Highlight Review

Theoretical Calculations on Electronic Structure and Catalytic Reaction of Organo-f-element Complexes

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Abstract

The use of lanthanide complexes as catalysts in organic synthesis is currently of intense interest. In particular, organolanthanide complexes are of rapidly growing importance, and hence the understanding of the binding behavior of f orbital as well as the ionic/covalent characteristics of lanthanocene-based complexes is of significance with respect to their reactivity and their role as catalyst in organic synthesis. The purpose of this review is to give a survey of recent progress in theoretical studies on organo-f-element complexes and to highlight successful applications of density functional and quantum chemical molecular dynamics methods.

♦ 1. Introduction

The application of quantum chemistry to f-block elements is a considerable challenge and has been attempted only by a comparatively small number of researchers. Several complications prevent standard quantum chemical approaches from being successful in all respects of this field. However, the rapid development of computer technology as well as quantum chemistry methodology resulted in a considerable progress in 1990s. Since then, theoretical studies steadily grown.[1–5] In recent years, ab initio and density functional methods were applied to organo-f-element complexes to investigate the molecular structure and electronic states as well as the interaction of metal–ligands. Studies were also focused on the catalysts containing cerium employing density functional theory (DFT) and quantum chemical molecular dynamics (QCMD) as well as empirical potentials.[6–9] Eisenstein and co-workers[10,11] have published some typical works on organo-f-element complexes while the studies on catalytic reaction mechanism of organolanthanides are limited.[12] On the other

hand, the widespread applications in the fields of chemistry, physics, biology, and medicine, lanthanides and actinides offer a new frontier in organometallic chemistry. Hence, organo-f-element complexes stimulated much more experimental studies. Organolanthanide and organoactinide catalysts in organic synthesis account for one half of this amount and are at the center of very intense activity. As is the case in many high technology areas, lanthanide usage in catalysts is expected to grow because of their specific properties and is substantiated by the large number of research papers and patents that appear since last decade. However, the development of organolanthanide and organoactinide catalyst usually suffers from difficulties in the interpretation of reaction mechanism, understanding of the electronic structure, etc. The recent progress in the computational chemistry field allows to compute at the full quantum mechanical level of realistic structures. As a result, we have witnessed a considerable growth in the theoretical studies on lathanides.[13,14] In this review, we address the recent progress on the theoretical calculations of organo-f-elements with the purpose of stimulating further interest in this field with a special emphasis on our recent work on the applications of theoretical methods such as DFT and QCMD.

♦ 2. Theoretical Method

Relativistic effect is very important for the calculation of heavy elements. This can be done at various levels, such as four-component spinors and two-component spinors. Four-component relativistic approach is the rigorous relativistic treatment using the four-component spinors explicitly and well suited to studies of molecular properties as well as of total electronic energies. However, this method is still very costly mainly because of the use of large basis sets needed for a proper description of

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the small component. In the framework of DFT, two-component Pauli formalism[15] and zero-order regular approximation (ZORA) approach[16] are often used. There are deficiencies in Pauli formalism based on first-order relativistic correction due to the singular behavior of Pauli Hamiltonian at the nucleus. For dealing with heavy elements, ZORA is recommended to give more reliable results. On the other hand, generalized gradient approximation (GGA), such as Lee–Yang–Parr (LYP),[17] Perdew,[18] Perdew and Wang (PW),[19] and the recent revised Perdew–Burke–Ernzerhodf (RPBE),[20] is well proved to improve the accuracy in the energetic estimation. Hence, in our DFT calculations, two-component relativistic calculations on atoms were considered by ZORA relativistic equation implanted in ADF (Amsterdam Density Functional) package, which is an excellent approximation to the fully relativistic Dirac equation with respect to proper CPU cost.

