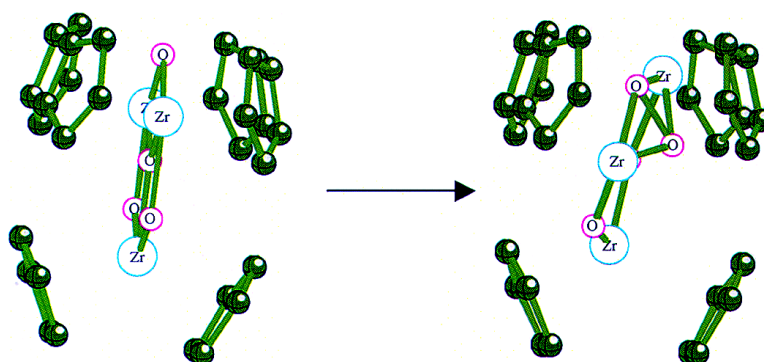Article

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Using Effective Group Potential Methodology for Predicting Organometallic Complex Properties

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Abstract: Using the Effective Group Potentials (EGP) method, optimal geometries, harmonic vibrational frequencies, and relative energies of different sets of metal complexes are calculated. All of the systems under consideration contain the cyclopentadienyl (Cp) ligand. They are as follows: (i) Group V metal Atom complexes showing one Cp ligand, (ii) a tetrameric Al−Cp compound with four Cp ligands, (iii) homometallic lutetium hydrides containing six cyclopentadienyl rings. Various electron correlation treatments have been carried out. All of the results compare very satisfactorily with available experimental data and with all-electron ab initio calculations performed for this work or published in the literature. Furthermore, the performance of the EGP method was tested on a rather large complex for which experimental evidence exists, but no all-electron calculation has been reported so far.

Introduction

The study of the reactivity of metal complexes, despite the growing power of modern computers, is still computationally demanding. There are two major reasons for this fact. The first is structural, i.e, transition metal complexes are often quite large systems involving bulky ligands. The second is due to the chemical complexity of these compounds. An accurate description of their electronic structure can only be achieved by using methods including electronic correlation. Perturbation theory, Coupled Cluster, or hybrid DFT methods greatly increase the computer cost of an ab initio calculation. However, there is a great need for methods that enable one to do rapid and reliable calculations on a laboratory computer (PC, Work Station). In the same spirit, if a theoretical chemist can draw a correlation diagram on a single sheet of paper, a computational chemist could do a quick calculation at almost the same accuracy as a complete ab initio calculation. However, these swift calculations must offer sufficient accuracy to draw qualitative if not quantitative conclusions.

The first possibility to overcome the size problem is to reduce the number of atoms and electrons and therefore reduce the "silico cost". For this purpose, modeling is a solution, i.e., the calculation is not carried out on the real system but on a simplified version of it. Simplification could mean substitution, for instance PR_3 phosphine by PH_3, or utilization of the so-called hybrid methods which combine a high-level of calculation for the active part of the molecular system and a low level of calculation for the spectator part. QM/MM or IMMOM[1] approaches combine quantum and molecular mechanics, whereas the ONIOM[2] formulation of IMMOM may combine ab initio and semiempirical methods. Applications have shown that the IMMOM approach is successful, especially if large steric effects are present. The picture of the situation would not be complete if no mention was made of semiempirical methods, such as PM3 (tm), which is parametrized for calculations on transition metal complexes. The performance of the semiempirical PM3 (tm) method is highly variable; some results are indeed excellent, but unfortunately, others are less reliable.[3]

Another approach is supported by the theory of separability of a many electron system developed by McWeeny et al.[4] and Huzinaga et al.[5] These theoretical foundations have allowed the development of various strategies for constructing effective group potentials for the description of "spectator groups ". The underlying idea is well-known and can be considered as an extension of the Effective Core Potential (ECP) formulation. It consists of separating the electrons and the nuclei of a given molecule into two distinct subsets: the active and the inactive ones. It is assumed that the active ones are those we want to describe accurately, and the particles belonging to the inactive set should be considered as spectators. A drastic assumption is to remove them and to mimic their effect by an effective potential. Several tests have been reported in the literature with this approach. Some of them were successful, and effective potentials for NH_3,[6] COOH,[7] and HF[8,9] have been obtained and tested. More recently, a group potential for SiH_3[10] has been extracted. Stevens, Jensen and co-workers have developed with

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success potentials that can be used to describe solvent effects and environmental effects.[11,12] Recent developments of this method allow the treatment of links across covalent bonds.[12,13] It should be noticed that few of them have been widely used.

We have proposed a general approach for the definition and the determination of effective group potentials (EGP),[14] and EGP's for SiH_3, NH_3, PH_3, and cyclopentadienyl ligand have been obtained. We have demonstrated that this method produces structures in good agreement either with reference calculations where all valence electrons are included, or with experimental data. Extraction of the EGP is done at the Hartree−Fock level, but we have already shown that use of the EGP can be extended to methods including correlation energy, such as MP2,[15] DFT,[16,17] CASSCF,[18] CIS,[19] and SDCI(SC2).[20] Maron et al.[21] have recently published an example of the accuracy of this method in the optimization of geometries of a number of lanthanide complexes. According to their results, the agreement of the predicted geometries with reference calculations is good. Moreover, estimation of the low activation energy for the studied reaction, i.e., H exchange reaction, with an EGP leads to very accurate values (the average deviation from the value calculated with real Cp is only 1.6 kJ.mol^{-1}). Heully et al.[22] have tested the performance of the method for the calculation of electronic transition energies of various metal complexes containing NH_3 ligands. They have shown that both simple ligand-field d−d transitions and the lowest charge-transfer transitions are reproduced very well.

In the present work, we report new results of an improved EGP for the cyclopentadienyl ligand, which we call Cp#, for different types of metal complexes. The cyclopentadienyl ligand is one of the most common and popular ligand in organometallic chemistry; Cp complexes for all transition metals are known.

As a rule, as is described elsewhere,[14] the first step of the extraction procedure is to select a reference system among a set of molecules embodying the chemical group we want to model. We have always tried to choose the reference system in such a way that the transferability of the group potential to other systems was not affected, but we have not found a satisfactory principle to systematize this step. However, in some cases the definition of the EGP can be achieved independently of any reference system. This is the case for the Cp group potential. Such a Cp# was elaborated from the cyclopentadienyl anion, which has the advantage of being a closed-shell molecule. Likewise, the 6 π electrons correspond to the number formally assigned to the cyclopentadienyl ligand on the basis of electron counting. In this way, we elaborate an EGP for Cp the ligand

that is transferable by nature and ready to be linked to a transition metal or a lanthanide ion. To avoid any misunderstanding, we recall that the EGP was designed for the cyclopentadienyl anion but it is later used as a five-electron system. The very fact that we have an atomic basis set on the spectator atoms will allow donation and back-donation effects between active and spectator parts—so, in practice, the charge of the Cp# will be between five and six, as for a real Cp ligand.

The comparison between the EGP and the real Cp ligand shows that these two entities are strictly isolobal, in that all the statements based on the isolobal analogy,[23] (i.e., similarity in the number, symmetry properties, approximate energy, and shape of the frontier orbitals, as well as the same number of electrons) are respected here. This is not strictly the case when a Cp is substituted by a chlorine atom, which sometimes leads to unreliable results.[24] The differences in both the energy and shape of the Cp and Cl occupied orbitals are in some cases too large.[21]

In our method, most of the isolobal analogy criteria, especially energy and shape of the molecular orbitals, are sine qua non conditions in the definition of an effective group potential. The replacement of bulky ligands by isolobal EGPs should form a new compound with a similar valence electron shell, and even displaying a similar potential energy surface and reactivity.

