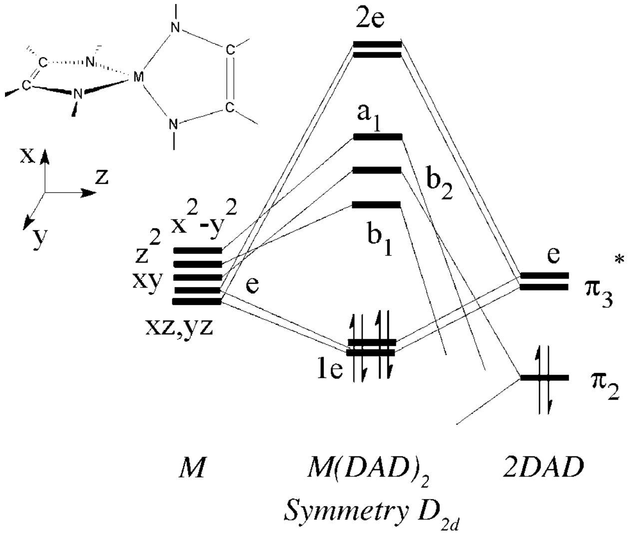
Fragment ML_2 typ	Simplified formula	CCDC refcode
ML_2	[$Ti(DAD)(OAr)_2$]	FOMZAI[53] FOMZIQ[53] HOZGAE[54] HOZGAE01[55]
	[$Zr(DAD)(OAr)_2$]	FOMZEM[56] FOMZEM10[56]
	[$Ti(DAD)(BH_4)Cl$]	JUWSID[57]
	[$Ti(DAD)(BH_4)_2$]	JUWSOJ[57]
	[$Ti(DAD)(BH_4)_2$]	JUWSUP[57]
	[$Ti(DAD)Cl_2$]	ZUJSEC[58]
Homoleptic		
$M(DAD)_2$	[$Ti\{(o\text{-}MeC_6H_4)NC(Me)C(Me)N(o\text{-}MeC_6H_4)\}_2$]	WEZXAA[59]
	[$Zr\{(iPr_3SiN)_2C_6H_4\}_2$]	ZUJSAY[58]
	[$Zr\{(Me_3SiN)_2C_6H_4\}_2$]	FIFQER[17]

system can, in principle, be related to classical tetrahedral complexes of the main group elements. On the other hand, the ability of a bent DAD to donate three electron pairs confirms that the d orbitals play a role, although they obviously cannot be saturated by a single DAD ligand. Thus, the two co-ligands (e.g. halides, phenoxides, and BH_4^-; see Table 4) also act as π donors. The electronic structure of [$X_2M(DAD)$] species has previously been investigated by us from a theoretical viewpoint[13] and will therefore not be addressed in detail here. [$L_2M(DAD)$] complexes have also been analyzed theoretically as the end-products of the intramolecular coupling of two η^2-iminoacyl ligands in bis(aryloxide) complexes of zirconium.[52] We therefore focus on the homoleptic species [$M(DAD)_2$] (see the lower part of Table 4), which raise the most intriguing questions because of the recently ascertained dichotomy of planar or bent metallacycles.

We start with a qualitative MO Scheme for a [$M(DAD)_2$] model with two planar perpendicularly oriented metallacycles (see Scheme 5).

Four low-lying σ bonding MOs, which correspond to the donation from nitrogen lone pairs into s and p metal orbitals, are not shown. It is evident from the frontier region of the diagram that a degenerate bonding set (1e) is formed between the metal *xz* and *yz* orbitals and suitable π_3* orbitals of the two ligands. The three remaining d orbitals are destabilized from other low-lying and filled ligand orbitals, which means that the HOMO–LUMO gap is sufficiently large (>1 eV). In particular, the *xy* orbital interacts with a combination of the π_2 ligand levels (see Scheme 2), while $x^2–y^2$ and z^2 are pushed higher by suitable combinations of the nitrogen σ lone pairs, which are already used for donation into high lying s and p metal orbitals. If the saturation of $x^2–y^2$ and z^2 is insufficient, folding of the two metallacycles may be induced by a second-order Jahn–Teller effect similar to that mentioned above for some pseudo-octahedral species.

