11324 *J. Phys. Chem. A* **2006,** *110,* 11324−11331

Structural and Electronic Analysis of Lanthanide Complexes: Reactivity May Not Necessarily Be Independent of the Identity of the Lanthanide Atom − A DFT Study

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Received: February 10, 2006; In Final Form: July 12, 2006

Density functional theory calculations were used to study a given complex for the whole series of lanthanide cations: [Ln(C_3H_5)Cp(OMe)] (**1**) [Ln = La ($Z = 57$)−Lu ($Z = 71$)], the radioactive lanthanide promethium ($Z = 61$) excepted. Contrary to the common assumptions, the calculations suggested a significant, albeit indirect, contribution of f electrons to bonding. Relativistic effects were considered in the calculations of the bonding energies, as well as in geometry optimizations in both spin-restricted and unrestricted formalisms. The unrestricted orbitals were finally used for the analysis of the charges and the composition of the frontier orbitals. It was confirmed that the ionic character was more pronounced for complexes of the late lanthanides.

Introduction

In recent years, the chemistry of lanthanides has attracted a great deal of interest, due to their high potential in molecular catalysis.[1−7]

It is commonly assumed that the f electrons of lanthanides are not involved in the chemistry of their complexes, because the f orbitals are significantly more contracted than the valence d or s orbitals in rare earths. This is widely understood because of the dependence of the orbital radii with the principal quantum number, which makes the 4f orbitals closer to the nuclei than the 5d and further than the 6s orbitals. Moreover, the relativistic effects will contract s and p orbitals with respect to nonrelativistic ones, and because the nuclei are accordingly more shielded, the f and d orbitals are on the contrary slightly relaxed, leading to destabilized energy levels.[8,9] Typical orbital radii are given in Table 1.[10]

Because most of the electronic density originating from the f orbitals exhibits a rather small overlap with the density of neighbor atoms, taking into account the f orbitals into geometry optimization calculations usually leads to geometries quite close to that obtained in calculations where the f orbitals are frozen into the so-called pseudopotentials (or effective core potentials), or frozen core approximations. This has been shown on many occasions[11−16] and provides a substantial economy in computation power. On the other hand, although the f orbitals exhibit a rather small overlap with interacting ligand orbitals, they possess energies that can become rather close to the corresponding ligand ones, and therefore, they can be significantly involved in the reactivity of lanthanide complexes, as already postulated by several authors.[17−21]

Moreover, the degree of covalency/ionicity in lanthanide−carbon bonds may be related to the catalytic behavior of rare earth complexes (e.g., for diene polymerization),[22,23] and careful examination of the nature of bonding in active species is therefore of interest, because a slight difference in the ratio may induce significant differences in catalytic properties that respond rather exponentially to energy-related differences. Other properties related to the valence electronic densities may also be affected: in a recent study, Sénéchal et al. observed a variation of nonlinear optical (NLO) properties along a series of lanthanide complexes.[24] NLO properties are known to be sensitive to (valence) electron density localization. Quite recently, Tancrez et al. observed a strong variation of the hyperpolarizability of lanthanide terpyridyl complexes with the f orbital filling, suggesting the direct contribution of f electrons to the hyperpolarizability.[25] In an already old study, Chatterjee et al.[26] showed in X-ray diffraction studies that the coordination environment in Ln(H_2O)$_9^{3+}$ may vary significantly along the series and that an excess in charge density located in trans of each ligand could be observed, the maxima being located on a sphere of ca. 70 pm radius, a value close to the radii of 4f orbitals (see Table 1).

TABLE 1: Orbital Radii (pm) of Some 4f Metals (from ref 10)

metal	6s	5d	4f
Ce	217	113	37
Gd	201	102	30
Lu	187	95	25

The purpose of the present article is to present numerical evidence of this behavior, which leads to differentiated reactivity of lanthanide complexes with their atomic number, an effect that has often been seen experimentally.[7,27,28] Therefore, since all rare earths are not equivalent, they have to be carefully selected for new syntheses, and other parameters, such as some economical features like their natural abundance (the lighter ones are the most common, and therefore the cheapest), need to be taken into consideration.

Computational Details

The density functional theory within the Kohn−Sham methodology has been used. Zhang and Wang modified Perdew−

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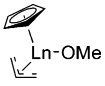
10.1021/jp060876d CCC: $33.50

SCHEME 1



Burke−Ernzerhof (PBE) exchange functional (revPBE) coupled to the PBE correlation term have been employed in the generalized gradient approximation (GGA).[29,30] This functional retains the robustness of PBE and gives improved atomic energies with respect to PBE. The local density approximation (LDA) has been used in a first step for a preliminary geometry optimization of the lanthanum complex. The calculations have been performed using the ADF03 and ADF04 program packages.[31] When not specified, the basis set is of double-ξ quality (basis II according to ADF02 terminology) and a small frozen core was employed. Therefore, the 4f electrons belong to the valence electrons. Relativistic effects are expected to be significant for heavy elements, and hence these effects have been taken into account for all electrons in the present calculation with the zero-order regular approximation (ZORA).[32−34] Finally, the integration grid parameter, setting the numerical integration accuracy, has been fixed to 4.5 or 5.0.