This paper is organized as follows: section 1 deals with theoretical aspects, with a brief sketch of the different steps involved in the definition of an EGP. In section 2, we have chosen different situations representative of the various difficulties commonly encountered in applications of ab initio methods to the field of organometallic chemistry. The first one concerns $CpMH_4$ systems (M = V, Nb, Ta), where the system fluxionality corresponding to exchange between H atoms is known as a touchstone for theoretical methods.

As underlined in the presentation of EGP's, a characteristic of the method is to use a limited orbital basis in the spectator region. This feature thus allows electron flows between the active and spectator parts. The reliability of our EGPs to reproduce these effects correctly is tested on Al_4Cp_4, a highly symmetric system for which previous ab initio calculations have been reported. As a third example of the potential of our methods, we have carried out investigations of the PES for very large systems including six Cp ligands ($Cp_6Lu_3H_3$ and $Cp_6Lu_3H_4$). In these cases, all-electron calculations are so time consuming that the PES exploration is currently carried out under strict restrictions. Finally, with some confidence in the accuracy obtained with the Cp EGP in the previous calculations, we have tried to elucidate a controversy provoked by the publication of a quite bizarre structure for $Cp_6Zr_3O_4$.

1. Theoretical Method. 1.1 Definition of the EGP Operator. As the EGP method was detailed in previous papers,[14] the derivation of a new EGP for Cp is outlined only to recall the two fundamental steps of the procedure.

The first fundamental step is the generation of molecular valence pseudo orbitals (MVPO), which are designed to reproduce the original Fock molecular orbitals of the active part of the molecule.

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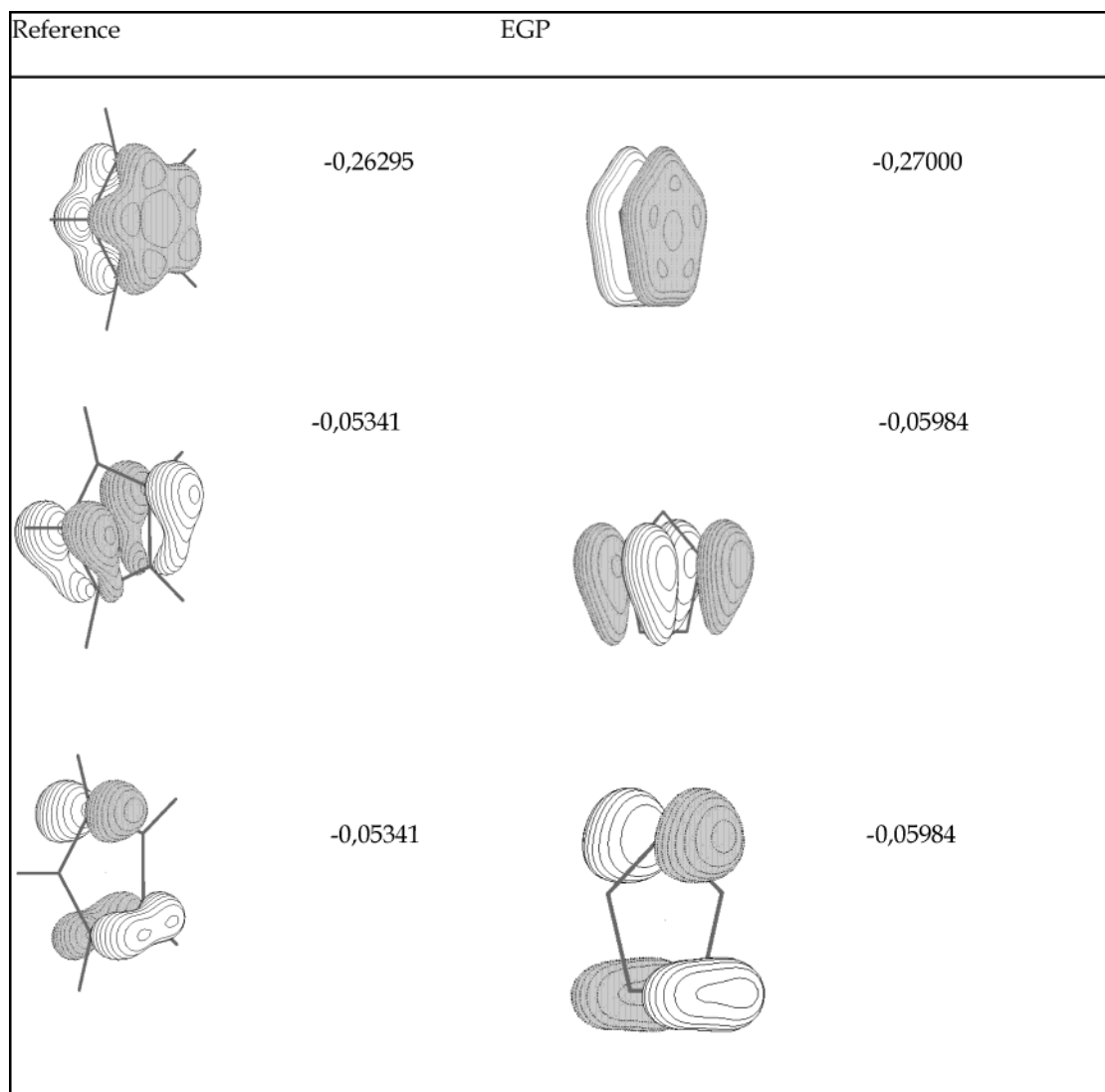
Figure 1. Isovalue representation and eigenvalues (in au) of the π orbitals of the Cyclopentadienyl anion and of the EGP representation.

The main improvement with respect to previous situations is that the Cp$^\#$ EGP was extracted from the Cp$^-$ reference system, so no definition of active and spectator parts is necessary in the extraction process. The choice seems to be rather satisfactory, because the transferability problems should be less pronounced. Among the 13 valence occupied MOs of the Cp$^-$ anion only three of them, called the molecular reference orbitals, are of interest to reproduce the chemical behavior of the pentahapto η^5-C$_5$H$_5$ group in typical organometallic complexes. As the HF canonical MOs are already separated into σ or π symmetry types, no localization procedure is needed. The system is then reduced to a fictitious one and a specific truncated basis set is optimized. The cyclopentadienyl group is reduced to a perfect pentagonal system R$_5$ with pseudo-carbon atoms C$^\#$, each bearing one electron in the π system. In this study, the best MVPO were obtained with a p function (exponent 0.3124). This value compares well with those of the p exponents of the basis set of carbon ECPs optimized by Bergner et al.,[25] (0.55, 0.15), and with those optimized by Baradiaran and Seijo,[26] (0.39–0.12).

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The second fundamental step is the generation of the nonlocal molecular pseudopotential W$_{EGP}$ by requiring that the solutions of the pseudo-Fock operator (eq 1) should be as close as possible to the MVPO 's and their respective eigenvalues

$$\hat{F}(i) = \hat{h}(i) + \hat{W}_{EGP}(i) + \sum_{j=1}^{n_{active}} (\hat{J}_j(i) - \hat{K}_j(i)) \qquad (1)$$

The role of W_{EGP} written in the usual nonlocal form (eq 2) is to fill in the difference between the reference and reduced systems, i.e., Cp$^-$ and R$_5$

$$W_{EGP} = \sum_n \sum_m \alpha_{nm} |g_n\rangle \langle g_m| \qquad (2)$$

In this study, to determine the nonlocal operator, we need a set of Gaussian functions $\{g_n\}$, located on each C$^\#$, defined as an even-tempered basis set (exponent = 3, 1.5, 0.75, 0.375) and an efficient optimization procedure[27] to determine the coefficients α_{nm}.