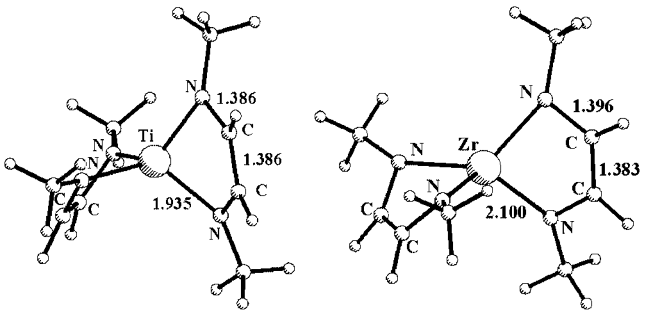
The first two complexes of the type [$M(DAD)_2$] to be characterized, namely [$Ti\{(o\text{-}MeC_6H_4)N(CMe)\}_2$] (**5**; WEZXAA[59]) and [$Zr\{(iPr_3SiN)_2C_6H_4\}_2$] (**6**; ZUJSAY[58]) are bent metallacycles, while in the more recently characterized species [$Zr\{(Me_3SiN)_2C_6H_4\}_2$] (**7**; FIFQER[17]) the two rings are perfectly planar and orthogonal. It is noteworthy that the two non-isostructural zirconium complexes **6** and **7** have the same C_6H_4 backbone and differ only in the nature of the silyl substituents at the N atoms. The subtle electronic factors that affect the dichotomy have therefore been examined by different computational techniques.



Scheme 5. Simplified MO diagram for D_{2d}-symmetric [$M(DAD)_2$] complexes.

The simplest models [$M\{MeNC(H)=C(H)NMe\}_2$] (M = Ti **5a**, Zr **6a**) with C_2 symmetry were optimized first at the DFT level. The absolute minima invariably contain bent metallacycles, as indicated in Figure 7.

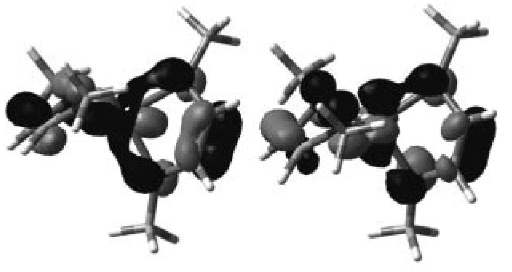
The pseudo-tetrahedral geometry observed in the X-ray structures of **5** and **6** is satisfactorily reproduced, as is the amount of twisting of each metallacycle (about 50° about the N···N vector). The shorter C–C distance in **6a** (by 0.05 Å) is most likely a consequence of the replacement of the more delocalized C_6H_4 backbone with the CH=CH grouping in the DAD ligand.



5a **6a**

Figure 7. Optimized structures of the homoleptic model complexes [M(Me-DAD)$_2$] (M = Ti **5a**, Zr **6a**) with bent metallacycles.

With respect to the MOs in Scheme 5, the lowering of the symmetry from D_{2d} to C_2 mixes the character of the barely saturated $x^2–y^2$ and z^2 orbitals into the highest two filled MOs (the previous 1e HOMOs). As pointed out in our original work on [TiCl$_2$(DAD)][13] and here for some [L$_4$M(DAD)] species, bending transforms most of the dπ–pπ bonding character of the frontier orbitals into a σ-type interaction between the nitrogen pπ lobes and single lobes of the $x^2–y^2$ and z^2 orbitals. This aspect is highlighted by the HOMO and HOMO–1 for complex **5a** (see Figure 8).



HOMO HOMO-1

Figure 8. 3D isosurfaces corresponding to the computed HOMO and HOMO–1 of **5a**.