Recently, we have developed QCMD method implanted into "Colors" code, which is based on tight-binding theory and has been successfully applied to the investigation of electronic structures and reaction issues covering lanthanides.[9,21–23] In order to save CPU time and maintain the accuracy, we have introduced various parameters, which are determined by two-component ZORA relativistic calculations at the level of PW. References are available for the details of DFT parameterization.[24,25]

♦ 3. Calculations of Electronic Structure

3.1 Binding behavior of f orbital

Numerous and unique properties of lanthanides and actinides compounds are widely considered to be associated with f electron. Although the complexity of the open shells of 4f and 5f orbitals poses a great challenge to theoretical work, modern DFT and QCMD have been found to challenge this issue at the edge of success.
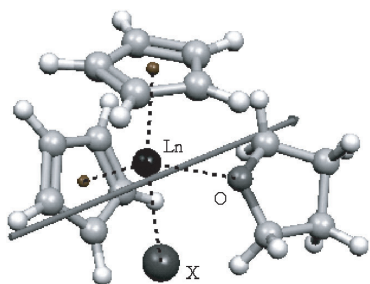

Figure 1. The geometry structure of $Cp_2LnX(THF)$. (Cp = cyclopentadienyl, THF = tetrahydrofuran, Ln = La–Lu and X = halides. Unmarked white and gray balls represent hydrogen and carbon, respectively. The arrow indicates the direction of dipole moment.)

In the framework of organo-4f-element complexes, typical theoretical investigations can be found for $Ln(NH_2)_3$[26] and $Cp_2LnX(THF)$[27] (Ln = lanthanides; Cp = cyclopentadienyl; X = halogen; THF = tetrahydrofuran) complexes, where 4f orbital shows nonparticipation in binding with ligands. Figure 1 shows the optimized structure of mixed-ligand complex $Cp_2LnX(THF)$ where the tetrahedral structure was described. Their optimized geometrical parameters and the available experimental data are summarized in Table 1. The calculated data is in good agreement

with experimental results except for the overestimated Lu–O and Lu–Cp distances (Table 1). In the DFT framework, the same overestimation for covalent bond length was also observed.[28] The overestimation is assumed to be due to intramolecular dispersion forces for which the present computational theories do not account.[29] The fact that Lu–Cl bond length can be well reproduced by the same theoretical method may result from its weaker covalent character compared to Lu–O and Lu–Cp bond in Cp_2LuCl complex.

Table 1. The selected bond length (in Å) and angles (in deg.) in $Cp_2LnX·THF^a$

Complex	Parameters	X = F	X = Cl	X = Br	X = I
$Cp_2LaX·THF$	La–X	2.176	2.708	2.889	3.140
(^1A)	La–O	2.460	2.463	2.464	2.463
	La–Cp	2.519	2.490	2.485	2.475
	Cp–Ln–Cp	115.3	117.4	117.8	118.6
	O–Ln–X	87.8	92.7	94.1	95.5
$Cp_2GdX·THF$	Gd–X	2.081	2.580	2.759	3.013
(^8A)	Gd–O	2.428	2.437	2.440	2.443
	Gd–Cp	2.418	2.402	2.401	2.397
	Cp–Ln–Cp	123.4	124.8	124.9	121.1
	O–Ln–X	85.5	90.1	91.2	92.7
$Cp_2LuX·THF$	Lu–X	2.007	2.493 (2.50)^b	2.672	2.936
(^1A)	Lu–O	2.422	2.445 (2.27)^b	2.447	2.448
	Lu–Cp	2.373	2.361 (2.29)^b	2.360	2.352
	Cp–Ln–Cp	127.5	128.7 (129.0)^b	128.8	129.6
	O–Ln–X	85.0	88.2 (91.6)^b	89.1	90.1