The first column of Figure 1 shows the three π MO's of the system that we want to reproduce. They correspond to the

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Table 1. Comparison of Computational Parameters for the
Cp₆Lu₃H₃ Complex

| model	ECP on lutetium	ECP+EGP
atoms	66	36
electrons	246	66
basis set functions	563	201

frontier orbitals of the cyclopentadienyl anion MO's. The third
column is the three-dimensional representation of the Cp#
molecular orbitals. The lowest energy orbital a''_2 and the two
e'' set of degenerate orbitals, labeled according to D_{5h} symmetry,
are obviously comparable in shape and in energy.

1.2 Computational Details. EGP Calculations. All EGP
calculations were carried out with Gaussian 98,[28] which was
modified to calculate matrix elements, first and second-order
derivatives for W_{EGP}.

Harmonic vibrational frequencies have been calculated for
the active part of the system in order to establish the nature of
the optimized structure (minimum, saddle point). Geometry
optimizations at the Hartree−Fock (HF), MP2, LDA, B3LYP,
and B3PW91 level of theory were carried out with Relativistic
Effective Core Potentials optimized by the Stuttgart group[29−31]
in the case of vanadium, niobium, tantalum, zirconium and
lutetium atoms. All of the Gaussian basis sets are of double-ζ
plus polarization quality unless otherwise mentioned.

To improve our chances of locating all the important
nontrivial geometries, all structures were optimized without any
symmetry constraints, except for the preliminary calculations
on zirconium complexes.

**Reference Calculations for Complete Systems or Valence
Electrons Calculations.** Due to the size of the molecules, we
systematically used ECP and their basis sets for all atoms in
the reference ab initio calculations. The ECP used are the same
as in the EGP calculations, i.e., the Stuttgart type ones. The
QC chemistry packages used were mainly NWchem,[32] Turbo-
mole,[33] and Jaguar.[34] To reduce computing times the highest
symmetry group was always used, even during geometry
optimization. A comparison of the number of electrons and basis
set functions involved in EGP calculations and in all-valence
electrons calculations of Cp₆Lu₃H₃ is given in Table 1. In the
all-electron calculation, standard programs use ECP only on
heavy atoms. The reduction of the number of atoms, electrons,
and basis functions in EGP calculations with respect to standard
calculations appears clearly.
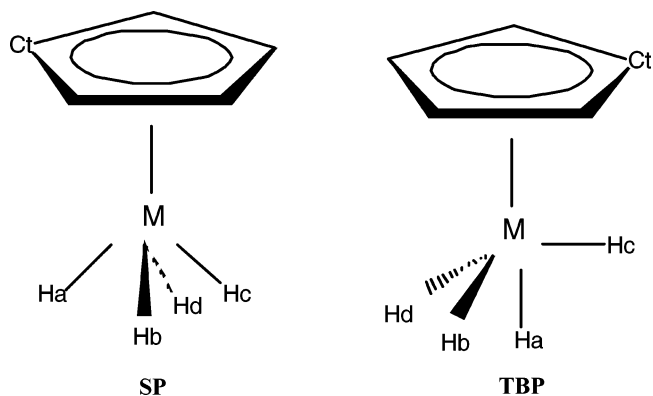
Figure 2. Basic structures for CpMH₄, square pyramid (**SP**) and trigonal
bipyramid (**TBP**). Ct is a carbon of the Cp ring.

**2. Application to Organometallic Complexes. 2.1. Flux-
ionality and H Exchange in Piano-Stool Complexes CpMH₄
(M = V, Nb, Ta).** In a preceding paper,[35] we have already
presented results with another EGP Cp# concerning piano-stool
complexes considered as pattern test molecules. It is a great
challenge for our method to be able to reproduce the potential
energy surfaces (PES) of such highly fluxional molecules as
these CpMH₄ complexes.

The CpMH₄ complexes, where M is a Group V metal atom,
belong to a group of seven coordinated molecules which are
found either with 3:4 coordination, i.e., a square planar structure,
or with 3:3:1 coordination, i.e., a trigonal bipyramid structure.
These two conformations are shown schematically in Figure 2.
The interconversion of the two geometries can occur in a simple
way via the Berry pseudorotation process.[36] In the absence of
polydentate ligands that enforce the geometry, the energies of
the various geometries are very close, and some five coordinated
complexes can exist as both square-pyramidal (SP) and trigonal-
bipyramidal (TBP) conformations in the same crystal.[37]

The geometries of all CpMH₄ complexes were optimized at
several levels of theory (HF, MP2, DFT). Direct comparisons
between the geometrical parameters obtained with Cp#, and in
reference calculations are presented in Table 2, and the relative
energies of the two conformers are given in Table 3 for niobium
and tantalum derivatives. All of the geometry optimizations were
followed by a vibrational analysis at the same level of
calculation, ensuring that the geometry corresponds to a
minimum on the PES.

Exploration of the PES reveals that SP and TBP stationary
points are found for CpMH₄ complexes and that these two
structures are local minima in all cases, the TBP form always
being the lowest energy structure. In Table 2, results with HF
calculations have been selected to show that EGP calculations
are able to reproduce SP structures and results obtained with
the correlated methods allow comparisons to be made between
reference and EGP calculations for the TBP forms. Close
agreement is obtained in each series, because the largest
difference between reference and EGP calculations is 0.04 Å
for bond lengths, 4° for valence angles and around 8° for
dihedral angles. The overall trend, for instance the increase of
M−H bond lengths down the group V, is reproduced well. This

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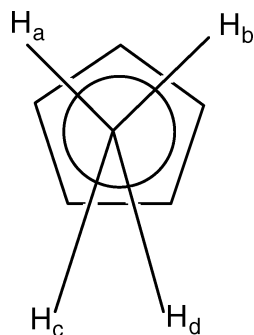Oxford, 1999.

Figure 3. Schematic representation of the η^2 structure.

Table 2. Important Bond Distances (Å) and Angles (deg) for the Optimized Geometry of CpMH$_4$ Complexes at Various Levels of Theory

CpMH$_4$	M = V		M = Nb		M = Ta	
	ref	EGP	ref	EGP	ref	EGP
HF	η^2 [a]	η^2	SP	SP	SP	SP
M-Ha	1.68	1.67	1.71	1.75	1.78	1.78
M-Hc	2.20	2.30	1.80	1.76	1.78	1.78
HaMHc	99.7	97.00	120.9	123.1	130.4	126.6
Ct[b]MHa Hc	−128.5	−134.4	−180.0	−178.9	−179.4	−179.5
MP2	TBP	TBP	TBP	TBP	TBP	TBP
M-Ha	1.64	1.60	1.76	1.76	1.77	1.77
M-Hc	1.65	1.64	1.75	1.76	1.76	1.77
HaMHc	79.9	75.0	79.5	79.5	80.0	80.1
CtMHaHc	0.0	−7.6	0.0	−4.9	0.4	−5.1
B3LYP	TBP	TBP	TBP	TBP	TBP	TBP
M-Ha	1.59	1.57	1.78	1.77	1.78	1.78
M-Hc	1.61	1.60	1.78	1.76	1.77	1.78
HaMHc	74.1	69.6	79.9	78.4	79.9	79.2
CtMHa Hc	−6.1	−2.2	37.0	42.8	37.0	43.2

[a] η^2 makes reference to the structure found at the HF level for M = V. [b] Ct is one of the carbons of the Cp ring (see Figure 2), used to define dihedral angles.

