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Folded 2,5-diazapent-3-ene metallacycle in ene-diamido group 4 metal compounds: DFT and AIM analyses

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Abstract

Mononuclear complexes, which contain a dianionic ene-diamido ligand bound to a group 4 metal atom in the formal d^0 configuration, are analyzed by the DFT method to interpret the electronic origin of the folding at the five-membered 2,5-diazapent-3-ene metallacycle moiety. Geometry optimizations were carried out for the following models, $TiCl_2[o\text{-}(Me_3SiN)_2C_6H_4]$, $Ti(OPh)_2(DAD)$, $CpTiCl(DAD)$, $CpTiMe(DAD)$ and $Cp_2Zr(DAD)$ $(DAD = HNCHCHNH)$. They show some common electronic features, the nature of the HOMO, in particular. In all cases, the latter results from the donation of a filled π_3^* ene-diamido level into an empty σ metal orbital, this being maximized upon the folding of the metallacycle. Such a geometric rearrangement involves the filled nitrogen p_π lobes, while the C=C π bond remains essentially uninvolved. The feature is confirmed by the application of the atom in molecules (AIM) theory, that provides no evidence of critical points between the metal center and the pair of two carbon atoms.
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1. Introduction

A few years ago, the electronic structure of the ene-diamido transition metal compounds, that contain a folded 2,5-diazapent-3-ene metallacycle (see **I**), attracted our interest. In a first study, the implications for the non-planarity of the ring in presence of d^0 metal center, were critically addressed from the theoretical viewpoint [1]. Subsequently, Group 5 mononuclear complexes that contain this dianionic functionality [2,3] were systematically analyzed from the structural and theoretical view-

points. Our familiarity with the electronic properties of the *o*-phenylenediamido ligands prompted us to extend the analysis to group 6 [4] and group 8 [5] metal complexes for which ring-folding is not so common. In this paper, we consider high-valent group 4 metals and, through a detailed analysis of the electron density, we are able to confirm the lack of direct metal–carbon interactions in the folded metallacycle.

I

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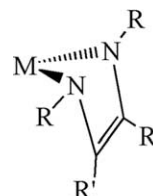
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2. Results and discussion

A search in the Cambridge Structural Database [6] for ene-diamido group 4 mononuclear compounds containing a folded 2,5-diazapent-3-ene metallacycle affords a number of species with different supporting metal fragments (MX$_2$, CpML$_n$ and Cp$_2$M) but common d$_0$ electron count [7–27]. Nitrogen–carbon distances (range 1.33–1.46 Å with mean value 1.39(3) Å), which are larger than a C=N double bond, and carbon–carbon distances (range 1.33–1.45 Å with mean value 1.38(3) Å), which are shorter than a C–C single bond, support the ene-diamido formulation. The metallacycle folding is characterized by torsion angles M–N–N–C in the range 119–145° (mean value 128(1)°) and bond angles around the nitrogen atoms that sum up to ca. 360° (planar environment). Upon folding, the separation between the metal and the two carbon atoms of the chelate is shortened almost to suggest a direct metal–carbon interaction. According to the previous analysis of other similar systems [1–3], there is no evident MO argument to support such a hypothesis. However, with the intention of dismissing any residual doubt on the point, we have carried out new DFT calculations on some representative models of the retrieved structures such as, for instance, TiCl$_2$[o-(H$_3$SiN)$_2$C$_6$H$_4$], **1**; Ti(OPh)$_2$(DAD), **2**; CpTiCl(DAD), **3**; CpTiMe(DAD), **4**, and Cp$_2$Zr-(DAD), **5**, (DAD = HNCHCHNH). Further compelling evidence is obtained from the topological analysis of the electron density of the species **3** and **4**, which has been performed with the usage of the atoms in molecules (AIM) theory [28].

