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Journal of Organometallic Chemistry 655 (2002) 16–22

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Theoretical study of the bonding capabilities of 1,4-diaza-1,3-butadiene and *cis*-1,3-butadiene ligands in cyclopentadienyl tantalum(V) complexes

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Received 10 December 2001; received in revised form 10 December 2001; accepted 22 March 2002

Abstract

A folded envelope geometry is generally encountered in structurally characterized high valent early transition metal compounds containing a substituted 1,4-diaza-1,3-butadiene ligand. In these cases the diazabutadiene ligand can be regarded as dianionic ene-diamido ligand and the folded five-membered ring can be described as a metallacyclo-2,5-diazapent-3-ene. A comparable metallacyclopent-3-ene description is attributed to η^4-butadiene complexes of early transition metals, in which the ligand exhibits a σ^2, π-character. For this reason, a parallel description was initially adopted by several authors for the ene-diamido ligands and the origin of the folding of the five-membered ring was attributed to the saturation of the metal center through the C=C double bond. The aim of this paper is to discriminate the bonding capabilities of the 1,4-diaza-1,3-butadiene and *cis*-1,3-butadiene ligands on high-valent tantalum complexes, and to establish the origin of the folding of the 1,4-diaza-1,3-butadiene ligand. A Density Functional study (DFT) of the model complex [CpTaCl$_2$(HNCHCHNH)] (**1**) and compound [CpTaCl$_2$(η^4-butadiene)] (**2**) has been carried out. The differences in the bonding description of these ligands coordinated to the identical [CpTaCl$_2$] moiety are discussed through the examination of the HOMOs of **1** and **2** and on the basis of a FMO analysis. In complex **1**, there is no evidence of any positive overlap between the tantalum center and the inner carbon atoms of the diazabutadiene ligand, while for **2** the classical σ^2,π-description for the η^4-butadiene ligand is well-founded. Consequently, the generally accepted bonding description of 1,4-diaza-1,3-butadiene ligands coordinated to high valent early transition complexes should be modified. The origin of the folding is the reorientation of the N hybrid orbitals with the purpose of saturating the metal center and no significant donation through the C=C bond occurs.

Keywords: Tantalum; Ene-diamido; Diazabutadiene; Butadiene; DFT

1. Introduction

A vast number of transition metal complexes containing ligands derived from the diazadiene skeleton are known. Recently, substituted 1,4-diaza-1,3-butadiene (α-diimine) compounds have attracted considerable interest as useful ancillary ligands in a number of stoichiometric and catalytic reactions. In particular, nickel(II) and palladium(II) complexes containing these ligands, reported by Brookhart and co-workers [1], were the first examples of late transition metal catalysts capable of polymerizing ethylene and higher α-olefins to high molecular weight polymers. Several coordination modes have been reported [2] for transition metal complexes containing substituted 1,4-diaza-1,3-butadiene ligands (from now abbreviated as R,R′-DAD [3]). Scheme 1 shows a representation of the bonding modes found in mononuclear complexes in which the DAD ligand is bonded to a single metal center through both N atoms. Consequently, dinuclear derivatives and compounds with only one N atom bonded to the metal (η^2-CN bonding) are not incorporated to the Scheme. In the majority of early transition metals the diazabutadiene ligand acts as dianionic ene-diamido chelate (mode **A**) and the metal-DAD moiety is characterized in almost all the examples by a non-planar disposition of the five-membered metallacycle (folded envelope) [4–7].

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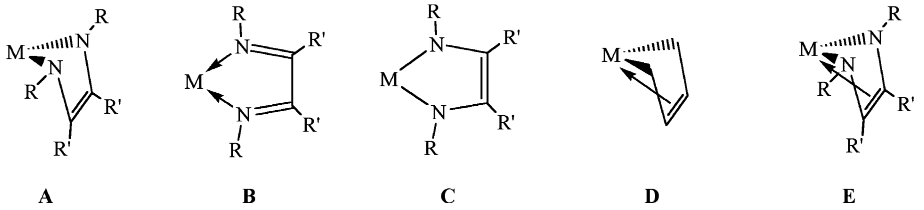
PII: S0022-328X(02)01404-3



Scheme 1.