Table 3. Relative Energy (kJ·mol^{-1}) of Optimized Molecular Structures at HF, MP2, B3LYP Levels for M = Nb and Ta[a]

	Nb		Ta	
	ref	EGP	ref	EGP
ΔE_{HF}	9.15	13.19	9.99	18.05
ΔE_{MP2}	17.43	27.42	25.08	42.00
ΔE_{B3LYP}	19.70	32.02	30.40	49.40

[a] $\Delta E = E_{SP} - E_{TBP}$.

is due to the expansion of the nd orbitals, resulting in large Ta−H bonds. Moreover, relativistic effects, included in the ECP, are more important for the tantalum atom and explain the lengthening of the M−H distance.[38] An orbital correlation diagram for the metal d orbitals that connects SP and TBP geometries for d^0 systems, i.e., our case, indicates that our observation coincides with the fact that these molecules are found either as TBP or SP conformation because of the slight energy difference between the two forms. As is shown in Table 3, the relative energies between the two conformers for the EGP calculations compare fairly well with the reference values.

The optimized structure of CpVH$_4$ at the HF level presents an artifactual stabilization of a nonclassical complex (Figure 3) both in reference and EGP calculations. The H$_c$−H$_d$ calculated distance of 0.76 Å is very close to that in the H$_2$ molecule (0.75 Å). The large distance between V and the η^2-H$_2$ (2.30 Å with the EGP, 2.20 Å with the reference calculation) indicates that we can consider that the CpVH$_4$ complex does

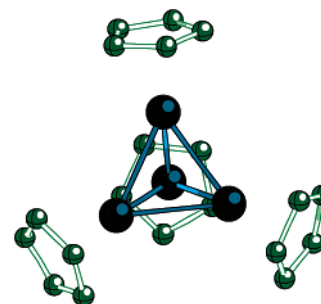(38) Desclaux, J. P.; Pyykkö, O. *Acc. Chem. Research* **1979**, *12*, 276.

Figure 4. Drawing of optimized geometry (T$_d$) of Al$_4$Cp$_4$.

not behave like a piano-stool complex on the HF PES. This peculiar structure, specific to the vanadium complex at the HF level, is certainly due to the small metallic radius (more contracted atomic orbitals) of V compared to those of Nb and Ta.[39] The existence of the η^2-H$_2$ form in the vanadium complex can be explained by a weak back-donation of metal d electrons to the H−H σ^* antibonding orbital. This implies that the transfer of d electrons to the hydrides H$_c$ and H$_d$ should not occur to form two covalent M−H bonds, unlike the case of the Nb and Ta complexes.

In view of these preliminary results, three comments can be made:

(i) Use of the EGP does not modify the shape of the potential energy surface of the active part at any level of calculation.

(ii) Use of the EGP does not perturb the virtual molecular orbitals spectral characteristics, because MP2 calculations give correct results

(iii) Results obtained with DFT calculations show that utilization of an EGP does not alter the electronic density of the active part, because in this case, also the reference and model results are almost identical.

2.2. Weak Bonding and Back-Donation: Structure of Al$_4$Cp$_4$. In this section, we report and discuss results of calculations carried out to test the ability of the Cp$^\#$ potential to reproduce the particularly weak Al$_4$ bonding in the Al$_4$Cp$_4$ cage compound (Figure 4). This remarkable characteristic will be governed by a pronounced π back-bonding effect in the monomer.

This part is intended to show that the Cp$^\#$ group potential is adequately defined to mimic this subtle effect.

In a first step, calculations on the monomer AlCp$^\#$ were performed, and in a second step computations on the tetramer were undertaken both at HF and post HF levels of theory. In Table 4 we have collected geometrical and energetic data relevant for comparison with results obtained by Ahlrichs et al.[40] on the same complexes. Due to the fact that, at post HF level, Ahlrichs et al. made estimate of correlation only, we have redone some calculations at the all-electron level. In the last column of Table 4, we recall the results obtained by Ahlrichs et al when Cp is modeled by a chlorine atom.

Regarding the monomer, the most important result is the perfect agreement between the population of the Aluminum p$_x$ and p$_y$ orbitals (0.39), which is attributable to the π back-bonding from the Cp ligand, in the reference and in the EGP calculations. Examination of the other orbital populations also shows an excellent agreement.

(39) Froese Fischer, C. *The Hartree−Fock Method for Atoms*; John Wiley & Sons: NewYork, 1977.
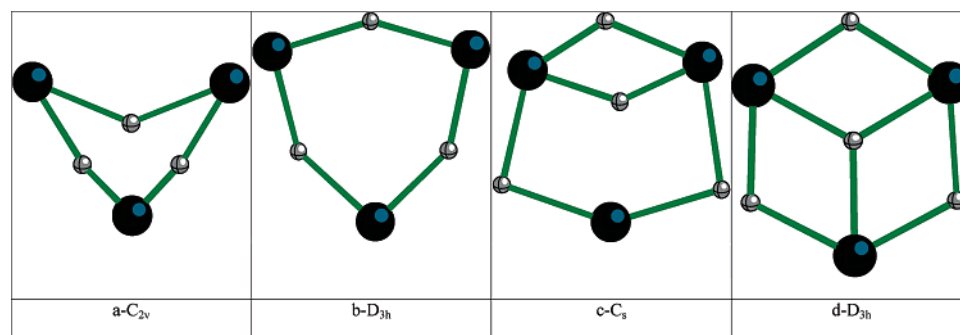(40) Ahlrichs, R.; Ehrig, M.; Horn, H. *Chem. Phys. Lett.* **1991**, *183*, 227.

Figure 5. Drawings of Lutetium complexes. The six Cp ligands are omitted for clarity.

Table 4. Computed Properties of the Monomer and the Tetramer for X = Cp, Cp#, Cl[f]

		ref X = Cp[d]	EGP X = Cp#	X = Cl[d]
AlX	AlX[a]	2.04	2.05	2.15
	q (Al3s)	1.89	1.89	1.86
	q (Al3p)	0.39	0.39	0.16
	q (Al)	0.46	0.44	0.47
Al$_4$X$_4$	AlX	2.06	2.06	
	Al−Al (HF)	2.80	2.85	2.64
	Al−Al (MP2)		2.78	
	Al−Al(B3LYP)	2.75[e]	2.80	
	q(Al)	0.38	0.40	0.40
	ΔE_{HF}[b]	42.00[d], 33.05[e]	−121.46	−145.
	ΔE_{MP2}[b]	−160.[c]	−345.	−363.
	ΔE_{B3LYP}[b]	−86.6[e]	−261.	

[a] Distance to the center of Cp. [b] $\Delta E = E_{Al_4Cp_4} - 4E_{AlCp}$. [c] Estimate of the correlation effect on tetramer stabilization. [d] see ref 40, [e] our reference calculations. [f] Bond distances in Å, valence shell occupations and atomic charges q from Mulliken population analyses, energy in kJ·mol^{-1}.