^{a}The electronic states are shown in the first column. The Cp in the second column represents the centroid of Cp ring.
^{b}Experimental data are given in the parenthesis taken from reference. (Z. Ni, Z. M. Zhang, D. L. Deng and C. T. Qian, *J. Organomet. Chem.*, **306**, 209 (1986).)
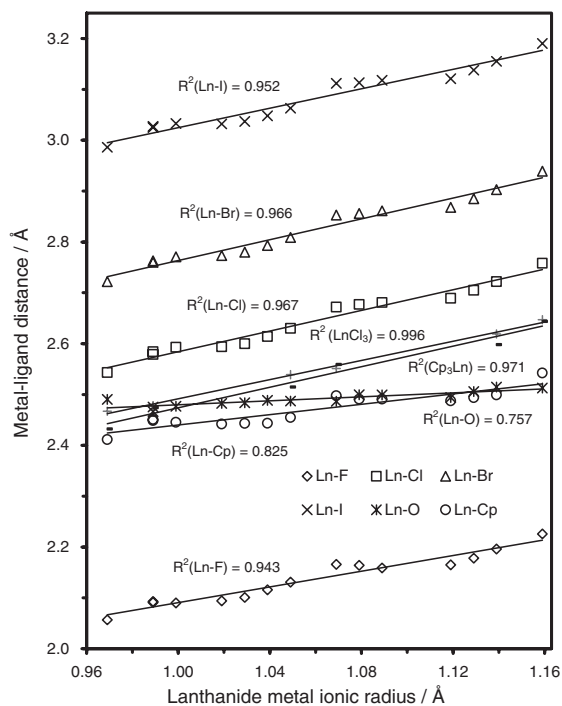

Figure 2. The relationship between the metal–ligands distances (Ln–X, Ln–O, and Ln–Cp) and metal ionic radius in $Cp_2LnX(THF)$ complex.

The consistency in the calculation and experiment can be also seen from the relationship of metal–ligand distance and metal ionic radius. As shown in Figure 2, the metal–ligand distances follow a linear trend along with the increasing metal ionic radius. For a comparison, the data of several binary compounds, viz. MCl_3 and Cp_3M (M = La, Ce, Eu, Gd, Yb, and Lu), are also included in this figure. Such linear relationship was also observed experimentally for organolanthanide compounds. Moreover, the periodical deviations from the lines were noticed. It may be due to the $5d^n$ ($n = 0$ and 1) electronic configuration[2] and 4f electron character, and the similar deviation in geometry and energy was also observed for other lanthanide complexes.[11] The metal atomic orbital (AO) population and the composition of highest occupied molecular orbital (HOMO) are depicted in Table 2. For the sake of simplicity, we only selected three kinds of metal complexes, Cp₂LaX(THF), Cp₂GdX(THF), and Cp₂LuX(THF) in which the central metal is picked up at the beginning, middle and end of lanthanide series. It was found that the 4f orbital mainly contributes to lowest unoccupied molecular orbital (LUMO) in the mixed-ligand complexes.

From Table 2, it is also clear that all of the Ln-5d populations are more than 1 in the complexes, which indicates that Ln-5d orbital act as electron acceptor in the interaction of Ln with ligands. Table 2 also indicates that the HOMO mainly consists of the AO in Cp and X-np (X = halides; $n = 3$, 4, and 5) orbital. It is important to mention here that the contribution lower than 5% is not considered for this analysis. In each kind of metal complex, the contribution of the AO in Cp to HOMO decreases in the following sequence: F > Cl > Br > I. However, the contribution of X-np orbital increases in accordance with the order of F < Cl < Br < I. On the other hand, the compositions of LUMO depend clearly upon the metal ions. The empty La-4f and partially filled Ln-4f as well as Ln-5d orbitals contribute to LUMO. In the case of La and Lu complexes, the AOs in Cp also contribute to LUMO. However, in the case of Gd complex, LUMO mainly consists of half-filled Gd-4f orbital. The nonparticipation of 4f-orbital in metal–ligand bond was also found for various trivalent organo-4f-element complexes.[30,31] The same is true for tetravalent cerium sandwich complex $Ce(C_8H_8)_2$.[32] However, on the basis of our recent result, the or-

bital overlap of Ce-4f with Cu-3d through bridged O-2p orbital was observed in $Ce_{1-x}Cu_xO_{2-\delta}$ system.[9] On the other hand, with respect to the magnetic properties, the binding behavior of 4f orbital was found in binuclear complexes (f–f interaction).[33] In order to understand the valence transition and magnetic phenomena of rare earth systems, Strange et al.[34] have performed electronic-structure calculation and found that f electrons can be treated as two types: (i) localized core-like f electrons and (ii) delocalized band-like f electrons. The latter hybridizes with outer s–d band and participates in bonding. Thus, the participation in bonding of 4f electron may occur in solid system due to the splitting of f-band into two subbands. One of the subbands lies just Fermi energy and hybridize the s–d band to participate bonding.[34] However, in organo-4f-element complexes without f-band splitting, the bonding of 4f electron with ligands was not found because 4f electrons are contracted into the core and difficult to participate in bonding. Hence, it is well acceptable for the treatment of organo-4f-element complexes to leaving 4f electrons in core described by relativistic effective core potential.[35–37]