Fig. 1 shows the optimized geometries of **1–5**. Selected structural parameters for these model compounds are reported as Supplementary Material. In general, there is a reasonable agreement between the experimental X-ray data and the computed model structures. The calculations confirm that the C–C distances in the metallacycle (1.38–1.44 Å range) are somewhat shorter than that expected for a single C–C bond, while the N–C bond lengths (1.37–1.41 Å range) are longer than the N=C double bond. These parameters substantiate the dianionic ene-diamido character of the DAD ligand. The computed M–N–N–C torsion angles for **3** and **4** reproduce nicely the folding of the metallacycle experimentally observed. Also, the corresponding value for **5** is in the range experimentally found for Cp$_2'$Zr-(R, R′–DAD) complexes. Only for the models **1** and **2**, the computed folding is less pronounced than in the experiment (the M–N–N–C angles are about 9° more
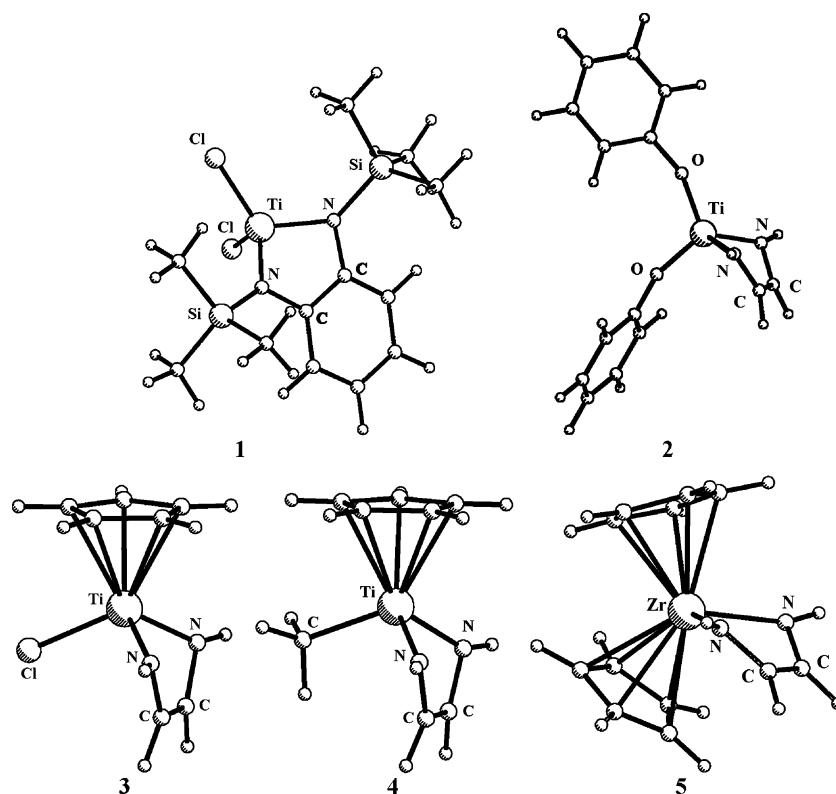

Fig. 1. Optimized structures of TiCl$_2$[o-(Me$_3$SiN)$_2$C$_6$H$_4$], **1**, Ti(PhO)$_2$(DAD), **2**, CpTiCl(DAD), **3**, CpTiMe(DAD), **4**, and Cp$_2$Zr(DAD), **5**, model complexes.

opened) and, consequently, the Ti···C contacts are longer (by about 0.1 Å).

The relevant MOs of ene-diamido ligand [2,29] and the optimized geometry and electronic properties of the simplest $TiCl_2(DAD)$ model compound have been already discussed by some of us [1]. Folding of the metallacycle is evidently triggered by the electron donation from the frontier π_3^* MO of the dianionic chelate (shown in **II**) into an empty metal σ orbital. On the other hand, no important steric effect is foreseen, which may originate the geometric feature. The point is fully confirmed also by the present DFT calculations and by the rather similar HOMOs, exhibited by all of the models **1–5** (see Fig. 2). Importantly, the respective drawings do not show overlap between any metal lobe and the C=C π bonding portion of the π_3^* level. Similar conclusions have been obtained by Reinhold and coworkers concerning the origin of the folding of dithiolene ligands in titanocene complexes [30]. Interestingly, the bonding scheme proposed for the ene-diamido ligand contrasts significantly with that of the early transition metals with a η⁴-coordinated butadiene ligand. In the latter, the involvement of all of the carbon atoms is most evident and theoretically justified [3,31].
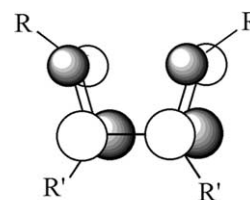
II

