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A Theoretical Study on Interaction of Cyclopentadienyl Ligand with Alkali and Alkaline Earth Metals

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Ab initio and density functional theory calculations are performed on half-sandwich (M-Cp) and sandwich (Cp-M-Cp) complexes of alkali and alkaline earth metals (M = Li, Na, K, Mg, and Ca) with cyclopentadienyl ligand (Cp). A comparison of dissociation energies demonstrates the ease of dissociation of the complex as ions in solvent phase and preference for dissociation as radicals in gas phase. Atoms in molecules analysis is used to characterize this cation- π interaction based on electron density values obtained at the cage critical point. The contribution of various components to the complex energy is estimated using reduced variational space analysis confirming maximum contribution from the coulomb exchange followed by contributions from polarization and charge transfer components of cyclopentadienyl ligand.

Introduction

Metallocenes are organometallic complexes that contain π -bonded cyclopentadienyl (Cp) ligands with the general formula Cp_nM (Cp = C_5R_5^- , R = H, Me, Ph, etc.; M = metal atom). The nature of interaction that is seen in these complexes is representative of a typical cation- π interaction, which is one of the most important noncovalent interactions. Cation- π interactions play a ubiquitous role in various areas of chemistry and biology, both to understand supramolecular assembly and in elucidating function.^{1–14} Pioneering studies by Dougherty et al. show the relevance of cation- π interactions to structural biology and their contribution to protein secondary structure based on studies of interactions between side chains of aromatic amino acids phenylalanine, tyrosine, tryptophan with lysine and arginine.^{1–4} The strength of a cation- π interaction depends on the nature of aromatic system and charge of cation involved.^{1,2}

A vast majority of studies focus on metallocenes which contain transition metals and their derivatives on account of the wide range of their applications.^{15–17} On the other hand main group metallocenes have the ability to adopt a wide variety of molecular geometries, show a number of interesting bonding types and hapticities and form structurally and chemically divergent group of compounds.^{18–23} They are among the most commonly used reagents for synthesis of many other types of metallocenes.

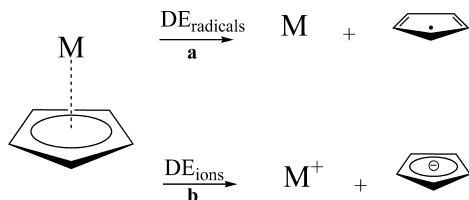
Several experimental studies focus on the polymeric structures of main group metallocenes.^{24–29} Solid-state information on these complexes was not available for a long time. Harder et al. later structurally characterized lithocene anion by employing single crystals.²⁴ The results of a crystallographic investigation where the structures of the base-free unsubstituted compounds LiCp, NaCp, and KCp were solved through powder diffraction methods using high-resolution synchrotron radiation are now available.²⁶ Schurko et al. employed solid-state NMR experiments, corresponding spectral simulations, and theoretical calculations for sodacenes and potassium metallocenes as a means of gauging the purity of the sample, the local electronic

environments of the quadrupolar nuclei, as well as the temperature-dependent motion of the metal atoms and cyclopentadienyl rings.^{27,28}

Quantum chemical calculations have been extensively employed on main-group metallocenes in recent years.^{30–33} Theoretical studies have been employed typically as tools to explain the bewildering variety of bonding arrangements to cyclopentadienyl (Cp) groups.¹⁸ Frenking et al. reported theoretical studies on the geometries, metal ligand bond dissociation energies, and heats of formation of 20 sandwich and half-sandwich complexes of the main-group elements of Groups 1, 2, 13, and 14 and Zn. The nature of the metal ligand bonding has been analyzed with an energy-partitioning method, and the results give quantitative information about the strength of the covalent and electrostatic interactions between M^{n+} and $(\text{Cp}^-)_n$ ($n = 1, 2$).³⁰ Studies on multimetallocenes CpM_nCp , (where M = Be, Mg, Ca, and Zn with $n = 2–5$) predict that the CpM_nCp species with $n > 2$ are thermodynamically unstable with respect to loss of one metal atom except for the beryllium compounds.³² Merino et al. explored atypical metallocene complexes having a symmetric bipyramidal double-cone structure for Group 13 elements,³³ and their study reveals heteroleptic species $[\text{E-Cp-E}]^+$ to be less stable than the homoleptic complexes $[\text{E-Cp-E}]^+$. They suggest that the lowest energy pathway for dissociation is through the loss of the positively charged heavier atom E^+ . Thus, the topic of alkali and alkaline earth metallocenes and their derivatives is of high interest to theoreticians and experimentalists.