The calculated Al−Al bond distances in the tetramer are in the range of expected values. The inclusion of electron correlation either at the MP2 or B3LYP levels leads to a marked decrease of bond lengths compared to the uncorrelated HF calculations, and so correlated results are in excellent agreement with the 2.77 Å value reported experimentally. A substantial difference concerning, the binding energy was observed. We found that Al$_4$Cp$_4$ is stable with respect to 4 AlCp by 120 kJ·mol^{-1} at the HF level whereas, Ahlrichs et al as well as our reference calculations found a metastable state at around 40 kJ·mol^{-1}. The very fact that we found this geometry—which is a rather small minimum—make us think that, in our case, the brute application of the formula $\Delta E = E_{Al_4Cp_4} - 4 E_{AlCp}$ is rather dangerous. Indeed, since hydrogen atoms are missing and because the effective nuclear charge on the pseudo carbon is set to 1, energy terms corresponding to the interaction between two AlCp fragments in Al$_4$Cp$_4$ are not correctly evaluated. We assumed that this yields to an excessive stabilization of Al$_4$Cp$_4$ with respect to four AlCps. However, this missing term is the same in correlated and uncorrelated calculations. As a matter of fact we can see that the stabilization by the correlation, mainly between the four Al, is very well reproduced; 120 kJ·mol^{-1} vs 140 kJ·mol^{-1} at the B3LYP level. In addition, we also note that the computed charge transfer between Al and Cp is very close to that obtained in the reference calculation (0.40 vs 0.38). Note finally that the use of a chlorine atom to model the Cp ligand leads to an underestimation of important π back-bonding effects and consequently to a shortening of the Al−Al bond length in the Al$_4$ cage.

The overall agreement of our results with those published by Ahlrichs or our calculations ensures that the Cp effective

Scheme 1. Atom Numbering of Cp#$_6$Lu$_3$H$_3$ and Cp#$_6$Lu$_3$H$_4$ Anion
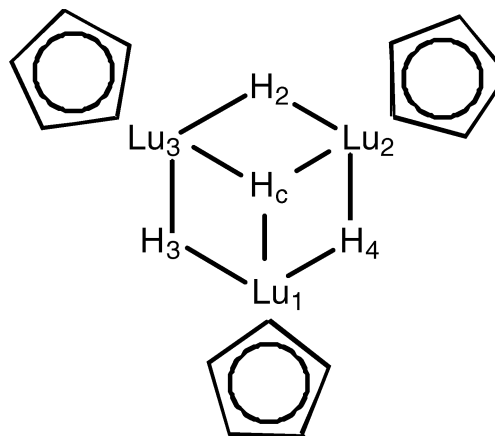
group potential can be used to study chemical problems where a back-bonding effect in weak bonding phenomena has to be reproduced.

2.3. Challenge for ab initio Calculations Cp#$_6$Lu$_3$H$_3$ and Cp#$_6$Lu$_3$H$_4$. Ten years ago, an unexpected trimeric arrangement of Cp$_2$LuH was characterized by X-ray crystallography.[41] The $[(\eta^5\text{-}C_5H_5)_2Lu]_3-(\mu_2\text{-}H)_2(\mu_3\text{-}H)$ experimental structure is represented in Figure 5a. This structure presents non−equivalent lutetium atoms, one of which is coordinated by three hydrogens. The most striking feature of this C_{2v} symmetry complex is the unusual distance (1.56Å) between Lu$_1$ and H$_3$ (see Scheme 1 for the numbering of the atoms of all structures) in comparison with the common value of 1.95 Å for Lu−H found in the literature.

In 1982, Evans et al.[42] have characterized by NMR spectroscopy the first trimetallic organolanthanide hydride: Cp$_6$Lu$_3$H$_4^-$. Interpretation of C NMR and H NMR spectra, which exhibit two inequivalent H environments in the ratio 3:1, allowed them to propose a D_{3h} structure for the anion $[\{(\eta^5\text{-}C_5H_5)_2 Lu-H\}_3(\mu_3\text{-}H)]^-$ (Figure 5d). A dozen years later, from an X-ray structural determination, Protchenko et al.[43] suggested a C_s structure for the same compound (Figure 5c). It should be noticed that this C_s structure also contains some unusual Lu−H bond lengths. In this case, a value of 2.75 Å for a Lu−H distance was reported.

The aim of the ab initio calculations reported in this part is to reproduce and to understand the unusual arrangement of

(41) Knjazhanskij, S. Y.; Bulychev, B. M.; Kireeva, O. K.; Belsky, V. K.; Soloveichik G. L. *J. Organomet. Chem.* **1991**, *414*, 11.
(42) Evans, W.; J.; Meadows, J. H; Wayda, A. L.; Hunter, W. E; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015.
(43) Protchenko, A.V.; Fedorova, E. A.; Bochkarev, M. N.; Schumann, H.; Loebel, J.; Kociok-Köhn, G.; *Izvestia. Akademii. Nauk. Rossijskaa. Akademia. Nauk. Seria. Himiceskaa* **1994**, *11*, 2027.

Table 5. Bond Lengths in Å, Angle in Degrees[a]

	experiment	valence electron calculation (LDA)	EGP (LDA)
Lu_1-H_3	1.56	2.06	2.12
$H_3-Lu_1-H_4$	88.3	143.0	146.0
ΔE [b]	-	610	501

[a] Experimental data in ref 41. Energy in kJ·mol^{-1}. [b] estimate, from single point calculations, of the energy difference for the $C_{2v} \rightarrow D_{3h}$ rearrangement.

Table 6. Bond Lengths in Å, Angles in Degrees[a]

	experiment (X-ray)	valence electron calculation (LDA)	EGP (LDA)	dimmer (X-ray)
Lu_2-H_4	2.75	2.36	2.40	-
Lu_2-H_2	2.13	2.36	2.40	2.13
Lu_2-H_c	2.04	2.36	2.35	1.98
$Lu_3-H_2-Lu_2$	115.5	120.0	116.0	118.0

[a] Experimental data from refs 43 and 44.

hydrogen atoms in Figure 5a and to make some structural investigations to solve apparent contradictions between different experimental results for both the $Cp_6Lu_3H_3$ complex and the $Cp_6Lu_3H_4$ anion. Due to their large size, these compounds are good candidates for calculations with EGP's. For this purpose, we used the EGP methodology with $Cp^\#$ instead of the real cyclopentadienyl ligand for the $Cp_6Lu_3H_3$ complex and in the $Cp_6Lu_3H_4$ anion.

$Cp^\#_6Lu_3H_3$. Geometries were optimized at both the Hartree−Fock and LDA levels. Vibrational frequencies analyses can be reasonably carried out in the EGP case. They are computed at the same level of theory to determine the nature of the optimized structure (minimum, saddle point).

Calculations failed to reproduce the structure 5a. Starting from the crystallographic structure, a lengthening of the Lu_1-H_2 distance takes place, during the Hartree−Fock optimization. This motion induces a rearrangement of the C_{2v} starting structure. The resulting optimized geometry shown in Figure 5b has D_{3h} symmetry; it is a true minimum. At the Hartree−Fock level there is no minimum in the region of the experimental structure because the molecule goes directly to the structure 5b.

When correlation is included with the LDA functional, the molecule tends to stay in this first region but the geometry optimization never really converges. So there is some singular point around the geometry proposed by Knjazhanskij et al.[41] Starting from the optimized D_{3h} Hartree−Fock structure, LDA geometry optimization and vibrational analysis let us identify the same D_{3h} structure as a minimum on the DFT PES.