Test calculations have been performed with a larger basis set, namely a triple-ξ + polarization quality (TZP, basis IV in ADF02 terminology) for three complexes, namely those of lanthanum, dysprosium, and neodymium. No significant difference with the DZ calculation has been obtained, validating the use of the DZ basis sets for the set of calculations. Supplementary calculations with TZP basis set have also been performed as single points at geometries optimized with the DZ basis set. Finally, bonding energies have also been calculated with respect to atoms in open shell state, within a configuration corresponding to the (high spin) ground state, or an average of states of lowest energy. (For this purpose, $C_{\infty v}$ and C_{2v} symmetries have been retained, which do not, however, lead straightforward to f^{5-9} configuration.) The spin contamination has been small in all calculations, and the expectation values of $\langle S^2\rangle$, calculated by the algorithm of Bulo et al.,[35] deviated only by a few percents above the theoretical value. Detailed validation of the basis set used and the spin contamination are shown in the Supporting Information.

All lanthanide complexes have been considered, promethium excepted, because, due to its radioactive-only state, its experimental preparation is more expensive and no real interest in its chemistry can be found.

Results and Discussion

The studied lanthanide complexes [Ln(C_3H_5)Cp(OMe)] (**1**) (Ln = La−Lu, Cp = C_5H_5) (see Scheme 1) have three mononegative ligands.

Therefore, the metal centers are formally at the +3 oxidation state. The Cp ligand, as well as the allyl ligand, is sometimes considered to exhibit a radical-like behavior in opposition to more ionic ligands (see, for example, ref 36). Therefore, if one assigns a negative one-half formal charge to each of them and keeps the methoxy as a single electron acceptor, one obtains a formal charge of +2 for the lanthanide charge. An oxidation degree (OD) 2 is still realistic for covalent compounds of lanthanide, whereas the OD 3 is known to be traditional in ionic compounds. We will see further on that this formal OD = 2 is not far from the theoretical computed charges. Finally, the hapticity of the complex is 9, a value quite common in complexes of elements in the $Z = 57$ (La) to $Z = 73$ (Ta) range. If the ligands could be considered as points (their centroids), the complex could be regarded as trigonal planar. If we consider more classically that ligands Cp and allyl take three and two coordination sites, respectively, we have a standard 6-fold coordinated complex. This kind of complex was chosen because we wished to consider a potentially reactive molecule. Actually, **1** fits well with this criteria: it bears two moieties, Ln−allyl and Ln−alkoxide, which are known as active species, respectively, toward apolar (e.g., conjugated dienes)[37] and polar (e.g., ϵ-caprolactone)[38] monomer polymerization. The stereoelectronic environment is completed by a Cp ligand, and monocyclopentadienyl lanthanide complexes are known to exhibit a catalytic activity toward a large variety of substrates.[39] Among the most recent results in the field of lanthanide-based polymerization catalysis, those involving monoCp derivatives are undoubtedly the most spectacular (i.e., the copolymerization of ethylene with dicyclopentadiene[40] or the insertion of ethylene into syndiotactic sequences of polystyrene[41] and also the references mentioned in ref 39.)

It is generally accepted that the active moiety in styrene and butadiene (isoprene) coordination polymerization is a metal−allyl one. Actually, a CpLnOR(allyl) molecule represents a highly probable active species that intervenes in the block copolymerization of styrene with ethylene carried out with a divalent Cp*LnOAr initiator[42] (this initiator is oxidized in a trivalent derivative, Cp*LnOAr($CHPhCH_2PS$) − PS is the growing polystyrene chain − in the presence of styrene). Moreover, it was postulated that the mechanism could exhibit an ionic character, and thus it is of interest to evaluate, as done in our study, the nature of bonding in such compounds, especially concerning the active Ln−allyl moiety. As already said, **1**, the molecule under study, is just derived, for evident saving of computational resources, from a Cp*LnOR(allyl) molecule, with Cp instead of Cp* and OMe instead of OAr.

In the first step, the lanthanum complex [La(C_3H_5)Cp(OMe)] (**1a**) geometry was optimized by using a medium frozen core and the LDA approximation (the medium frozen core differs from the small frozen core through freezing Ln 5s and 5p orbitals in the medium core). In the great majority of systems, the LDA leads to realistic structures with generally too strong bonds, and sometimes too short distances.[43] Introducing GGA or most sophisticated exchange-correlation functionals usually leads to larger bond lengths (and of course more reliable energies), but quasi-homothetic structures. In some cases, however, in particular when weak bonds are present (e.g., explicit solvent molecules), LDA structure may be artifactually distorted.[44] Relativistic effects were not taken into account for this first optimization. To check the quality of the basis set, **1a** was recalculated with a small frozen core, so that the 5s and 5p electrons do belong to the valence orbitals. Significantly smaller bond lengths were obtained, indicating that a polarization of the density by the ligands is significant and needs its description by occupied s+p+d (and f) orbitals. Moreover, the 4f electrons may contribute to the lanthanide complex bonding since the 4f orbital occupation is significantly smaller than its value in a free Ln atom. One can stress that this by no means indicates a direct participation of an f orbital to the bond, but rather, through a noninteger occupation (e.g., 0.3 e^- in a Mulliken population analysis of the La complex, see below), a subsequent depletion of the 5d orbital, which is more involved in the bonding, is obtained (if one assumes that the 6s orbital is quasi-totally depleted in agreement with the oxidation state of the rare earth center). Therefore, the observed effect in the bond length can be considered as an indirect core−valence correlation effect induced by the differences in the (valence) basis set. This effect

TABLE 2: Bond Length (Å) for [La(C_3H_5)Cp(OMe)] (2) Computed with the LDA Approximation and No Relativistic Corrections

	d(La−Cn)[a]	*d*(La−C(1))	*d*(La−C(2))	*d*(La−C(3))	*d*(La−O)	*d*(O−C(4))
core medium	2.621	2.766	2.834	2.792	2.141	1.427
core small	2.555	2.697	2.783	2.740	2.098	1.429

[a] Cn is the centroid of the cyclopentadienyl ring.