The optimized model complexes **5b** and **6b** with planar metallacycles (D_{2d} symmetry) are associated with two high imaginary frequencies, which clearly indicates the preference of the two ligands to fold. The total energy is higher than that at the absolute C_2 minimum by as much as 20 kcal mol^{-1}. The energy difference between the planar and bent forms is reduced to the order of only 1–3 kcal mol^{-1}, when the calculations are repeated with DAD ligands having a C_6H_4 backbone. This is most likely due to a significant delocalization of the electron density toward the aromatic ring and away from the nitrogen atoms. This reduces the possibility of the latter jointly becoming the donors of a third electron pair when the metallacycle is bent. Under these circumstances, it is possible for DAD to maintain the enediamido character associated with the planar conformation, which means that the dichotomy of the two geometries and the existence of two isomers is plausible. Since the zirconium complexes **6** and **7** have different ring geometries and differ only in having *i*Pr$_3$Si or Me$_3$Si substituents, respectively, the relative effects of the latter on the stability of each isomer must be rationalized.

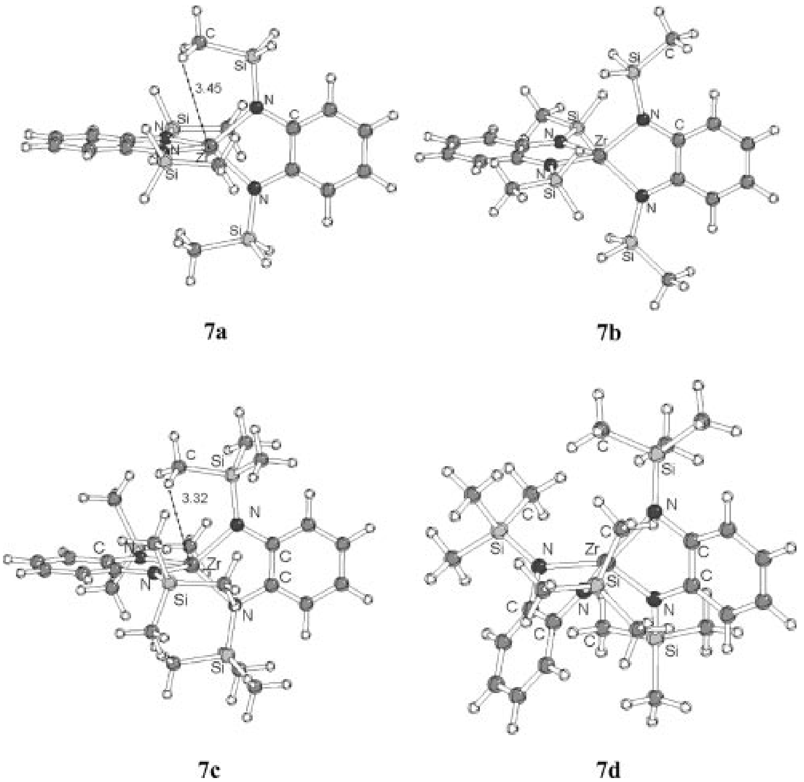
One CH$_3$ group of each silyl substituent in the experimental structure of **7** hangs over the metal atom with two relatively close H atoms and one C–H vector pointing away. Although the shortest Zr···H separation is as long as 3.04 Å, such an arrangement is reminiscent of the Zr–η^3-CH$_2$ agostic interactions that have been classified by some of us recently,[60] and this is also the classical bonding mode between a metal center and a free alkane.[61] Thus, the metal center in **7** seems to be involved in four simultaneous interactions of the latter type with four different CH$_3$ groups, which are pairwise aligned roughly along the two main perpendicular directions.

To verify whether the agostic interactions really exist, various models of **7** have been investigated (see Figure 9).

First of all two D_{2d} structures (**7a** and **7b** in Figure 9) were optimized with MeH$_2$Si substituents in place of the Me$_3$Si ones. These model complexes have imposed planar metallacycles but differ in the orientation of the unique methyl groups, which can either lie close to or away from the metal center. The shortest Zr···H distances in **7a** are much longer than the experimental ones (3.45 vs. 3.043 Å) and the computed N–Si–C angle is less closed [107.5° vs. 103.5(1)°], which suggests that the agostic interactions, if real, are not reproduced by the calculations. Further information was expected from model **7b** which, due to its stereochemistry, cannot feature any agostic interaction. This conformer, which is not even a minimum on the PES (imaginary frequencies are present), is energetically disfavored with respect to **7a** by 22 kcal mol^{-1}. This difference is not a proof of the agostic interactions in **7a** but has a clear steric origin. In fact, the significantly open N–Si–C angles (120.7°) best highlight the short contacts between the C_6H_4 backbone and the coplanar methyl groups, and hence their repulsive effects.