Expensive all-electron calculations carried out for the sake of comparison confirm the results of the EGP calculations. Examination of Table 5 shows the agreement in both the geometrical parameters and energy values between EGP and reference calculations. The origin of the discrepancy between our results and the experimental X-ray data cannot be attributed to the use of the EGP. It is clear that the large energy difference between the C_{2v} and D_{3h} conformations does not allow us to confirm the possible existence of this unusual complex. Moreover, it should be noticed that Knajazhanskij et al. emphasize that they cannot completely rule out the contribution from two fragments: i.e., $[(Cp_2Lu)_2H]^+$ and $[Cp_2LuH_2]^-$ in the crystallographic sample of the trimer·. This suggestion has the advantage of supporting the observation of nonequivalent Cp_2-LuH fragments in the crystallographic structure of the trimer. Electrostatic interactions between the two ionic moieties in cooperation with crystal packing effects could be involved to explain the profound difference with our structure which exhibits three equivalent Cp_2LuH fragments.

$Cp^\#_6Lu_3H_4$. Calculations on the $Cp^\#_6Lu_3H_4$ anion were carried out at the LDA level because this method is well adapted to reproduce structural parameters quantitatively at a reasonable computational cost. Calculations with other types of functional, i.e., B3LYP and B3PW91, have also been carried out. Only the LDA results will be mentioned here, because the differences with the two other functionals are very small and because valence electron calculations have only been done with LDA, the two other functionals still being too time consuming for such a large chemical system. Pertinent bond lengths and angles are collected in Table 6 and compared with the corresponding X-ray data. Comparison with the experimental X-ray data is difficult, because it clearly appears that geometry optimization of structure 5c (X-ray data) at LDA level results in the structure shown in Figure 5d, which obviously corresponds to that proposed by Evans from NMR data. The D_{3h} structure has been found to be a minimum on the PES of the model anion.

Once again valence-electron calculations lead to the same conclusion even if we have no guarantee that the structure obtained is a minimum. The third and fourth columns of Table 6 show the very good agreement between reference and EGP geometrical parameters.

Despite our efforts the experimental X-ray structure was not located on the PES. According to our results, the D_{3h} geometry was the only one found in both cases ($Cp_6Lu_3H_3$ and $Cp_6Lu_3H_4^-$), in agreement with Evans et al. for the latter case. The Protchenko et al. structure does not seem to correspond to a stationary point on the PES. Examination of the structural parameters of the crystallographic complex observed by Protchenko et al. and symmetry arguments led us to postulate that the anion structure can be viewed as being formed by the combination of $(Cp_2LuH)_2$ and $[Cp_2LuH_2]^-$ fragments. In support of such a postulate, we note (i) the unusual bond distance Lu_2-H_4 (2. 75 Å) attributable to a hydrogen bond connecting the two interacting species, and (ii) the ability of the Cp_2LuH hydride to form an asymmetric dimer whose geometrical parameters are displayed in the last column of Table 6.[44] It is worth noting that the $[Cp_2LuH_2]^-$ moiety exhibits significant differences in the two complexes studied and that the hydrogen bond distance is longer than that found in the $Cp_6Lu_3H_3$ complex (distance $Lu_2-H_4 = 2.13$Å). Such structural changes are consistent with the different strength of the electrostatic interactions. In the first complex, the interaction take place between two ionic moieties, while in the latter case the electrostatic interaction involves an interaction between a neutral and an anionic species.

2.4. Controversial Experimental Result: What is the Structure of $Cp_6Zr_3O_4$? A few years ago, the structure of a trinuclear complex $[\{(\eta^5\text{-}C_5H_5)_2 Zr-O\}_3(\mu_3\text{-}O)]$ (Figure 7) with unusual distances and angles and a peculiar planar μ_{3-O} ligand

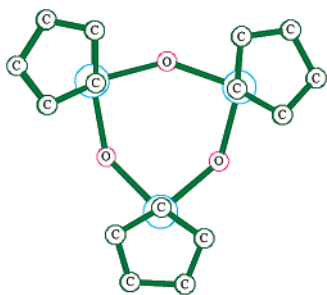(44) Schumann, H.; Genthe, W.; Hahn, E.; Hossain, M. B.; Van Der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67.

Figure 6. Optimized D_{3h} structure of $\{(\eta^5\text{-}C_5H_5)_2\,Zr\text{-}O\}_3$.
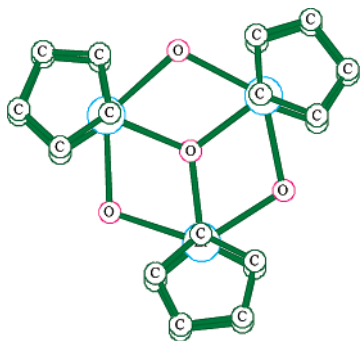

Figure 7. Drawing of the optimized O_4 planar structure.

in its center was reported.[45] The crystal structure was highly controversial, because it implies an oxygen atom with a fractional oxidation state. This neutral complex was obtained in small yield as an unexpected product of the hydrolysis reaction of a phosphane zirconocene complex, and the controversial crystal structure has attracted our attention. It gave us the opportunity to test our method on a case where reference calculations are missing, and the possibility to obtain a better understanding of this problem.

In a first step, we checked that EGP methodology was able to reproduce the structure of a well-known zirconium trinuclear complex: $\{(\eta^5\text{-}C_5H_5)_2\,Zr\text{-}O\}_3$ (Figure 6). Geometry optimization was undertaken for the trinuclear complex.

The geometry resulting from optimization is depicted in Figure 6 and in Table 7. The experimental X-ray structure is very satisfactorily reproduced. Bond lengths calculated at the HF level are slightly overestimated. As expected, inclusion of correlation with the B3PW91 method makes them closer to the crystallographic data.

With such a good agreement for the O_3 complex, a similar accuracy should be expected for the O_4 complex. Starting from experimental coordinates, geometry optimization of the O_4 complex leads to the structure shown in Figure 7. Some of the bond lengths and angles are collected in Table 7, together with the corresponding X-ray data. The environment of the zirconium atoms is well reproduced, since the largest uncertainty for the Zr–O bonds is 0.01Å and the calculated Zr–O–Zr valence angles are larger than the experimental ones by only 1.8°.

This preliminary result shows that the experimental O_4 planar structure is indeed quite reasonable. It can be rationalized by simple orbital interaction diagrams. In fact, the O_4 structure can be seen as a trimethylene methane type symmetry adapted orbitals.[46] In this scheme, the π interactions between the O_3

(45) Boutonnet, F.; Zablocka, M.; Igau, A.; Jaud, J.; Majoral, J. P.; Schamberger, J.; Erker, G.; Werner, S.; Kruger, C. *J. Chem. Soc. Chem. Commun*. **1995**, 823.

Table 7. Comparison between Experimental, HF and B3PW91 optimized Parameters for O_3 and O_4 Planar Structures[a]

		experiment	EGP–HF	EGP–B3PW91
$Cp_6Zr_3O_3$	ZrO	1.95	2.01	2.00
	Zr–O–Zr	146.1	145.7	145.8
$Cp_6Zr_3O_4$	ZrO	2.21	2.22	2.20_5
	ZrOc[b]	2.09	2.10	2.09
	Zr–O–Zr	108.5	110.3	110.3

[a] Bond Distances in Angstroms and Angles in Degrees. [b] O_C is the central oxygen of the O_4 planar structure.