TABLE 3: Computed GGA Bond Length (Å) for [Ln(C_3H_5)Cp(OMe)] (1) [Ln = La−Lu] at the ZORA Relativistic Level, DZ Basis Set, Small Frozen Core

	d(Ln−Cn)[a]	*d*(Ln−C(1))	*d*(Ln−C(2))	*d*(Ln−C(3))	*d*(Ln−O)	*d*(O−C(4))
La	2.624	2.766	2.831	2.894	2.128	1.459
Ce	2.566	2.718	2.774	2.747	2.105	1.459
Pr	2.559	2.724	2.779	2.742	2.094	1.458
Nd	2.541	2.720	2.764	2.723	2.090	1.456
Sm	2.529	2.772	2.786	2.779	2.085	1.452
Eu	2.521	2.796	2.807	2.880	2.094	1.450
Gd	2.477	2.646	2.685	2.650	2.045	1.452
Tb	2.436	2.634	2.660	2.637	2.041	1.451
Dy	2.444	2.630	2.659	2.635	2.032	1.449
Ho	2.431	2.633	2.653	2.641	2.032	1.447
Er	2.427	2.632	2.665	2.692	2.031	1.446
Tm	2.416	2.684	2.673	2.702	2.032	1.444
Yb	2.405	2.691	2.681	2.807	2.032	1.453
Lu	2.354	2.544	2.566	2.548	1.983	1.445

[a] Cn is the centroid of the cyclopentadienyl ring.

is similar to that observed by Dolg and Cao in their post Hartree−Fock calculation of La and Lu compounds where a significant change in the bond length was found for different sizes of their active space.[45] Table 2 shows the bond lengths for [La(C_3H_5)Cp(OMe)] compared with the LDA approximation and no relativistic corrections.

The GGA approximation was employed for further calculations and took into account the relativistic effects within the ZORA formalism. Compared to the previous calculation, for which the LDA approximation and no relativistic effects were used, a significant, but expected,[43] bond length increase was obtained (Table 3). It is noteworthy that the values of the bond distances calculated are comprised in the usual ranges for half-metallocenes of the lanthanides: *d*(Ln−Cp) = ca. 2.40−2.60 Å, *d*(Ln−C(allyl)) = ca. 2.60−2.80 Å, *d*(Ln−O) = ca. 2.00−2.1 Å (see, for example, refs 46 and 47).

No strong variation in the bond angles can be noticed, and the largest variations are related to:

(i) the Cp−Ln−O angle, which increases from 119 ± 1 for La−Sm to 124 ± 1.5 for Gd−Lu,

(ii) the central C(allyl)−Ln−O angle, which decreases from 104 for La−Eu to 101 ± 1.5 for Gd−Lu, and

(iii) the terminal C(Me)−O−Ln angle, which varies from 174 ± 1 for La, Ce, and Lu to 178 ± 1.5 for others, whereas angles such as C−C−C(allyl) remain constant, equal to 125 ± 0.5. A selection of angles is reported in Table 14 of the Supporting Information.

Variation of the Lanthanide Center. The heavier the lanthanide atom, the more important the relativistic effects. Therefore, the s and p orbitals of the later lanthanides are more contracted, so that the bond lengths are smaller than those for the early lanthanides. This trend known as the "lanthanide contraction" is of course well-known and widely described in textbooks.[48] More precisely, the contraction is enhanced by a poor screening effect of the f orbitals, an effect that is not additive to the relativistic effect.[49,50] It has already been observed during the past 10 years, in different contexts, although many calculations were limited to a few Ln atoms of the series.[51,52] The general trend obtained here is therefore a quasi regular decrease of *d*(Ln−Cp), *d*(Ln−C_3H_5), and *d*(Ln−O) when the atomic number of the rare earth increases (Table 3). This regular trend is, however, broken for *d*(Ln−C_3H_5). The results can be summarized as follows:

For the heavier elements, if one excepts the special cases of Eu and Yb, discussed later, one obtains a quasi-similar Ln−C(1) and Ln−C(3) distance, slightly smaller than Ln−C(2). This is typical of the allyl coordination, the asymmetry Ln−C(1)/Ln−C(3), possibly connected to the absence of symmetry in the complex (because of the methoxy group), being in fact related to a differential localization of the π system (see further).

For the lighter elements, a marked difference, particularly with La, is noticed. This could be tentatively related to the chemical reactivity: it was shown in many occasions that the larger lanthanides (La, Nd) are much more active in conjugated diene polymerization.[7,28] Moreover, in general, allylic molecular catalysts in this series exhibit dissymmetric allylic ligands with one shorter Ln−C distance, for example, (C_5Me_5)Ln(allyl)$_2$(dioxane) (Ln = La, Nd),[46] or similarly in an allyl−neodymium complex for styrene polymerization[53] preceding a possible $\sigma-\pi$ allylic rearrangement, and hence insertion of the monomer.[54,55] On the other hand, Nd(allyl)Cl(THF)$_5^+$, proved as inactive, bears a symmetric allyl group.[46]

When the series crosses the europium and ytterbium cases, the Ln−allyl bonding involves preferentially Ln−C(1) and Ln−C(2). The splitting up of the two distances Ln−C(1) and Ln−C(3) observed indicates that one external carbon of the allylic group is much less bonded to the central Ln atom than the two other carbons, keeping an enhanced radical character of the allyl. Said differently, the allylic group does not exhibit such a strong delocalization of its π system as in other complexes. In the HOMO − 1 of these two complexes, the coefficient of the p orbital for the further of the two outer carbons is bigger than that for the closest one (Figure 1; Table 4).