Finally, the most complete model of complex **7**, with actual Me$_3$Si substituents, was optimized in both D_{2d} and C_2 symmetries (**7c** and **7d**, respectively, in Figure 9). The results with these complexes show that the molecule can exist in the gas phase with either planar or bent metallacycles since both models are real minima on the PES. Importantly, the folding of the ligand in **7d** still causes a stabilization of only 2 kcal mol^{-1}, which is one order of magnitude smaller than that found for species without the aryl backbone. For this reason, it is not totally surprising that isomer **7c** is found in the solid state. Furthermore, the small energy difference is in agreement with the fluxional behavior observed in several [X$_2$M(DAD)] complexes,[38,47,58,59] as shown schematically in Scheme 6.

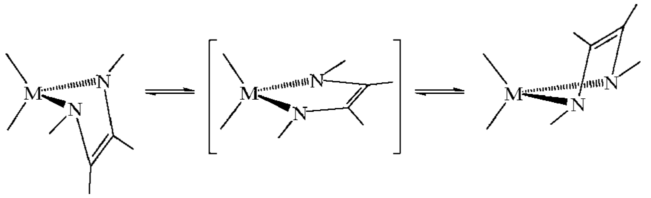
With regard to the critical geometrical parameters of the Me$_3$Si displacement in **7c**, the agreement with those of the experimental structure is good but not excellent. In any case, the trends with respect to **7a** indicate shorter Zr···H contact distances (3.30 Å) and more acute N–Si–C angles (105.5°). Again, the closeness of one methyl group to the metal atom seems due to the steric repulsions between the C_6H_4 ring and the other methyl groups rather than to an actual agostic interaction.



7a **7b**

7c **7d**

Figure 9. Optimized D_{2d} structures of [Zr{(MeH$_2$SiN)$_2$C$_6$H$_4$}$_2$] with 180°-reoriented MeH$_2$Si substituents (models **7a** and **7b**). Structures **7c** and **7d** are D_{2d}- (planar metallacycles) and C_2-symmetric (bent metallacycles) models of complex **7** with Me$_3$Si substituents. The dotted lines in **7a** and **7c** highlight one of the equivalent shortest Zr···H contacts.



Scheme 6. Dynamic equilibrium between the conformers of folded DAD complexes.

7. QTAIM Analysis of the Homoleptic [Zr(DAD)$_2$] Species

In order to find a reasonable answer to the nature of the interaction, which in complex **7** pushes four methyl groups toward the inner coordination sphere of the metal, a QTAIM[51] analysis was carried out for model **7c** as other QTAIM studies have been able to clearly highlight Ti···H and Zr···H interactions in systems where they really exist.[62]

The structures in Figure 10 (see part A) show all the expected bond critical points (bcp's) for the normal interatomic interactions, none of which appears in the region of possible Zr···H interactions. Furthermore, the Laplacian map indicates a localized depletion in these regions, which means that no confirmation of the agostic bonds is found. A similar study by Coppens et al., also using the QTAIM method, was also unable to detect any agostic interactions in the open zirconocene complex [Zr(2,4-C$_7$H$_{11}$){(*i*Pr)NCHPhCH$_2$-CMe=CHCMe=CH$_2$}].[63]

Remarkably, another type of attractive interaction can be seen from Figure 10 (A), namely eight bcp's appear between the N atoms and the methyl H atoms, which were initially supposed to participate in agostic interactions with the metal. These bcp's essentially correspond to weak C–H···N hydrogen bonds, although it remains questionable whether these can be the driving force for the Me$_3$Si group to lean toward the metal. The computed N···H separations of 3.12 Å (av.) are somewhat longer than the experimental average value of 3.05 Å, which also means that the electron density at the bcp's is rather small (0.005 e Å^{-3}). In any case, the cumulative strength of as many as eight interactions of this type could be stabilizing. Incidentally, an equivalent situation (not shown) is found for the structure of [Zr{(Me$_3$SiN)$_2$C$_6$H$_{10}$}$_2$],[64] which differs from **7** in having a cyclohexyl backbone instead of an aryl one (in other words the carbon atoms of the metallacycle are fully saturated). The DFT calculations for this molecule indicate that there is only one conformer with two quasi-planar and perpendicular metallacycles.