Table 8. Bond Lengths (Å) and Angles (deg) for the Deck-Chair Conformation

	B3PW91
Zr_1–O_4	2.09
Zr_3–O_5	2.08
Zr_1–O_6–Zr_3	138.20
Zr_3–O_5–Zr_2	137.00
O_5–O_7	1.54
O_5–Zr_3–O_6–Zr_1	26.00

Scheme 2. Dashed Arrows Indicate a Motion Away from the Reader. Bold Arrows Indicate a Motion toward the Reader
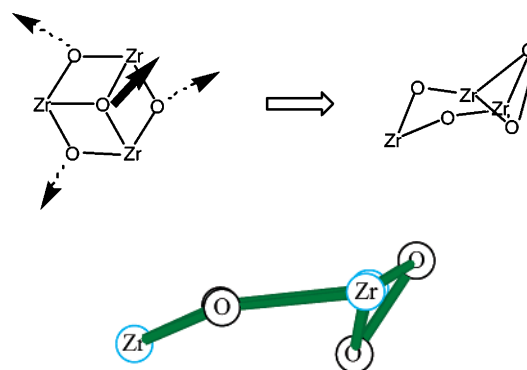

Figure 8. Drawing of the deck-chair structure. The six Cp ligands are omitted for clarity.

pattern and the empty atomic orbital p_π of the added oxygen provide possible stabilizing factors of great importance.

Vibrational analysis of this optimized D_{3h} planar geometry clearly indicates that this structure is a saddle point on B3PW91 potential energy surface. The imaginary frequency corresponds to a deformation that can be seen as the ring-puckering mode which leads on the DFT potential surface to the deformation illustrated on Scheme 2.

The resulting puckered structure, called the deck-chair structure, is presented in Figure 8 and in Table 8. This unexpected structure of C_s symmetry is characterized as a local minimum on the B3PW91 potential energy surface. The relative energetic data for each stationary point as determined at the DFT level along an idealized reaction pathway are shown schematically in Figure 9. The planar structure lies no less than 313 kJ·mol^{-1} above the puckered structure. To understand the nature of the interaction providing stabilization of the deck-chair form, we have examined the molecular orbital spectrum of the three structures. Examination of the occupied molecular orbitals from our calculation reveals π delocalization between the p_π orbital of the central oxygen atom and the rest of the molecule. The energies of the π molecular orbitals of the O_3

(46) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985.
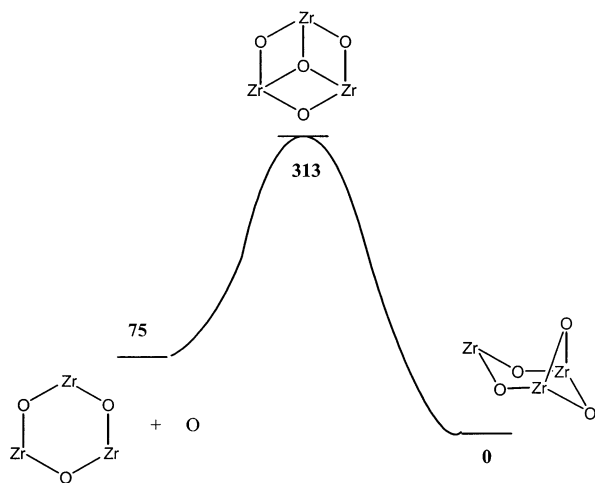
Figure 9. Relative energy diagram (kJ·mol^{-1}) for the stationary points determined at the DFT level. Cp ligands are omitted for clarity.

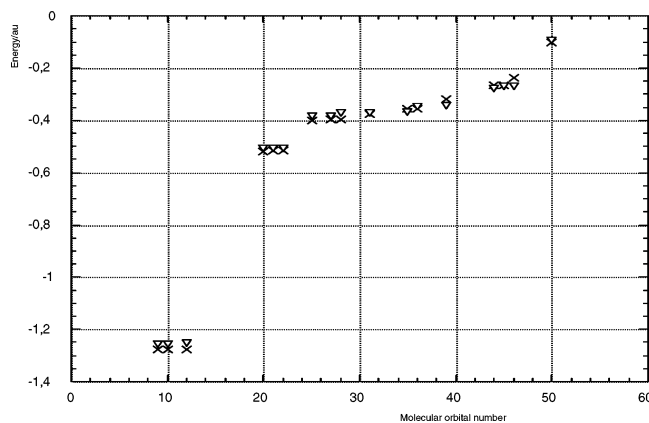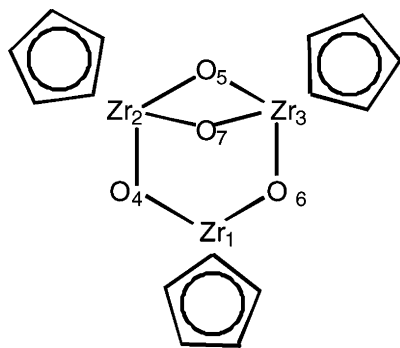**Scheme 3.** Atom Numbering of Deck-Chair Structure

Figure 10. Energy of π molecular orbitals of the O$_3$ ($\triangledown$) and planar O$_4$ ($\times$) systems

and the O$_4$ systems are shown in Figure 10. In fact the planar structure is only slightly stabilized by π-type interactions.

Among the MOs of the planar structure, only one shows a significant bonding π interaction between the p$_\pi$ orbital of the central oxygen and the zirconium atom, but none of them with the O$_3$ ring. Others are nonbonding or antibonding MOs with respect to the central oxygen atom. The stabilization is clearly less important than that involved in the trimethylene methane system. π delocalization seems insufficient to prevent the folding of the six-membered ring, which provides the appearance of an unusual oxo-bridged arrangement characterized by an O$_5$–O$_7$ distance (1.54 Å) which can be compared to the calculated distance in the dianion O$_2^{2-}$ molecule (1.66 Å).

Table 9. Mulliken Population Analysis of O$_3$ and O$_4$ in the Deck-chair Conformation

atom	O$_3$	deck-chair O$_4$
Zr$_1$	1.48	1.47
Zr$_2$		1.38
Zr$_3$		1.38
O$_4$	−0.35	−0.34
O$_6$		−0.34
O$_5$		−0.28
O$_7$		0.04

Mulliken population analysis of the three complexes confirms the existence of an O$_2^{2-}$ fragment in the puckered ring. In the planar O$_3$ complex the charges are +1.48 and −0.35 for Zr and O respectively, which are consistent with the usual formal oxidation states of +IV for the metal and −II for the oxygen atom. As seen in Table 9 this correspondence allows us to assign an oxidation state of −II for each equivalent oxygen (charge of −0.34) in the deck-chair structure, the total contribution of the two remaining oxygen atoms (−0.28 plus 0.04) leading to a charge distribution which can be considered equivalent to −II.

To our knowledge, no oxo-bridged structure with a Cp$_2$ Zr pattern has been reported in the literature. We only found some structures with a similar pattern of dioxygen internuclear distances in the range of 1.3–1.6 Å. Nevertheless, a very similar structure is reported with a rhenium instead of a zirconium atom.[47]

On the other hand, the most favorable bonding contributions between the O$_7$ and the O$_5$ atomic orbitals appear when the ring puckers. The MO spectrum of the deck-chair structure exhibits the well-known set of MO of an O$_2^{2-}$ unit. These MO show significant stabilization by a bonding interaction of the fragment orbital corresponding to the O$_2$ part and the two nearest zirconium Atoms. Two of the MOs that give stability to the molecule in its deck-chair form are represented in Figure 11. The first one (Figure 11a) corresponds to an antibonding interaction between a σ_g orbital of O$_2$ fragment and p orbitals of the zirconium atoms. The second one clearly shows (Figure 11b) interactions between one of the π_g orbital of O$_2$ and the d$_{xy}$ orbitals of the metal.

The puckering allows bonding interactions between the O$_2$ fragment and the two remaining oxygens which cannot occur when the structure is planar. One of these interactions is shown in Figure 11c.