This is directly connected to the differences in the corresponding bond lengths, reported in Table 3.

Furthermore, the values *d*(Ln−Cp) and *d*(Ln−O) are also special for these two elements. For example, the Eu−O or Eu−Cp is slightly longer than that expected from an extrapolation of the corresponding bond lengths for the Ce−Sm complexes. Indeed, one knows that Eu and Yb elements exhibit easily a

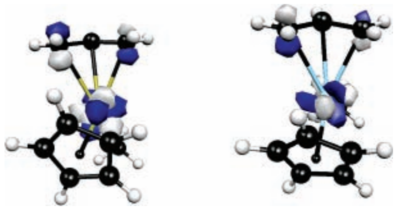


Figure 1. Homo − 1 of compound **1**. Left: Ln = Eu. Right: Ln = Yb (the left carbon is the longer bonded one).

TABLE 4: HOMO − 1 Composition for Ln(C_3H_5)Cp(OMe)] (1) [Ln = Eu, Yb] and Energy (eV)

	C(1)	C(3)	Ln	other atoms	energy
Eu	4.9% p	6.8% p	74.8% f	13.6%	−4.739
Yb	4.3% p	6.4% p	81.4% f	7.9%	−4.818

formal oxidation state of +2 rather than +3, because in such cases they have one half-occupied f shells. This assumption is confirmed by the charge analysis (Table 5). If an atom has a lower oxidation state, its covalent radius is larger than what is found for these two elements. By way of illustration, the Yb−ketyl complex ($C_5Me_4SiMe_2NPh$)Yb($OC_{13}H_8$)(THF)$_2$, in which the Yb element exhibits some divalent character, displays a Yb−O distance[47] (2.15 vs 2.04 Å) significantly higher than that in the pure Yb(III) dimeric [($C_5Me_4SiMe_2NPh$)Yb(μ-$OC_{13}H_8$)-(THF)]$_2$.

The following discussion will be related to the atom charges. One knows that they are pure theoretical objects that cannot be measured. However, they provide great insight into the chemical properties. The most widely used are Mulliken[56] charges, which can be divided into s, p, d, and f subcharges, but which are basis set-dependent and sometimes unrealistic. Hirshfeld[57] charges, on the contrary, are more robust, and often preferred, but less often calculated by quantum chemical software. Looking at the Mulliken charges of the lanthanide center, an increase from La to Lu is observed, except for Eu and Yb for the reasons just mentioned (see above), corresponding to a decrease of the Mulliken charge by ca. 0.15 e$^-$ below the interpolated charge of the $Z \pm 1$ complexes. The ligands are negatively charged. The charge of the oxygen atom decreases in the same way as the charge of the lanthanide center increases. Hence, the bonding La−O has a very strong ionic character with a charge difference larger than 2.5. This ionic character becomes more important for the late lanthanides (Table 5). Such a conclusion could not be drawn from a similar study involving cyclopentadienyl lanthanide complexes.[58] In a study bearing on a few lanthanide trihalides, Adamo and Maldivi[59] reached an opposite conclusion, but their compounds were significantly different from ours because of a stronger ionic character of the bonds and a clearly defined formal OD +3 of the Ln atom, in contrast to our complex.

The special cases of Eu and Yb already mentioned for the bond lengths lead also to different charges on some atoms of the complex. The Mulliken charge on the Ln atom is significantly smaller than could be obtained from an extrapolation of the charges at the beginning of the La−Sm or the Gd−Tm series. This is directly related to the already mentioned tendency of these elements to accept OD = 2 instead of 3. As a consequence, the allyl anion should exhibit a structure closer to that of an allyl radical. The Mulliken population of its C

TABLE 5: Mulliken Charge Analysis for [Ln(C_3H_5)Cp(OMe)] (1) [Ln = La−Lu]

	Ln	C(1)	C(2)	C(3)	O	C(Cp)$_{ave}$	Δ(Ln − O)[a]	C(1+2+3)[b]	Δq C(1+2+3)[c]	C(1)−C(3)[d]
La	1.900	−0.818	−0.363	−0.827	−0.784	−0.432	2.684	−2.008	0.000	0.0086
Ce	1.905	−0.812	−0.373	−0.829	−0.781	−0.434	2.686	−2.014	−0.003	−0.017
Pr	1.980	−0.831	−0.373	−0.839	−0.786	−0.441	2.766	−2.043	−0.051	−0.0079
Nd	1.938	−0.824	−0.374	−0.827	−0.788	−0.439	2.725	−2.025	−0.124	−0.0009
Sm	1.946	−0.797	−0.391	−0.799	−0.805	−0.443	2.751	−1.987	−0.324	−0.0015
Eu	1.877	−0.742	−0.413	−0.762	−0.825	−0.443	2.702	−1.917	−0.480	−0.0201
Gd	2.158	−0.866	−0.394	−0.866	−0.832	−0.455	2.990	−2.126	−0.010	0.0007
Tb	2.190	−0.842	−0.403	−0.845	−0.836	−0.450	3.026	−2.090	0.010	0.0171
Dy	2.138	−0.857	−0.397	−0.858	−0.841	−0.454	2.979	−2.112	0.091	−0.0004
Ho	2.168	−0.846	−0.406	−0.850	−0.840	−0.458	3.008	−2.102	0.171	−0.0041
Er	2.175	−0.818	−0.412	−0.848	−0.850	−0.461	3.024	−2.078	0.260	0.0298
Tm	2.117	−0.801	−0.422	−0.810	−0.852	−0.461	2.969	−2.033	0.361	0.0089
Yb	2.004	−0.738	−0.438	−0.774	−0.861	−0.455	2.865	−1.950	0.494	0.0355
Lu	2.254	−0.886	−0.404	−0.888	−0.875	−0.460	3.129	−2.178	0.000	−0.0026