The coordination mode B, α-diimine ligand, is well represented for many late transition metal complexes [2]; meanwhile the bonding type C, a planar metalla-2,5-diazacyclopent-3-ene is found in some middle transition elements and it is less common in early transition metals [8]. In the last years, it has been reported the synthesis and characterization of a series of tantalum complexes containing 1,4-diaza-1,3-diene R,R′-DAD ligands [6c, f, h, i] (or closely related *o*-phenylenediamido ligands [6d, g]) in which the diazabutadiene behaves as dianionic ene-diamido ligand and shows a folded envelope geometry (mode **A**).

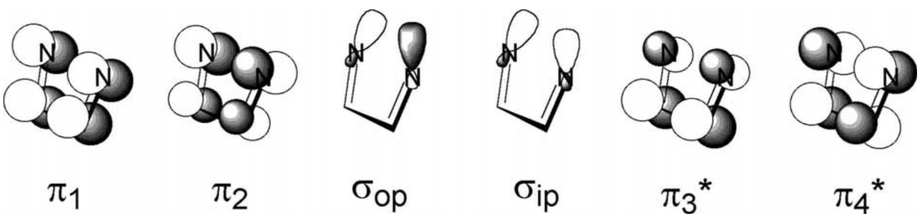
In this paper, we report a theoretical comparative investigation (Density Functional study, DFT) of the 1,4-diaza-1,3-butadiene and *cis*-1,3-butadiene ligands coordinated to the same [CpTaCl$_2$] moiety, in order to distinguish the bonding capabilities of the 1,4-diaza-1,3-butadiene and 1,3-butadiene ligands on high-valent complexes of early transition metals. A similar study has been carried out on related niobium complexes [9].

2. Results and discussion

1,4-Diaza-1,3-butadiene compounds behave as 'non-innocent' ligands and when the coordination to a single metal center occurs, two descriptions are possible: a metallacyclo-2,5-diazapenta-2,4-diene (**B** in Scheme 1) or a metallacyclo-2,5-diazapent-3-ene. In the latter situation, the ligand acts as dianionic ene-diamido ligand and the conformation of the five-membered ring can be approximately planar (bonding mode **C**) or folded (mode **A**). The folding of the five-membered ring occurs through the concerted torsion of the NR groups about the C–N bonds (ca. 25–35°), bending the C=C fragment toward the metal and producing short M–C contacts. The folded envelope geometry is encountered in high valent early transition metal compounds and it is characterized (CSD analysis [10]) by: (a) a torsional angle M–N–N–C in the range of 111–144°; (b) a relatively short metal-carbon contacts; (c) a carbon–carbon bond length shorter than that expected for a single C–C bond; and (d) the bond angles around the nitrogen atoms summing up to ca. 360°. Some of these features are related with those observed in butadiene complexes of early transition metals, in which the ligand exhibits a σ^2,π-character (**D**), and for similarity a parallel description was initially adopted by several authors for folded ene-diamido ligands (**E**). In this paper, we criticize this bonding picture.

The conformational preferences and other properties of 1,4-diaza-1,3-butadiene molecule and related conjugated systems have been recently studied by DFT methods [11]. Previously, ab initio studies of this molecule [12] and related species [13] were also performed. From a qualitative point of view, when considering the substitution of 1,3-butadiene by the 1,4-diaza-1,3-butadiene ligand, we are replacing a ligand capable of donating two pair of π electrons (π_1 and π_2) by other ligand which is able to donate up to a maximum of four electron pairs (the equivalent to the previous two π pair plus two in-plane σ pair). The qualitative MO picture of this ligand has been recently discussed [14]. A representation of the frontier MOs corresponding to the 1,4-diaza-1,3-butadiene ligand is shown in Scheme 2. The main MOs include two filled σ lone pairs (in phase σ_{ip} of symmetry a_1 and out phase σ_{op} of symmetry b_2) that correspond to the HOMO and HOMO-1 of the molecule; two filled, lower in energy, π_1 and π_2 combinations (symmetries b_1 and a_2, respectively) and two empty π* combinations (π_3^* and π_4^* of symmetries b_1 and a_2, respectively). Consequently, the bonding capabilities of DAD ligands arise from the two nitrogen σ lone pairs and the two filled π MOs. The LUMO of the molecule is the MO π_3^*. If the ene-diamido form is contemplated two additional electrons occupy this FMO and π_3^* becomes the HOMO of the ligand.