In the present paper two novel aspects of main group metallocenes have been explored. These include gauging impact of solvation on the dissociation of these complexes and understanding the contribution of different factors to stability of complex by using energy decomposition analysis. Solvation of metal ions and that of cation- π interactions is interesting in its own right.³⁴ There is a tremendous disparity in the behavior of these interactions in gas and condensed phases.^{35,36} We thus feel that it is important to analyze the effect of solvent on the structure and stability of metallocenes. In this study two plausible dissociation pathways of half-sandwich complex of selected main group metallocenes has been considered and

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SCHEME 1: Pictorial Representation of Two Plausible Modes of M-Cp Complex Dissociation^a


^a DE represents dissociation energy in kcal/mol.

nature of these paths as a function of metal ion and solvent has been explored (Scheme 1).

Obviously, solvent will have a significant effect on the relative preferences between these two paths, and in this study an implicit solvent method polarizable continuum model (PCM)³⁷ is used to demonstrate its effect. This impact of solvent on the dissociation preference is explored both for neutral complexes as well as charged complexes in order to ascertain whether there exists a relative preference for splitting into either an open or closed shell system. The structural, energetic and electron density distributions in all the complexes were analyzed to gauge the dependence on the nature of the metal considered. Previous studies by Frenking et al.^{30,31} have shown the application of an energy partitioning scheme using the program package ADF³⁸ on different main group metallocenes in order to perform bond analysis where the results give a picture of the nature of the chemical bond in terms of familiar concepts of traditional bonding models. In our study reduced variational space (RVS)³⁹ analysis, which is an energy decomposition scheme is employed to delineate the contribution of various factors in order to establish which factor dominates the total interaction energy of the complex.

Computational Details

Two types of systems are considered in this study, the first system where a metal ($M = \text{Li, Na, K, Mg, and Ca}$) interacts with a single cyclopentadienyl unit to form a half-sandwich structure (M-Cp) and the second system where a metal ($M = \text{Li, Na, K, Mg, and Ca}$) interacts with two cyclopentadienyl units to form a sandwich structure (Cp-M-Cp). In the case of Mg and Ca, both neutral as well as charged complexes are taken. This has been done in order to gauge the relative differences in preference of Mg and Ca complexes to dissociate either as closed-shell or open-shell systems. Geometry optimizations are performed at B3LYP/6-31G*, B3LYP/6-311++G**, MP2/6-31G*, MP2/6-311++G**, MP2/cc-pVDZ, and MP2/cc-pVTZ levels of theory in the gas phase for half-sandwich complexes. In the lone case of potassium complex optimizations using cc-pVDZ and cc-pVTZ were not performed on account of nonavailability of corresponding basis sets. For the sandwich complexes geometry optimizations are performed at B3LYP/6-31G*, B3LYP/6-311++G**, MP2/6-31G*, and MP2/6-311++G** levels of theory. Frequency calculations were done to ascertain nature of stationary points obtained for all the optimized geometries. The dissociation energy (DE in kcal/mol) for each half-sandwich complex is calculated as shown below (a and b correspond to the two paths shown in Scheme 1).

$$\text{DE}_{\text{radicals}} = (E_{M\text{-radical}} + E_{\text{Cp-radical}}) - E_{\text{complex}}^a \quad (1)$$

$$\text{DE}_{\text{ions}} = (E_{M\text{-ion}} + E_{\text{Cp-ion}}) - E_{\text{complex}}^b \quad (2)$$

where $E_{M\text{-radical}}$ = energy of metal radical, $E_{\text{Cp-radical}}$ = energy of cyclopentadiene radical, $E_{M\text{-ion}}$ = energy of metal cation, $E_{\text{Cp-ion}}$ = energy of cyclopentadiene anion, and E_{complex} = energy of complex.

The dissociation energy (DE in kcal/mol) for each sandwich complex is calculated as shown below.

$$\text{DE}_{\text{ions}} = (E_{M\text{-ion}} + 2 \times E_{\text{Cp-ion}}) - E_{\text{complex}} \quad (3)$$

where $E_{M\text{-ion}}$ = energy of metal cation, $E_{\text{Cp-ion}}$ = energy of cyclopentadiene anion, and E_{complex} = energy of complex.