In contrast to organo-4f-element complexes, the contributions of 5f orbital were found in actinide–ligand bond of some organo-5f-element complexes. Meyer and coworkers[38] have shown the orbital interaction between 5f (U) and s/p (C/H) type orbitals even if the contribution is very minor from s/p orbitals. However, the same authors also performed DFT calculations on several uranium complexes such as $[(ArO_3)tacn]U^{III}(NCCH_3)$, $[(ArO_3)tacn]U^V(NSi(CH_3)_3)$, and $[(ArO_3)tacn]U^{IV}(N_3)$,[38] and showed that U(III) and U(V) species are stabilized via π-bonding interaction, involving uranium-f-orbitals and the axial acetonitrile and imido ligands while the bonding in U(IV) azido complex has purely ionic character. Theoretical calculations on both $[(NH_2)_3(NH_3)U]_2(\mu^2-\eta^2:\eta^2-N_2)$ and $U_2(\mu^2-N_2)(\eta^5-C_5H_5)_2(\eta^8-C_8H_6)_2$ indicate that both these complexes contain two U(IV) $5f^2$ centers with substantial covalent interaction between the U-5f atomic orbitals and one component of the N_2 π_g orbitals.[39] Another DFT calculation on $I_3U–L$ (L = acetonitrile or pyrazine) also showed $5f–\pi^*$ ligand interaction.[40] In trivalent uranium $[(CH_2)_5]_4$-calix-tetrapyrrole complexes, a little 5f character with admixture of ligand character was also observed.[41] The DFT results also show the existence of antiferromagnetic coupling be-

Table 2. The population of atomic orbital and the composition of HOMO and LUMO in Cp₂LnX(THF) (Ln = La, Gd, and Lu, X = F, Cl, Br, and I)[a]

Complex	Metal Atomic Valence Shell				Composition of Molecular Orbital/%	
	s	p	d	f	HOMO	LUMO
Cp₂LaX(THF)						
F	2.03	5.85	1.00	0.35	96Cp	33La5d + 16La4f + 43Cp
Cl	2.08	5.98	1.28	0.34	81Cp	30La5d + 30La4f + 27Cp
Br	2.08	5.96	1.22	0.33	78Cp + 6Br4p	31La5d + 32La4f + 26Cp
I	2.12	6.08	1.53	0.32	45Cp + 41I5p	35La5d + 29La4f + 26Cp
Cp₂GdX(THF)						
F	2.06	5.97	1.05	7.17	83Cp	98Gd4f
Cl	2.14	6.14	1.33	7.17	67Cp + 12Cl3p	96Gd4f
Br	2.15	6.12	1.25	7.16	66Cp + 22Br4p	96Gd4f
I	2.19	6.27	1.60	7.17	38Cp + 53I5p	96Gd4f
Cp₂LuX(THF)						
F	2.03	6.18	1.16	14.02	83Cp	35Lu5d + 14Lu6s + 23Cp
Cl	2.16	6.37	1.38	14.02	74Cp + 15Cl3p	47Lu5d + 7Lu6s + 26Cp
Br	2.17	6.34	1.34	14.02	51Cp + 27Br4p	49Lu5d + 6Lu6s + 25Cp
I	2.25	6.50	1.57	14.02	34Cp + 56I5p	57Lu5d + 5Lu6s + 24Cp

[a]The data was taken from Ref. 27.

tween the two uranium metal centers as the only significant U–U interaction.