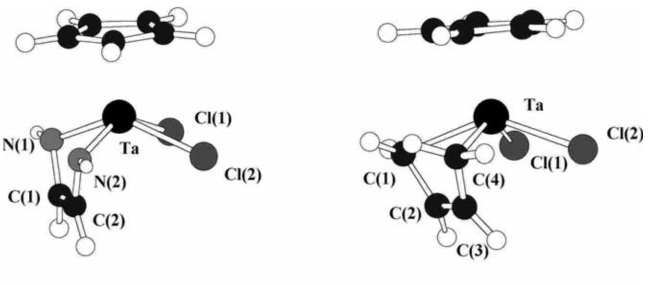
Mealli, Ienco and some of us have recently communicated a re-interpretation of the bonding scheme of the ene-diamido ligand in d^0 metal complexes [15]. Essentially, the folding of DAD ligand (folded envelope geometry, mode **A**) in such complexes cannot be explained by using the standard description σ^2,π adopted for the η^4 bonding of butadiene ligand to early transition metals. The experimentally observed folding cannot be attributed to the π donation from the central C=C linkage to the unsaturated metal center, because this interaction is negligible according to the calculations. In order to confirm this analysis, we have performed DFT studies on the model compound [CpTaCl$_2$(HNCHCHNH)] (**1**) and, for comparison, on the complex [CpTaCl$_2$(η^4-butadiene)] (**2**). Therefore, we can contrast the ligands 1,4-diaza-1,3-butadiene (in its ene-diamido form) and 1,3-butadiene (in its but-2-en-



Scheme 2.

1,4-diyl form) coordinated to the moiety CpTaCl$_2$ with a formal d^0 configuration. Full geometry optimizations were performed for **1** and **2**. The resulting final optimized geometries are shown in Fig. 1 and their coordinates are included as supporting information. Selected calculated parameters of complexes **1** and **2** and, for comparison, selected experimental data from X-ray crystallography have been collected in Tables 1 and 2, respectively.

As pointed out Mashima et al. [16] in the majority of cyclopentadienyl-dichloro compounds the DAD ligand adopts a supine conformation, except for a bulky substituted ^{t}Bu,H-DAD derivative [Cp*TaCl$_2$(^{t}Bu,H-DAD)] [6h] and for the bis(trialkylsilyl)-*o*-phenylene-diamido complexes [Cp*TaCl2{(^{i}Pr3SiN)2-*o*-C$_6$H$_4$}] [6d] and [Ta{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}Cl$_2${(Me$_3$SiN)$_2$-*o*-C$_6$H$_4$}] [6g]. No steric crowding can be expected in model complex **1**, because it contains the simplest DAD ligand and, consequently, only the *supine* conformation was considered in the calculation, In Table 1, we contrast selected experimental data for several complexes containing a DAD ligand (excluding the *o*-phenylenediamido derivatives) coordinated to the [Cp′TaCl$_2$] moiety (Cp′ = Cp or Cp*) with the computed parameters. A general satisfactory agreement between the calculated and experimental values of geometrical parameters is found. The DAD ligand is folded towards the metal center and the computed torsional angles of 118.0°, affords Ta–C contacts within the range of bonding distances. The C1–C2 bond distance, 1.410 Å, is shorter than that expected for a single C–C bond, while the N1–C1 and N2–C2 bond lengths, 1.384 Å, are longer than expected for a double N=C bond. These parameters are in agreement with a dianionic ene-diamido constitution of the DAD ligand.



1 **2**

Fig. 1. Optimized structures of model complex [CpTaCl$_2$(HNCHCHNH)] (**1**), and compound [CpTaCl$_2$(η^4-butadiene)] (**2**).

Table 2 shows selected data for [CpTaCl$_2$(η^4-butadiene)] complex. A quite satisfactory accord is found between the calculated and experimental values of geometrical parameters. Bond distances agree within ca. 0.03 Å and the good agreement found with respect to the bond angles is noticeable. The largest deviation appears to be less than 4°. The folded envelope geometry is characterized for torsional angles (for example, Ta–C1–C4–C3, 93.7°, computed; 94.7°, experimental) appreciably lower than those found in DAD derivatives (116–122° range in Table 1). This folding affords bond distances between the Ta atom and the inner carbon atoms of butadiene shorter than the Ta–C contacts in DAD complexes. The computed bond lengths in the butadiene fragment show the expected long-short-long bond alternation, indicating the involvement of the σ^2,π bonding contribution of the formally but-2-en-1,4-diyl ligand (**D**). Fig. 2 shows the superimposition of the molecular structures, calculated and experimental, of complex **2**. The major discrepancies are found in the hydrogen atoms of butadiene ligand. In spite of these atoms being located in the difference Fourier maps in the refinement of the experimental structure [17], they do not show any sign about the expectable bending back of the hydrogen atoms of CH$_2$ groups.