At this point, we have decided to exploit other methods to settle the question of the possible Ti···C interaction in the present complexes. Thus, we have carried out a topological analysis of the electron density in CpTiCl(DAD), **3**, and CpTiMe(DAD), **4**, by using the AIM theory. The exclusion of the bonding interaction can be made on account of the lack of suitable bond paths [28]. A total of 25 bond critical points, 7 ring critical points and 1 cage critical point are found for **3** (the results for **4** are comparable and are not explicitly discussed here). By taking into account that **3** contains 20 nuclei, there are no missing critical points because the Poincaré–Hopf relationship is satisfied [28,32]. The CpTi moiety is characterized by bond paths reproducing
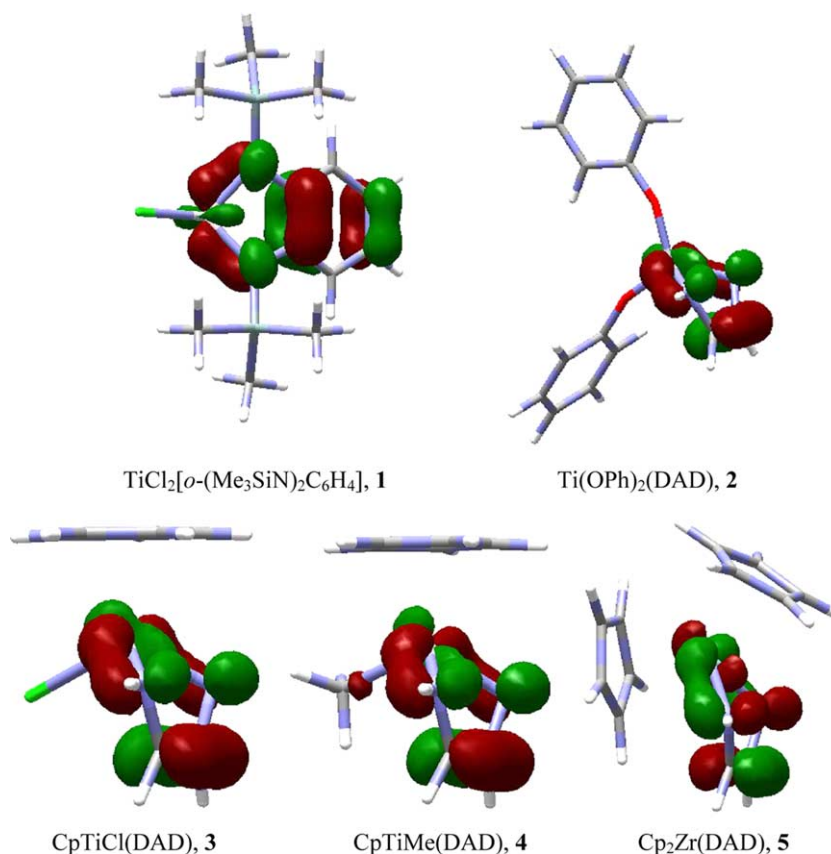

$TiCl_2[o-(Me_3SiN)_2C_6H_4]$, **1** $Ti(OPh)_2(DAD)$, **2**

CpTiCl(DAD), **3**   CpTiMe(DAD), **4** $Cp_2Zr(DAD)$, **5**

Fig. 2. 3D isosurfaces corresponding to the HOMOs of the model compounds **1–5**.

Table 1
Charge density, ρ, laplacian of the electron density, $\nabla^2\rho$, energy density, $E(r)$, and ellipticity, ϵ, for some bond critical points (cp) and the ring critical point (rcp) of the Ti–DAD five-membered ring in **3** (all values in a.u.)

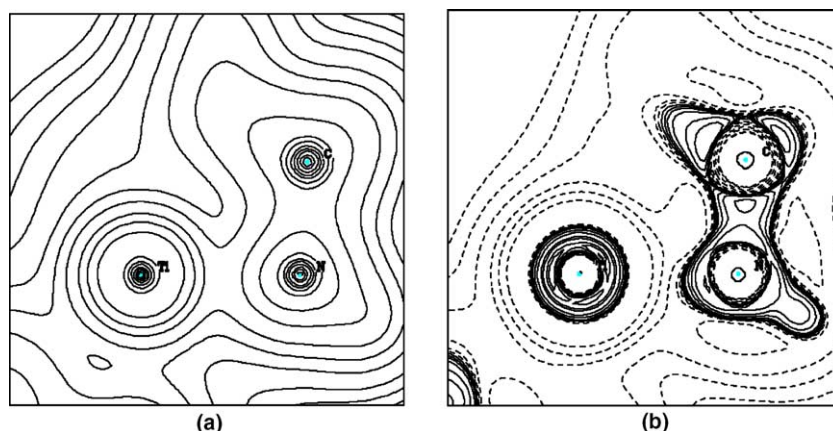| cp and rcp	ρ	$\nabla^2\rho$	$E(r)$	ϵ
Ti–N	0.119	0.481	−0.037	0.318
	0.118	0.480	−0.037	0.315
N–C	0.312	−0.943	−0.468	0.137
	0.312	−0.945	−0.468	0.137
C–C	0.317	−0.862	−0.324	0.370
rcp	0.035	0.175	0.005	–