Rather different results are obtained from the QTAIM analysis of the C_2 isomer **7d** with bent metallacycles (Figure 10, B). Recall that the latter conformation is observed in complex **6** (ZUJSAY) with *i*Pr$_3$Si substituents in place of the Me$_3$Si ones. Only two of the eight C–H···N bcp's remain in isomer **7d**, and their densities are at least 20% lower than those in **7c**.

In conclusion, the larger number of stabilizing N···H interactions in **7a** seem to justify the reduced energy difference

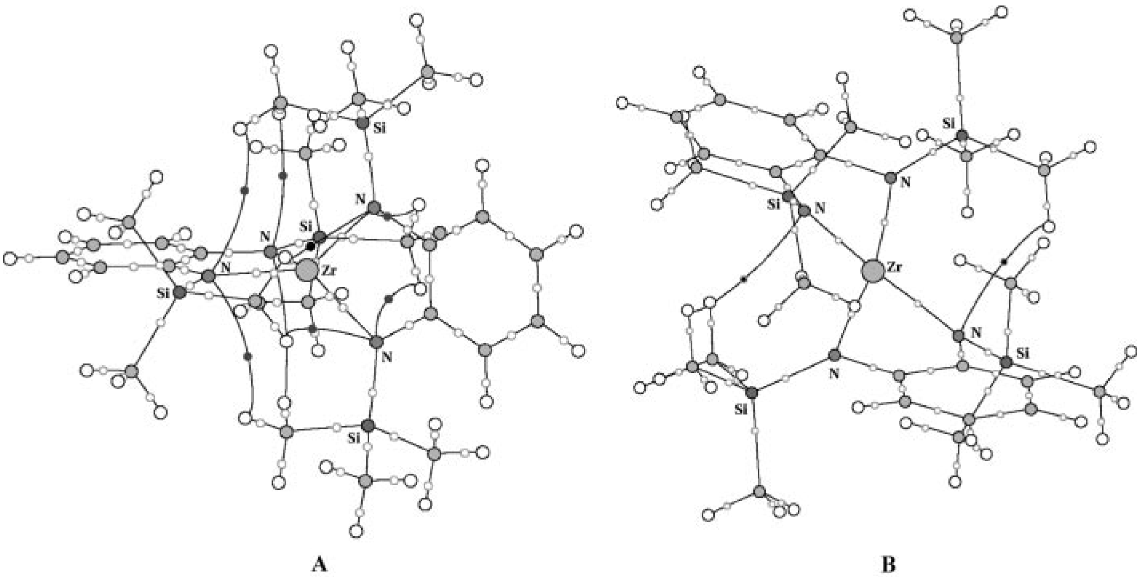


Figure 10. Molecular graphs of the D_{2d}- and C_2-symmetric models **7c** and **7d** (A and B, respectively). All calculated bcp's are shown except for ring and cage critical points. The black bcp's represent curves associated with the N···H interactions.

between the isomers and the isolation of this complex in the solid state. Recall that when the metallacycles are folded, the N pπ orbitals of the DAD ligands (lone pair combinations) give rise to σ-type interactions with the metal center. In this case, the feature is contrasted by the hydrogen bonding, which, by restricting the added donor capabilities of the combined nitrogen atoms, can partially favor the planar conformation.