3.2 Ionic/covalent characteristics and charge population

The ionic and covalent character of coordination bond dominates crucial role in coordination chemistry, which naturally depends on the lanthanide metal and ligands. The chemical description of the lanthanide–ligand interaction of the bonding characteristics, viz., ionic versus covalent, is one of the challenging problems in lanthanide complexes. The ionic and covalent characteristics of organic complexes are associated with the binding nature of metal with ligand as well as hardness–softness and acid–base (HSAB) character. Hence, in the framework of DFT, the approach of charge population and the concept of HSAB have been proposed to describe qualitatively the ionic and covalent character of metal–ligand bond.[42] On the other hand, since the ionization potential and electron affinity are related to the energies of HOMO and LUMO, the chemical hardness can be represented approximately by the half of HOMO–LUMO energy gap.[43] There are several methods available for charge partitioning, viz., Mulliken[44] and Hirshfeld.[45] However, it was found that Mulliken charge population failed to describe the trend in ionic/covalent character of organolanthanides along with lanthanide series.[27] In the case of $Cp_2LnX(THF)$ complexes, chloride carries less negative (Mulliken) charge than bromide, which is in contradiction with the chemical concept that the electronegativity of the latter is smaller than that of the former. Here, it is well known that the Mulliken population analysis gives peculiar results for the molecules which have diffused basis sets.[46] On the other hand, the Hirshfeld method successfully describes the ionic/covalent trend and the charge population on both bromide and chloride ions, as shown in Figure 3.
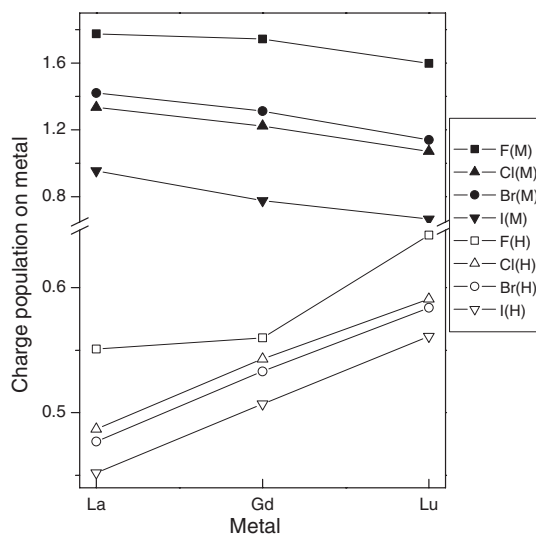

Figure 3. Mulliken (M) and Hirshfeld (H) charge population on Ln in $Cp_2LnX\cdot THF$ (Ln = La, Gd, Lu; X = F, Cl, Br, I).

It can be seen from this figure that the Mulliken charge decreases on gong from La to Lu while the charge trend with respect to halides follow the order: F > Br > Cl > I, which is clearly against the chemical hardness concept as well as the larger electronegativity of Cl as compared to Br. While the Hirshfeld

charge reflects the increasing ionic character along lanthanide series and the order of electronegativity as per Cl and Br. In another contribution,[47] it was found that Mulliken charge population on Ln metal decreases from La to Eu for a given complex, which is also contradicting the trend of ionic character. The increase in ionic character along with lanthanide series can also be understood by the increase of metal–ligand interaction energies.[48]

With respect to the problem of electronic structure, chemical bond, and optical spectra, bis(porphyrin)M(IV) (M = Ce and Th) complex was investigated by time-dependent density functional method.[49] In addition, agnostic interaction was also discussed. β-SiC agnostic interaction was found in tris(bis(trimethylsilyl)-methyl)lanthanum and samarium.[50] The same interaction was also declared for $La(CH(SiMe_3)_2)_3$, in which there is no γ-agnostic C–H bond.[51] Except for DFT, classical molecular dynamics method was also applied to simulate organo-f-element complex with respect to larger systems.[52–55] Using these methods, the real solvent phase can be considered with respect to the interaction of metal ions with solvent molecules. The coordination behavior of metal ions toward various ligand can be also investigated. However, it is difficult for classical molecular dynamic method to challenge chemical reaction issues.