Fig. 3. Contour maps of the electron density (a) and the laplacian of the electron density (b) within the Ti–N–C plane in **3**. In (b), solid contour lines correspond to regions of charge concentration ($\nabla^2\rho < 0$).

the C–C, C–H and Ti–C interactions with a total of 15 bond critical points, 6 ring critical points and 1 cage critical point. The situation is completely analogous to other complexes containing the same CpTi fragment [33]. Next, we have centered our attention in the Ti–DAD metallacycle and selected data from the topological analysis are presented in Table 1.

The DAD ligand is characterized by bond paths along the N–C, C–C, N–H and C–H bonds. The values of the bond critical points are typical of nonpolar interactions with ρ values in the 0.28–0.34 range and $\nabla^2\rho$ always negative. The largest value, 0.34 a.u., is found for N–H bonds, while C–H bonds display ρ values similar to those found in the C–H bonds of Cp fragment (ca. 0.28 a.u.). The C–C bond shows a ρ value of 0.317 a.u., somewhat higher than those found for the C–C bonds in Cp (around 0.30 a.u.). This fact suggests that the C–C bond order in the DAD ligand is higher than any of the C–C bonds in Cp and confirms the assumed ene-diamido formulation [34]. Additionally, the ellipticity of this bond is higher (0.370) than any other calculated C–C bond in Cp (around 0.24). This suggests a rather anisotropic distribution of the density along the bond. The Ti atom is bonded to the nitrogen atoms of

the DAD ligand and two bond critical points are found correspondingly. These critical points have the features of closed-shell interactions as, for example, small ρ and a positive value of $\nabla^2\rho$, while the energy density is negative (shared interactions). These peculiar properties of the critical points have been previously highlighted for the direct Ti–C σ bonds [33]. A ring critical point characterizes the five membered metallacycle, but no critical points are found between the Ti atom and any carbon atom of DAD. Fig. 3 shows the density and laplacian charge density within the plane containing three adjacent Ti, N and C atoms. Additional plots through different planes are collected as Supplementary Material. In conclusion, the present AIM analysis supports the idea that the ene functionality of the C=C linkage in the dianionic DAD ligand is not directly exploited to saturate the electron deficiency of the metal atom.

3. Conclusions

In this paper, we have extended to group 4 metal atoms our systematic theoretical investigations of the bonding capabilities of the ene-diamido ligands. The ex-

perimentally observed folded envelope geometry in these d^0 complexes must be attributed to electronic grounds and it was produced with the aim of maximizing the donation of the ene-diamido π_3^* MO to the metal. The use of AIM methodology allows us to confirm that the donation through the π component is basically contributed by the nitrogen atoms and the interaction between the metal centre and the carbon atoms of the DAD ligand is not significant.

4. Computational details

The electronic structure and geometries of the model complexes were computed within the density functional theory at the B3LYP [35,36] level using the LANL2DZ [37,38] basis set for the titanium and zirconium atoms. The basis set used for the remaining atoms was the 6-31G + (d,p). All the optimized geometries were characterized as local energy minima by diagonalization of the analytically computed Hessian (vibrational frequencies calculations). The DFT calculations were performed using the GAUSSIAN 98 suite of programs [39]. Molecular orbitals were visualized using the GAUSSVIEW program [40]. The AIM computations were generated with the XAIM suite of programs [41].

Acknowledgements

Appendix A. Supplementary material

Selected computed parameters of model compounds **1**–**5** (Tables S1–S4) and contour maps of the laplacian of the electron density for complex **3** (Fig. S1). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem. 2004.05.038.

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