A qualitative FMO analysis helps to elucidate the major bonding components between 1,4-diaza-1,3-butadiene and 1,3-butadiene ligands and the same [CpTaCl$_2$] fragment. The metal FMOs corresponding to a general CpMX$_2$ fragment have been discussed elsewhere [18]. A representation of these orbitals is sketched in Scheme 3. They are essentially a subset of three low lying frontier orbitals, two of a' ($1a'$, d_{x2-y2} and $2a'$, d_{z2}) and one of a'' ($1a''$, d_{xy}) symmetries, and a second subset, higher in energy, of two frontier orbitals ($3a'$, d_{xz} and $2a''$, d_{yz}). The interpretation of the bonding scheme of the η^4-butadiene ligand bound to early transition metals is well established [19]. In particular, a detailed EHMO analysis was early reported by Nakamura, Kasai and coworkers [17] for cyclopentadienyl–tantalum complexes containing the metalla-cyclopent-3-ene structure. The bonding description in **2** is similar and can be briefly resumed as follows. The strongest interactions are the donation of the π_2 orbital to $1a''$ and the donation of π_3^*

Table 1
Selected calculated data [bond distances (Å), angles and torsional angles (°)] for [CpTaCl$_2$ (HNCHCHNH)] model complex, **1**, and, for comparison, selected experimental data for compounds of general formulation [Cp′TaCl$_2$(DAD)]

Cp′, Refcode [10], DAD	Cp, Complex **1,** HNCHCHNH	Cp*, HESCAJ [6f], ^{i}Pr-DAD	Cp, POJQOU [6h], MeO-p-C$_6$H$_4$-DAD	Cp*, LIWVAO [6], MeO-p-C$_6$H$_4$-DAD	Cp*, LIWVIW [6h], p-tolyl-DAD	Cp*, LIWVOC [6h], Cy-DAD	Cp*, TIRBUR [6c], McO-p-C$_6$H$_4$, Me-DAD
Ta–Cl1	2.466	2.490(2)	2.465(4)	2.488(4)	2.467(2)	2.494(2)	2.472
Ta–Cl2	2.465	2.492(2)	2.454(4)	2.473(4)	2.456(2)	2.490(2)	2.469
Ta–N1	2.037	2.000(4)	2.026(10)	2.02(1)	2.028(5)	2.020(6)	2.022
Ta–C1	2.507	2.430(5)	2.46(1)	2.48(2)	2.480(7)	2.451(7)	2.470
Ta–C2	2.507	2.436(5)	2.45(2)	2.47(2)	2.474(7)	2.464(7)	2.451
Ta–N2	2.037	2.006(4)	2.01(1)	2.03(1)	2.045(5)	2.004(5)	1.990
C1–C2	1.410	1.380(7)	1.36(2)	1.30(2)	1.389(10)	1.392(9)	1.388
N1–C1	1.383	1.374(7)	1.38(2)	1.37(2)	1.373(8)	1.383(8)	1.399
C2–N2	1.384	1.370(7)	1.38(1)	1.37(2)	1.367(8)	1.383(8)	1.383
Cl1–Ta–Cl2	81.7	78.05(6)	79.9(1)	79.0(2)	78.64(8)	78.32(7)	79.1
N1–Ta–N2	80.3	84.1(2)	83.4(5)	81.4(5)	83.2(2)	84.0(2)	81.3
Ta–N1–C1	92.3	90.2(3)	90.4(8)	91(1)	91.6(4)	90.1(4)	90.5
Ta–N2–C2	92.3	90.3(3)	90.6(8)	91.1(10)	90.7(4)	91.5(4)	91.4
N1–C1–C2	116.0	118.3(5)	117(1)	117(1)	117.6(6)	118.7(6)	115.8
C1–C2–N2	116.0	118.4(5)	120(1)	120(1)	119.8(6)	117.4(6)	116.6
Ta–N2–N1–C1	118.0	119.7	117.3	120.8	121.0	119.6	116.5
Ta–N1–N2–C2	118.0	119.4	117.8	121.6	121.4	120.5	116.6