[a] Δ(Ln − O) is the difference of the charges of Ln and O. [b] Sum of the charges of the allylic carbons. [c] Sum of the spin densities of the allylic carbons (differences in α and β charges). [d] Difference of the charges of the terminal C(1) and c(3) allylic carbons.

TABLE 6: Hirshfeld Charge Analysis for [Ln(C_3H_5)Cp(OMe)] (1) [Ln = La−Lu]

	Ln	C(1)	C(2)	C(3)	O	C$_{ave}$	Δ(Ln − O)[a]	C(1+2+3)
La	0.705	−0.184	−0.055	−0.185	−0.342	−0.096	1.047	−0.424
Ce	0.676	−0.177	−0.058	−0.187	−0.330	−0.095	1.007	−0.422
Pr	0.783	−0.190	−0.063	−0.196	−0.365	−0.104	1.149	−0.449
Nd	0.759	−0.185	−0.062	−0.188	−0.361	−0.103	1.121	−0.435
Sm	0.712	−0.164	−0.059	−0.166	−0.364	−0.102	1.076	−0.389
Eu	0.701	−0.140	−0.057	−0.143	−0.379	−0.105	1.080	−0.340
Gd	0.659	−0.181	−0.048	−0.181	−0.333	−0.094	0.992	−0.410
Tb	0.804	−0.193	−0.061	−0.194	−0.371	−0.104	1.175	−0.448
Dy	0.792	−0.190	−0.058	−0.190	−0.374	−0.105	1.166	−0.438
Ho	0.761	−0.180	−0.057	−0.180	−0.368	−0.104	1.129	−0.417
Er	0.748	−0.165	−0.056	−0.176	−0.371	−0.104	1.119	−0.397
Tm	0.736	−0.154	−0.055	−0.157	−0.389	−0.106	1.125	−0.366
Yb	0.716	−0.134	−0.055	−0.138	−0.386	−0.107	1.102	−0.327
Lu	0.669	−0.187	−0.041	−0.188	−0.346	−0.093	1.015	−0.416

[a] Δ(Ln − O) is the difference of the charges of Ln and O.

atoms should reflect this point, and this is indeed visible in Table 5 where the sum of the Mulliken charges of the 3 C atoms is decreased (in absolute value) by ca. 0.10 electrons with respect to the charges for the other 11 complexes. Interestingly, the spin densities on the allyl C increase with the number of unpaired α f electrons in the first half of Ln (i.e., the number of unpaired f electrons) and with the number of β electrons in the second half of Ln (i.e., the complement to seven of the number of unpaired f electrons). As will be discussed later, the spin densities on the allyl carbons vary with the number of f electrons lying in the same energy band, as is illustrated in Figure 5. The sign of the spin density indicates an excess of α spin on the carbons for the late Ln, whereas for the early Ln, the opposite is observed (excess of β). As can be also seen in Table 5, the total charge on the allyl carbons decreases as the spin density increases (whatever its sign). Finally, a significant difference in the charges of the terminal C of allyl is only observed for Eu, Er, and Yb complexes.

However, the fact that the oxygen charge and the charge of the external allylic carbons have the same order of magnitude disagrees somewhat with the chemical intuition. Therefore, Hirshfeld charges, often considered as more trustworthy and more robust against a variation in the basis set,[57,60] are examined. The absolute values of the Hirshfeld charges, reported in Table 6, are smaller than the absolute values of the Mulliken charges. The same conclusion is valid for the charge differences between the Ln atom and the oxygen atom, which represents a measure of the ionic character. Whereas the Mulliken charge analysis indicates an increasing ionic character with *Z*, the atomic number of the Ln, the Hirshfeld charge analysis, in contrast, does not exhibit such a linear increase. For the oxygen atom as well as for the metal center, no uniform development of the Hirshfeld charge such as that in the case of the Mulliken charge is observed. Nevertheless, the special attitude for the complexes of Eu and Yb, also observed for the values of the external carbons of the allylic group, is even more visible than in Mulliken analysis, indicating again an increased tendency of the allyl ligand to behave more like an allyl radical.

Finally, the Lu charges show an opposite behavior within the two charge analysis schemes: Hirshfeld predicts one of the smallest charges, similar to Gd and Ce ones, whereas Mulliken predicts the largest charges of the series. More specifically, the ionic character of the Lu−allyl is one of the largest of the lanthanide series in both schemes, but the Lu−OMe is definitely less ionic in the Hirshfeld scheme, whereas it is more ionic in Mulliken analysis.