♦ 4. Chemical Reaction Assisted by Organolanthanides

Theoretical studies on chemical reaction assisted by organolanthanides are still relatively few owing to the fact that such studies require huge computational time and, moreover, the systems are highly complicated because of the large relativistic effects. The first theoretical investigation on catalytic reaction of organolanthanides was reported by Koga,[56] in which ab initio method was used with the replace of larger core containing 4f orbital by the relativistic effective core potentials (ECP). In this contribution,[56] the author investigated ethylene insertion into Sm–C bond of $H_2SiCp_2SmCH_3$ and found that MP3 and MP4SDQ energy profiles are almost parallel. It was pointed out that the theoretical treatment of such reaction of Sm complex 4f orbitals can be replaced by the ECP, as long as oxidation or reduction reaction in which an electron is removed from or added to 4f orbital are not included. Koga and co-workers[12] have also reported recently a DFT calculation on the coordination and insertion of butadiene to Cp^*_2SmH ($Cp^* = \eta^5\text{-}C_5Me_5$), in which the 4f orbital of Sm was not included in valence shell and treated by ECP. Eisenstein and co-workers[57–59] have investigated the activation of H–H, C–H, and SiH_4 by Cp_2LnH (Ln = lanthanides) with the method of DFT. Their results show that it is possible to perform such calculations on the structure and reactivity of cyclopentadienyl lanthanide complexes with larger core ECP. They have verified that the usual oxidation (trivalent) state of Ce, Eu, and Yb produced analogous results as compared to that of other trivalent lanthanide complexes. Moreover, anionic $Cp_2Eu^{II}H^-$ and $Cp_2Yb^{II}H^-$ as well as cationic $Cp_2Ce^{IV}H^+$ were also considered for comparison. The results showed that Ce(IV) resulted in shorter Ce–H distance and stronger dissociation energy of SiH_4 as compared to other Ln(III). On the other hand, anionic $Cp_2Eu^{II}H^-$ and $Cp_2Yb^{II}H^-$ have longer Eu–H and Yb–H distances as compared to Ln(III) complexes. Their stronger interactions with SiH_4 were also observed. These studies indi-

cate that larger core ECP, i.e., valence shells exclusive of 4f orbital, can be used for the investigation of catalytic reaction of organolanthanides as it may save CPU time without loss of accuracy. At this point of time, Gaussian program[57–59] and ECP as well as the associated basis sets optimized by Dolg et al.[60] were widely used. The analogous DFT calculation with the method of hybrid functional was performed on the cyclopropanation reactions of divalent samarium carbenoid $ISmCH_2I$ with ethylene.[61] As far as the estimation of energy barrier for chemical reaction is concerned, it is well known that HF theory usually overestimates barrier heights and DFT usually underestimates them.

Hence, hybrid functional B3LYP[15,62] has been widely used, which contains 20% HF exchange. Even if hybrid method does better than DFT for the energy barrier calculation, the B3LYP method still systematically underestimates barrier hights.[60] Recently, MPW1K method optimized against a kinetic database by Truhlar and co-workers[63,64] was found to be very good for barrier height calculations. Using double-numeric quality basis set with polarization functions, we recently performed DFT calculation on the ring opening mechanism of methylenecyclolopropane (MCP) over Cp_2LnH (Ln = La and Lu),[65] in which a novel η^4-coordination tetrahedral transition state (TS1) was found and hence enriched the transition state structure of insertion reaction of alkenes.
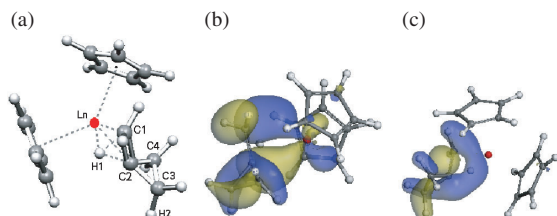

Figure 4. The new η^4-coordination tetrahedral TS1: (a) geometry; (b) 56a MO; La(5d) with 2p of C1 and C2. (c) 51a MO; H1(1s) with 2p of C1 and C2.
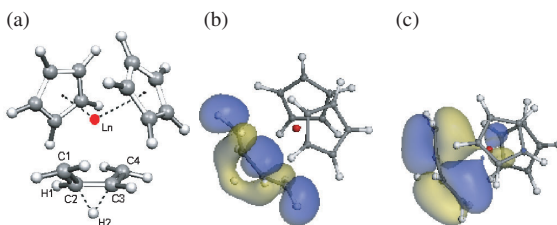

Figure 5. The orbital interaction isosurface of TS2: (a) geometry; (b) 50a MO; H2(1s) with 2p of C2 and C3; (c) 51a MO; La(5d) with π orbitals of C1=C2 and C3=C4.