Table 2
Selected structural data for calculated and experimental [CpTaCl$_2$ (η^4-butadiene)] complex

Bond distances (Å), angles and torsional angles (°)	[CpTaCl$_2$ (η^4-butadiene)]	
	Calculated	X-ray [17]
Ta–Cl1	2.424	2.423(3)
Ta–Cl2	2.423	2.405(3)
Ta–C(Cp)	2.440 (average)	2.393(13)–2.421(12) range
Ta–C1	2.270	2.258(12)
Ta–C2	2.425	2.424(11)
Ta–C3	2.425	2.410(12)
Ta–C4	2.269	2.257(11)
C2–C3	1.400	1.375(16)
C1–C2	1.465	1.458(16)
C3–C4	1.465	1.453(16)
Cl1–Ta–Cl2	92.9	89.5(1)
C1–Ta–C4	72.5	73.3(4)
Ta–C1–C2	77.7	78.2(7)
Ta–C4–C3	77.7	77.7(7)
C1–C2–C3	115.9	116.6(10)
C2–C3–C4	116.0	117.3(10)
Ta–C4–C1–C2	93.6	95.2
Ta–C1–C4–C3	93.7	94.7

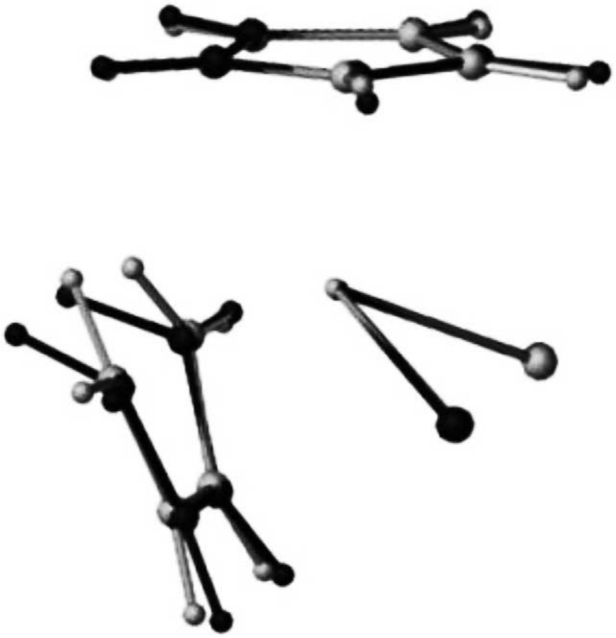


Fig. 2. Superimposed molecular structures of theoretical (black) and experimental (grey) [CpTaCl$_2$(η^4-butadiene)] complex.

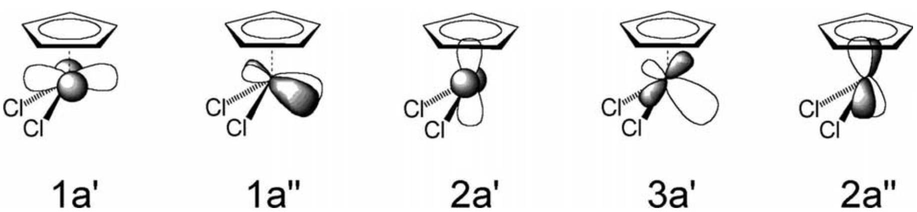
to $1a'$ and in minor proportion to $2a'$ FMOs. Other details require no further discussion and can be found in the above mentioned seminal paper [17].