The evolution of the HOMO and the LUMO (defined as the absolute highest HOMO or lowest LUMO of the α and β spin orbitals, whichever comes first) is shown in Figure 2. The energy of the HOMO (LUMO) decreases from Ce to Gd (Eu), then is shifted up and decreases again monotonically up to Lu (Yb) (the energy of the LUMO is higher for Lu, but in that case, it is not an f orbital anymore). The elements with an empty (La), half-occupied (Gd), or completely occupied (Lu) f shell have the greatest HOMO−LUMO gaps and are therefore (according to the maximum hardness principle of Pearson and Parr) the most stable complexes.[61−66]

In the simplest (closed shell) quantum chemical models, the orbital energy of the frontier occupied orbital(s) varies like the total energy. It is therefore tempting to look at some apparent correlation with the variation of the total energy with the atomic numbers, and Figure 2 can be compared to Figure 3.

The trend of this graph might be correlated in considering the total energy that decreases continuously as far as Gd. This agrees with the first half of the curve. The diminution of the Coulombic energy due to relativistic effects (shielding) can explain the decrease in the energy in the second half (Table 7). Finally, considering the total energy of these species, this Coulombic energy in the second half is compensated by the kinetic energy which increases if the orbitals are more contracted. A closer look at the kinetic energy shows that it (La and Ce complexes excepted) increases monotonically up to Gd, then is shifted down and increases again. The special behavior of the two La and Ce complexes is due to the relatively larger occupation of their 5d orbital with respect to their 4f (Table 8) orbital (let us recall that a 5d orbital, which has two nodes in its radial function, possesses larger curvatures and therefore larger kinetic energy than a 4f orbital which possess no nodes, although being confined in a smaller volume of space). Finally one can notice that these conclusions remain whatever the quality of the basis is used, TZP or DZ, for given geometries optimized at the DZ level of basis set (the average energy difference between the two basis sets is almost constant, amounting to 3.56 eV, with a standard deviation as small as 0.10 eV).

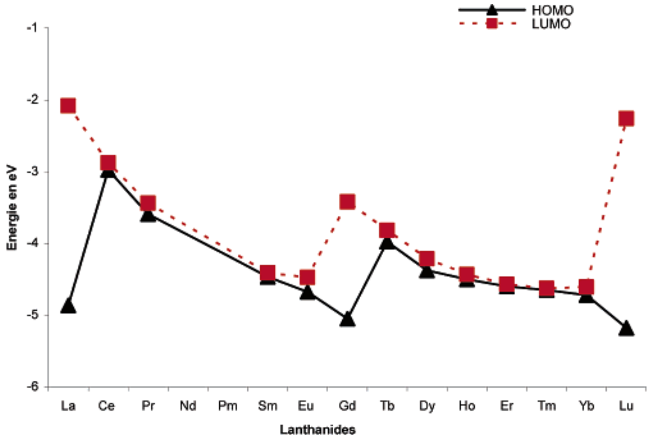


Figure 2. Evolution of the HOMO and LUMO energies within the Ln series.

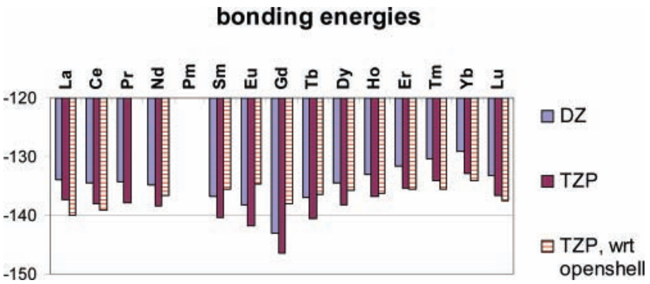


Figure 3. Bonding energy variation with the Ln atomic number. DZ and TZP basis sets (with respect to spherical atoms), and TZP binding energies with respect to open shell atoms. Energies in eV.

On the other hand, one should not expect too much from such a correlation, because the bonding energies provided by ADF are related to spherical, unrestricted atoms, and along the lanthanide series, the spin polarization varies, enhancing the difference with the atoms within a given spin state. To overcome this restriction, bonding energies have also been calculated with respect to open shell atoms, for which the ground-state energy has been calculated within the $C_{\infty v}$ or C_{2v} symmetry, leading to definite configurations for most of them. It is interesting to note that a similar correlation is found, although it is a decrease in the bonding energy that corresponds to an increase of the frontier orbital eigenvalue.

TABLE 7: Energies (eV) for [Ln(C_3H_5)Cp(OMe)] (1) [Ln = La−Lu][a]

	HOMO energy	LUMO energy	electrostatic energy	kinetic energy	Coulombic energy	XC energy	Total bonding energy DZ (TZP) [wrt open shell atoms, TZP]
La	−4.862	−2.084	−98.30	107.39	−18.57	−124.36	−133.84 (−137.33) [−109.99]
Ce	−2.976	−2.878	−99.03	103.00	−13.80	−124.69	−134.52 (−138.01) [−109.04]
Pr	−3.592	−3.441	−97.60	45.09	33.54	−115.30	−134.27 (−137.82)
Nd	−4.061	−3.988	−97.55	57.34	22.96	−117.59	−134.85 (−138.45) [−106.58]
Sm	−4.465	−4.410	−96.94	80.36	2.62	−122.89	−136.84 (−140.44) [−105.53]
Eu	−4.674	−4.475	−96.28	92.12	−8.35	−125.72	−138.23 (−141.82) [−104.60]
Gd	−5.047	−3.419	−99.50	127.53	−36.41	−134.69	−143.07 (−146.47) [−108.00]
Tb	−3.975	−3.819	−98.43	68.42	13.97	−120.93	−136.97 (−140.50) [−106.36]
Dy	−4.376	−4.215	−97.99	69.89	12.60	−119.01	−134.52 (−138.20) [−105.79]
Ho	−4.502	−4.432	−98.11	72.73	10.06	−117.76	−133.08 (−136.74) [−106.19]
Er	−4.599	−4.568	−97.73	76.82	5.97	−116.94	−131.59 (−135.28) [−105.47]
Tm	−4.647	−4.627	−97.33	76.43	6.22	−115.66	−130.33 (−134.08) [−105.54]
Yb	−4.721	−4.605	−97.00	80.17	2.77	−115.06	−129.13 (−132.85) [−104.04]
Lu	−5.177	−2.260	−100.87	101.31	−11.25	−122.36	−133.17 (−136.55) [−107.44]