In any case, the planar metallacycles observed in complex **7** must be considered rather exceptional and are only possible when at least three main factors occur simultaneously. These are: i) the peculiar conformation of the Me_3Si-substituted DAD ligands, which places one CH_3 group over the Zr–N bonds; ii) the role played by the eight N···H interactions; iii) the incorporation of the aromatic backbone in DAD. In fact, when [Zr(Me_3Si-DAD)$_2$] models are optimized with the simplest enediamido skeleton in place of the *o*-phenylenediamido one, the bent conformation is stabilized by as much as –19.3 kcal mol^{-1}. In this case, a QTAIM analysis reveals no bcp's associated with any N···H interaction.

8. Relationship Between [M(DAD)$_3$] and [M(DAD)$_2$] Complexes

The existence of both the 1:2 and 1:3 homoleptic species also raises the interesting problem of their interconvertibility. The energies of all the species that appear in Equation (1) are available, which means that it should be possible to gain some useful hints regarding their interconversion.

$$[\mathrm{Ti(Me\text{-}DAD)_2}] + \mathrm{Me\text{-}DAD} \rightleftharpoons [\mathrm{Ti(Me\text{-}DAD)_3}] \qquad (1)$$

The thermochemical values calculated for the gas phase indicate that the enthalpy of reaction and the Gibbs free energy (at 298 K) are –27.0 and –13.2 kcal mol^{-1}, respectively, which means that the reaction is exothermic, as would be expected in view of the better metal saturation in the [Ti(Me-DAD)$_3$] species. This result is compatible with some experimental findings. For example, tom Dieck and co-workers have reported that the addition of *i*Pr-DAD to [Ti(*i*Pr-DAD)$_2$] yields the complex [Ti(*i*Pr-DAD)$_3$],[65] and Scholz and co-workers have described that the reduction of [$TiCl_4$(thf)$_2$] in the presence of magnesium gives [Ti(DAD)$_2$] in the presence of two equivalents of DAD or [Ti(DAD)$_3$] with an excess of ligand.[59] As for the reverse reaction, the expulsion of one ligand from [M(DAD)$_3$] introduces significant metal unsaturation, which the system generally compensates for by ligand folding. In this regard, the nature of the substituents attached to the nitrogen centers can play a decisive role, as described previously. Two recent contributions with metals other than those of group 4 have demonstrated the decisive influence of the substituents. Thus, substitution of the *t*Bu groups with C_6F_5 ones in a diazabutadiene ligand induces a variation in the oxidation state of europium,[66] and the selection of alkyl or aryl substituents in α-diimino ligands coordinated to iron affects the spin state of the metal, which is correlated with a specific catalytic activity.[67]

9. Conclusions

We have extensively reviewed the known complexes formed by a metal of the group 4 and at least one α-diimino ligand. The latter, due to its *noninnocent* character, can also be described as a dianionic enediamido species. We have focused our attention on the electronic aspects of the metal–DAD bonding and on geometric effects, which are triggered depending on the ligand's electronic and steric properties and the number of co-ligands as well as the oxidation state of the metal. In particular, the frontier MOs are strongly affected by the folding of the metallacycles, which permits a greater electron donation ability from the ligand. In general, complexes with a higher coordination number (pseudo-octahedral), including the homoleptic [M(DAD)$_3$] class, feature planar metallacycles, which contrasts with the folding of the metallacycles observed in [L$_2$M(DAD)], CpLn, and [M(DAD)$_2$] complexes, where the metal is less saturated (higher oxidation state). Notable exceptions have been highlighted. The various cases have been analyzed in terms of DFT calculations and qualitative MO arguments. When the findings are ambiguous (where the DFT response does not allow for discerning the structural preferences) the QTAIM method has been adopted to extract useful information about the distribution of the electron density within the models. In particular, we have found that for a given stereochemistry, unpredicted C–H···N hydrogen bonding can contribute to the stability for specific types of planar metallacycles. Finally, we have analyzed the energetics behind the interconversion between [M(DAD)$_2$] and [M(DAD)$_3$] complexes, which has been found to be exclusive to group 4 metals.

Supporting Information (see also the footnote on the first page of this article): Seven tables (labeled S1–S7) with selected structural data (bond lengths and angles), relative energies, and optimized stuctures for calculated and experimental complexes. Five tables with optimized coordinates for compounds **7a**–**d**. Additional information regarding the QTAIM analyses is also provided.

Acknowledgments

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