With reference to the bonding of complex **1**, the FMO analysis shows that the strongest interaction is also the donation of the π_2 orbital (that is now substantially lower in energy in comparison with the similar π_2 orbital in the butadiene ligand) to $1a''$, but now this donation is completed by the participation of the *out-of-phase* σ_{op} contribution. The donation of π_3^* orbital is also active but now is directed preferentially to the $2a'$ FMO and only in small percentage to $1a'$. The latter metal orbital is substantially saturated by the donation of *in-phase* σ_{ip} FMO. These dissimilarities in the bonding analysis of **1** with respect to **2** are the source of the essential differences found in the HOMO of the two model complexes (see Fig. 3). In the HOMO of **1**, the nitrogen π lobes overlap significantly with the lobes of $2a'$ (d_{x2-y2}) orbital while the carbon π orbitals (part of the ligand's HOMO π_3*) do not overlap with the metal lobes and are only involved in C–C bonding interaction. Moreover, a detailed analysis of the fragment orbital interactions does not provide any evidence for carbon π electron donation toward the metal. Contrarily, the HOMO of *) do not overlap with the metal lobes and are only involved in C–C bonding interaction. Moreover, a detailed analysis of the fragment orbital interactions does not provide any evidence for carbon π electron donation toward the metal. Contrarily, the HOMO of **2** shows the overlap of all carbon π lobes of π_3^* with both the $1a'$ and $2a'$ FMOs. In conclusion, the bonding of the ene-diamido (or diazabutadiene) ligand is different with respect to the conventional σ^2,π-description of the butadiene ligand. The origin of the folding was initially ascribed by several authors to the donation of the C=C bond. However, according to the calculations, this folding can be attributed to the necessity of the reorientation of the filled N hybrid orbitals in order to saturate the metal center. The donation through the π component is basically contributed by the nitrogen atoms and, consequently, the interaction between the tantalum and the carbon atoms of DAD ligand is not significant.

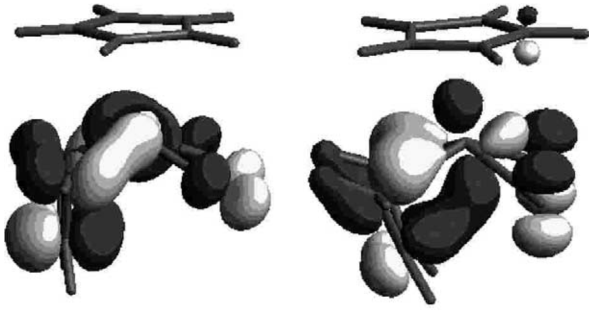
Work is in progress in order to study several butadiene ligands containing heteroatoms (1-aza-1,3-butadiene, 1,4-dioxa-1,3-butadiene or enediolate and so on) bonded to high valent early transition metals and verify the nature of the metal–ligand interaction.

3. Conclusions

This theoretical study has shown the bonding of the ene-diamido ligand is different with respect to the conventional σ^2,π-description of *cis*-1,3-butadiene ligand bonded to early transition metals. The experimentally observed folded envelope geometry in high valent early transition complexes containing a substituted 1,4-diaza-1,3-butadiene ligand (coordination mode **A** in Scheme 1) cannot be attributed to the π donation from the central C=C linkage. According to the calculations, the folding of the five-membered ring must be attributed to the necessity of the reorientation of the N hybrid



Scheme 3.



1 **2**

Fig. 3. 3D isosurfaces corresponding to the HOMOs of the [CpTaCl$_2$(HNCHCHNH)] (**1**), and [CpTaCl$_2$(η^4-butadiene)] (**2**) complexes.

orbitals in order to saturate the metal center. The donation through the π component is basically contributed by the nitrogen atoms and the interaction between the tantalum center and the carbon atoms of the DAD ligand is not significant. Consequently, the coordination mode depicted in **E** (Scheme 1) is not adequate to describe the bonding situation in high valent early transition complexes containing a substituted 1,4-diaza-1,3-butadiene ligand.

4. Computational details

The electronic structure and geometries of the model complexes were computed within the density functional theory at the BP86 [20] level using the LANL2DZ [21] basis set. A set of *d* polarization functions was added to Cl, C and N atoms. This computational approach has been used in similar systems with good results [9,15]. All the optimized geometries were characterized as local energy minima by diagonalization of the analytically computed Hessian (vibrational frequencies calculations). All the DFT calculations were performed using the GAUSSIAN 98 suite of programs [22]. Molecular orbitals were visualized using the CHEM3D PRO program [23]. The FMO analysis was made with CACAO [24] using the coordinates of the optimized model complexes.

5. Supplementary material

Tables of coordinates for the optimized structures of [CpTaCl$_2$(HNCHCHNH)] and [CpTaCl$_2$(η^4-butadiene)] complexes.

Acknowledgements

We are grateful to DGICYT (Project PB 97-0740) and Junta de Andalucia for financial support of this research. We thank the Spanish Ministerio de Educación, Cultura y Deporte for a research studentship (Diego del Río).

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