[a] Calculations with the DZ basis set. Total energies in parentheses are calculated with the TZP basis set at geometries optimized with DZ basis sets. Total energies in brackets are calculated with the TZP basis set with respect to open shell atoms (at geometries optimized with DZ basis sets).

TABLE 8: Ln Mulliken Populations in the Valence Orbitals for [Ln(C_3H_5)Cp(OMe)] (1) [Ln = La−Lu] and Corresponding Spin Polarization

	5s+6s		5d		4f		5p		6s+5d+5p	4f	total
spin	a	b	a	b	a	b	a	b	$\alpha - \beta$	$\alpha - \beta$	$\alpha - \beta$
La	1.035	1.035	0.435	0.435	0.147	0.147	2.934	2.934	0	0	0
Ce	1.034	1.031	0.473	0.410	1.116	0.176	2.931	2.925	0.072	0.940	1.012
Pr	1.033	1.025	0.410	0.361	2.214	0.154	2.917	2.910	0.064	2.060	2.124
Nd	1.042	1.029	0.395	0.335	3.300	0.133	2.920	2.909	0.084	3.167	3.251
Sm	1.033	1.016	0.354	0.266	5.473	0.083	2.914	2.902	0.117	5.390	5.507
Eu	1.036	1.012	0.335	0.251	6.558	0.061	2.940	2.920	0.128	6.497	6.625
Gd	1.038	1.023	0.426	0.320	7.012	0.175	2.936	2.908	0.149	6.837	6.986
Tb	1.070	1.062	0.369	0.290	7.000	1.204	2.922	2.898	0.111	5.796	5.907
Dy	1.041	1.034	0.341	0.271	7.011	2.296	2.946	2.922	0.101	4.715	4.816
Ho	1.027	1.025	0.293	0.240	7.007	3.377	2.941	2.922	0.074	3.630	3.704
Er	1.025	1.025	0.253	0.214	7.003	4.456	2.934	2.916	0.057	2.547	2.604
Tm	1.028	1.029	0.231	0.205	6.998	5.512	2.950	2.930	0.045	1.486	1.531
Yb	1.022	1.023	0.217	0.198	6.994	6.576	2.987	2.978	0.027	0.418	0.445
Lu	1.044	1.044	0.318	0.318	7.011	7.011	3.000	3.000	0	0	0

In general, no striking results are given by the Mulliken population analysis of the valence orbitals: the 5s and the 5p orbitals are almost completely occupied and the filling of the 4f orbitals (at first the orbitals with α-spin up to Gd) follows the general Hund's rule and textbook chemical laws.

One can notice that the Gd complex with the highest multiplicity (7) is energetically the most stable complex among all the calculated lanthanide ones and it has the greatest exchange-correlation energy (Table 7). This energy increases together with the spin polarization up to Gd (see Table 8, and below), and then it decreases. The spin polarization of the valence shell, 4f electrons excepted, increases regularly as the number of unpaired f electrons increases, as well as the total spin polarization, although the spin polarization in a $4f^n$ compound is always significantly larger than that in the associated $4f.^{14-n}$ Indeed, the excess in spin polarization in a $4f^n$ compound exceeds that of the $4f^{14-n}$ compound by a number of electrons amounting to 0.567, 0.593, 0.647, 0.691, and 0.718 for Ce, Pr, Nd, Sm, and Eu, respectively. It is interesting to notice that this spin polarization is greater than the number of f electrons for the early rare earths (La−Gd), and smaller than the number of holes in the 4f shell for the late rare earths (Tb−Lu). This is directly related to the spin polarization of the allylic group reported in Table 5, and the sum of both spin polarizations amounts quite closely the number of f electrons (weighting the allylic spin polarization by a factor near 1.2 would indeed further improve the agreement). This feature by itself indicates that the behavior of all the Ln ions may differ in their interaction with a ligand like allyl, the rare earth being not just a spectator. This aspect cannot be evidenced if calculations are performed with frozen cores or pseudopotential approximations, which do not let the 4f electrons relax through the bonding to the ligands.

A look at the frontier orbitals shows that the HOMO of the energetically most stable complexes (La, Gd, and Lu) is different from the HOMO of the other lanthanide complexes where the f character of the orbitals dominates. For La, Gd, and Lu, the f orbitals are more stabilized than the d orbitals. Therefore, their

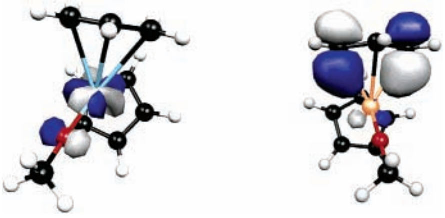


Figure 4. HOMO of compound **1**. Left: Ln = Yb. Right: Ln = Lu.