Finally, the orbital energies of the two conformations are compared in Figure 12. It is clear that all molecular orbital energies undergo relatively little change during the folding of the ring, except for those lying around −1 hartree. In the deck-chair structure, these MOs are those which support the appearance of the O$_2$ fragment, as represented in Figure 11a. However, the energy change of the MOs is not sufficient to explain the total energy difference (313.5 kJ·mol^{-1}). The conformational preference for the C_s structure over D_{3h} that emerges from our computations is the result of rather complicated and subtle orbital interactions. The calculated planar O$_4$ structure corresponds exactly to the one reported in ref 43. This result confirms that our method produces consistent structures in good agreement with experimental structure determinations. The fact that this compound was crystallized once and in a poor yield could

(47) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; Wiley & Sons: New York, 1999.
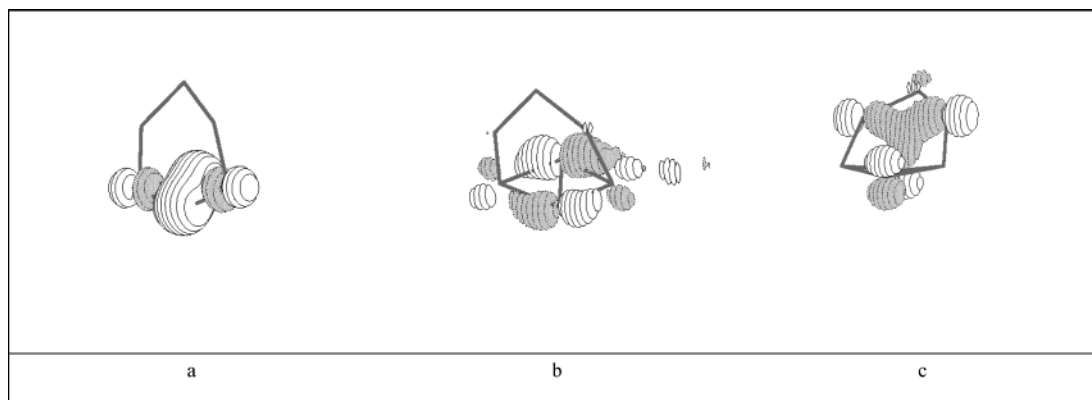
Figure 11. Three-dimensional representation of occupied molecular orbitals of the O_4 deck-chair structure.
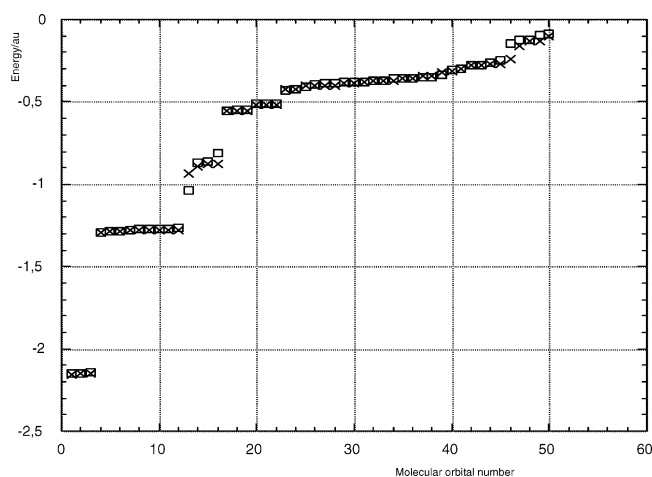

Figure 12. Energy of molecular orbitals of O_4 complexes: deck-chair ($\square$) and O_4 planar ($\times$).

be correlated with the frequency analysis which states that the O_4 planar structure in gaz phase is a saddle point on the potential energy surface.

In 2000, Niehues et al.[48] have suggested another formula for the planar species from a new hydrolytic pathway. They proposed a Zr_3O_3 hexagon with a μ_3-O in its center, but each of the three oxygens of the ring was protonated and connected to a THF molecule by a hydrogen bond in the crystal structure. The molecular structure of this cation exactly corresponds with the neutral planar structure proposed by Boutonnet et al. Calculations which take into account this last information may be necessary to resolve this issue fully.

Conclusion

The effective group potential for the cyclopentadienyl ligand, $Cp^\#$, presented and illustrated in this article shows that accurate calculations can now be performed with far less computational effort than previously. This approach to modeling opens a new route to perform electronic structure calculations on systems that are not easily amenable to standard ab initio calculations. The quantum potential generated by the $Cp^\#$ system successfully reproduces molecular orbital wave functions of the real Cp group. Consequently, this $Cp^\#$ can be successfully used in different molecules of different degrees of complexity at different levels of calculations, showing that such an EGP is

(48) Niehues, M.; Erker, G.; Meyer, O.; Fröhlich, R. *Organometallics* **2000**, *19*, 2813.

fully transferable to molecules and can be used at various levels of computations (with or without electronic correlation effects)

In a first step, tests have been performed to check that the use of $Cp^\#$ gives agreement with all-valence-electron calculations. Very cheap calculations provided quite accurate geometrical as well as vibrational information, and they succeeded in reproducing subtle physical chemistry features. The first test deals with the flatness of the $CpMH_4$ surfaces. Calculations on these systems show the robustness of this EGP. The potential energy surface of the active part, MH_4, of these complexes is accurately reproduced. Charge distribution in the active part of $Al_4Cp_4^\#$ appears not to be altered by the use of the group potential. Our results are comparable with those found by Ahlrichs on the real system: a pronounced π back-bonding effect in the Al $3p_\pi$ can be responsible for the large Al−Al distance in the Al_4 cage. This suggests that the mixing between the $Cp^\#$ wave function and the 3p orbital of Aluminum is well reproduced. These calculations are good illustrations of the degree of confidence one can place in the $Cp^\#$. The efficiency of the $Cp^\#$ potential is thus well established. However, improvements should be included in order to better take into account the repulsion between the fictitious groups and the active part of the molecule; especially when a large reorganization take place, as it is the case in the tetramerisation of AlCp in Al_4Cp_4.

Our future goals are now accessible: to be able to treat problems with large molecules at a high level of calculation (MP2, DFT) without any loss of accuracy. The elucidation of some controversial experimental structures of large molecules will be a matter for our method. Calculations on the Cp_6Lu series are fully satisfactory. They have left out the conformations with unexpected structural parameters, especially in the case of the Cp_6LuH_3 complex. Concerning $Cp_6LuH_4^-$ the results of our calculations confirm the structure predicted by NMR experiments. The D_{3h} structure was found to be a minimum on the potential energy surface, unlike the crystallographic structure which does not correspond to a stationary point. Successful application of the EGP method to these cases previously exposed allows us to question the very existence of a *neutral planar* $Cp_6Zr_3O_4$. We found this neutral planar structure was a saddle point on the potential energy surface. Searching for a minimum led to a puckered structure called a *deck-chair* conformation. The main feature of this structure is the emergence of an unusual peroxide ligand coordinated to two zirconium atoms with an O−O bond distance of 1.54Å. Analysis of the results of our

calculations allows us to make some additional general comments. The active part of the molecule, the part of interest, not only preserves all of its chemical properties but the simplification of the initial chemical system make the interpretation of results easier, especially for the large molecules case. The most obvious simplification is the one relative to the molecular wave functions from which molecular properties are usually discussed; qualitative understanding and quantitative predictions are still possible. A second important advantage is the reduction of the degrees of freedom in an optimization of geometry. Small and unimportant movements of the ligand are eliminated and thus rapid convergence is observed in most cases. A last comment concerns the use of density functionals. This work shows that the electronic density of the active part of the molecule is not spoiled by the use of an effective group potential.

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