Figure 4 depicts the new TS structure together with their orbital isosurface, which is different from the usual η^2-coordination planar TS structure of alkenes insertion. On the other hand, TS2 (Figure 5) represents yet another unusual structure where the coordination (η^4-form) between Ln and MCP takes place through all the four carbon atoms as a consequence of ring opening with a simultaneous "switching or oscillating" of H2 between C2 and C3.

Except static calculation, QCMD simulation was also performed on ring opening mechanism of MCP assisted by Cp_2LaH using "Colors" program.[22] The parameters for "Colors" pro-

gram were determined so as to reproduce the ionic potential, electron density of valence shell, interatomic potential curve, and geometries for atoms and small molecules obtained by DFT calculations. The calculation results by "Colors" code well reproduced the geometries of various organo-f-element complexes obtained by the DFT and experiments.[22] Figure 6 depicts the variation in bond population against the simulation time for the ring-opening process of MCP over lanthanocene catalyst. Although the usual MO and DFT discuss the catalytic reactions using only the electronic states and formation energy of transition states, QCMD calculations give us more detailed information on the catalytic reaction mechanism during the whole reaction path. Especially, the order and timing of the bond-breaking as well as bond-formation process can be analyzed as shown in Figure 6. Both QCMD and DFT results suggested the 1,2-insertion and proximal ring opening mechanism of MCP. It is also worth mentioning here that molecular mechanics and classical molecular dynamics methods were applied to investigate trivalent lanthanide complex formation with macrocyclic polyaminopolycarboxylate ligands.[66]
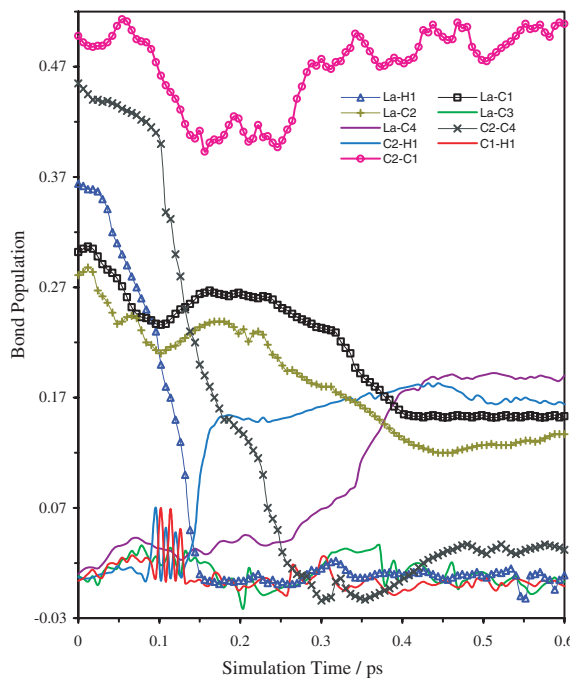

Figure 6. Bond population during the ring-opening of MCP over Cp_2LaH with a time interval of 0.2 fs under reaction temperature (298 K).

♦ 5. Outlook and Future Directions

In this article, we outlined the theoretical calculations on electronic structure and catalytic reaction of organo-f-element complexes. Although many advances have occurred in this field in recent past, calculations on organo-f-complexes still remain to be one of the most challenging areas for computational chemistry. As far as the investigation of electronic structure, it needs to address whether 5f orbitals participate in bonding with ligands even if 4f orbitals have been widely considered to be nonparticipation in bonding. Moreover, the theoretical calculation on the

catalytic reaction of organo-5f-complexes has not been reported yet in spite of numerous experimental findings in this field.[67] Hence, the theoretical outcomes as great as that in organotransition metals are expected for organo-f-element complexes. However, the relativistic effect and electron correlation make it difficult to challenge f-element compounds, especially for the open f shell. Thus, the development of theoretical method is essential for the purpose of accuracy and widespread application. With advent of computational efficiency, the studies of effective ligand models[11] and effective group potentials method[68] are in progress.

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