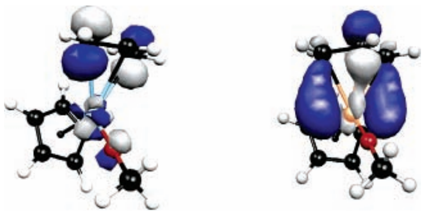


Figure 5. LUMO of compound **1**. Left: Ln = Yb. Right: Ln = Lu.

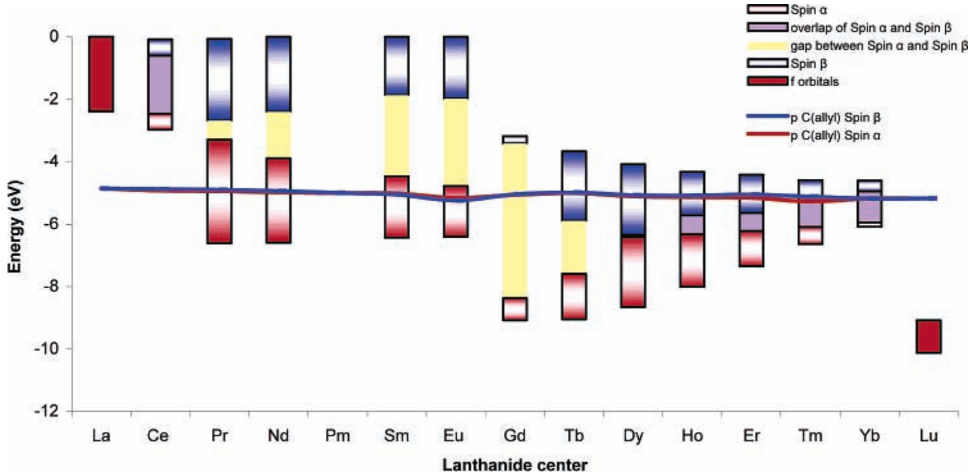


Figure 6. Evolution of the f orbital spin orbital energy band with respect to the allyl energy levels along the lanthanide series.

HOMO is dominated by the p orbitals of the allylic carbon and by the d orbitals of the lanthanide atom (Figure 4).

La and Lu have the same LUMO composition (La 4f, La 5d, and p allyl C) (Figure 5, right). But an interesting LUMO composition is observed for Yb and Eu. Here, the LUMO is composed of allylic carbon p orbitals and metal f orbitals (Figure 5, left). The LUMOs of the other complexes are almost only pure f orbitals. Going from La to Lu, one can notice that the energy of the HOMO allylic carbon p orbitals does not vary substantially, whereas the 4f orbital energies decrease strongly as their atomic number increases.

For La, the allylic carbon 2p orbitals have a lower energy than the f orbitals; for Lu it is the reverse. Starting from La, the allylic carbon p orbital penetrates more and more the occupied f orbital band (Figure 6).

As expected, the spin polarization, evaluated as the difference of the orbital energy levels for α and β spins, is noticed for all open shell systems. For Ce, an overlap of up and down f spin orbital bands is observed. However, for further open shell elements (Pr to Dy), a gap exists between the f spin orbitals of both spins. This gap is maximal for Gd with the highest multiplicity. Overlap is again found for the complexes of Ho to Yb.

The f orbital bandwidth is very small for Ce and very large for Pr. It becomes smaller up to Gd. Then, it becomes once more larger for Tb and decreases again. Generally, the gap between the 4f band and the energetically subsequent orbitals is found rather large, both for the lower energetic and for the higher energetic orbitals.

Conclusion

Theoretical studies of the lanthanide complexes are still difficult, although their number is increasing rapidly. It is shown that, within spin-unrestricted calculations, many interesting results can be obtained, overtaking the geometry optimizations that can provide structures in close agreement with experiment. Various properties such as the total energy, the charge distribution within the complexes, as well as the composition and the energy of the frontier orbitals can be calculated, giving insights in potential reactivity of families of complexes.

Contrary to the general opinion, the f orbitals are involved in bonding, but this is somewhat an indirect effect: because of the quasi-degeneracy of 4f and 5d Ln orbitals within the complexes, the 4f occupation (or population) may vary and induce a change in the bonding via the 5d orbital, or to a lesser extent (because of its higher energy) the 6s orbital (which, on the opposite, has a large possible overlap with ligand orbitals due to their diffuse spatial extension). As is now well established, relativistic effects are very important for lanthanide complexes. The decrease in the bonding distances from lanthane to lutetium is well described by these effects.

Furthermore, according Hund's rule, the complexes prefer having a half-occupied or an occupied shell. Gadolinium has a half-occupied shell and the multiplicity is the highest, the total energy as well as the corresponding maximal exchange-correlation energy.

Going from the early to the late lanthanides, the spin polarization is less acute and the f orbitals become more stable and less involved in possible reactivity schemes. The difference in the spin polarization within the Ln complexes lets us understand differences in catalytic properties, but this feature cannot be seen if frozen cores or pseudopotential approximations are used in the calculations.

These informative results, which confirm that the reactivity of rare earth complexes cannot be considered identical through the whole family, should encourage continued detailed analyses of lanthanide complexes.

Acknowledgment. The CINES is acknowledged for a grant of computer time (Project cpt2130). Dr. O. Maury is acknowledged for fruitful discussions.

Supporting Information Available: Detailed information on the validation of the model (basis set, spin value). This material is available free of charge via the Internet at http://pubs.acs.org.

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