The dissociation energy values obtained at each level are corrected for basis set superposition error (BSSE) using the counterpoise method (CP) described by Boys and Bernardi.⁴⁰ The "Counterpoise = N" keyword is used to calculate the BSSE corrected total energy of a complex, where N holds for the total number of fragments composing the complex. To gauge the impact of presence of solvent on dissociation of M-Cp complex, PCM optimization was performed with water as implicit solvent at B3LYP/6-311+G* level. All the above-mentioned calculations were carried out using the Gaussian 03 program.⁴¹

The topological properties of the electron density can be mapped with the help of the atoms-in-molecules (AIM) theory developed by Bader and co-workers.⁴² The electron density at bond critical points was taken into account for the characterization of chemical bonding. We employed AIM analysis to investigate and characterize the nature of nonbonded interactions in half-sandwich and sandwich complexes at MP2/6-31G* level of theory. Bader theory has several limitations;⁴³ however, it is one option to describe the nature of the chemical interactions. Following this, RVS⁴⁴ analysis was done to quantify contribution of various factors to the total energy in both the complexes. In this technique the interaction energy of any complex at a given instant is analyzed for contributions from Coulomb and exchange energy (CEX), polarization energy (POL), and charge transfer energy (CT). While the CEX term is the energetic contribution arising from the repulsion between the occupied molecular orbitals of the two fragments (metal and cyclopentadienyl ligand), the CT term measures the energetic contribution arising from electron transfer between the fragments and the POL term assesses the energetics of deformation of a fragment's electron density caused by the other fragment. RVS analysis was performed at HF/6-31G* level on B3LYP/6-31G* optimized geometries using the option "runtype = MOROKUMA" available in the GAMESS software.⁴⁵

Results and Discussion

The discussion in this section focuses on optimized geometries and dissociation energies of half-sandwich complexes and sandwich complexes in gas phase and water. This is followed by an analysis of the results obtained from AIM analysis and RVS analysis for all complexes. Table 1 of the manuscript gives a comparison of experimentally determined values of ionization potential (IP) for metals and electron affinity (EA) for cyclopentadiene,⁴⁶⁻⁵⁰ and their corresponding values were calculated at B3LYP and MP2 levels of theory with 6-31G* and 6-31++G** basis sets. The theoretical values obtained with the above-mentioned methods and basis sets match the experimental values quite closely and have thus been employed for further studies.

TABLE 1: Comparison of Experimental and Theoretical Values of IP and EA Values (in eV) of Metals and Cp Taken in Present Study

metal/metal cation	experimental IP value	B3LYP		MP2	
		6-31G*	6-311++G**	6-31G*	6-311++G**
Li/Li ⁺	5.39	5.61	5.61	5.32	5.33
Na/Na ⁺	5.13	5.40	5.42	4.95	4.94
K/K ⁺	4.34	4.50	4.49	4.12	4.23
Mg/Mg ⁺	7.64	7.72	7.72	7.20	7.20
Mg/Mg ²⁺	15.03	15.45	15.46	14.71	14.71
Ca/Ca ⁺	6.11	6.15	6.15	5.65	5.78
Ca/Ca ²⁺	11.87	12.08	12.08	11.45	11.68
Cp/Cp ^{-a}	1.789±0.047	1.04	1.76	1.28	2.19

^a Indicates experimental value for electron affinity of cyclopentadiene.

Optimized Geometries. Half-Sandwich Systems. The optimized geometries of all the half-sandwich complexes (M-Cp) are represented in Figure 1. All the structures have C_{5v} symmetry and are minima on the potential energy surface.

An exception to the C_{5v} symmetry was found in case of Mg-Cp complex with a +1 charge at MP2 level with 6-31G*, cc-pVDZ, and cc-pVTZ basis sets. The metal to centroid of Cp distance in Å for alkali complexes shows the trend Li-Cp < Na-Cp < K-Cp. A similar trend is observed with Mg and Ca in case of both neutral and +1 charged complexes, Mg-Cp < Ca-Cp Table S1 of Supporting Information.

Sandwich Systems. Optimized geometries of sandwich complexes containing two cyclopentadienyl units and one metal element at B3LYP level using 6-31G* and 6-311++G** basis sets and at MP2 level using 6-31G* basis sets are shown in Figure 2.

Similar to the case of half-sandwich structures, magnesium and calcium sandwich complexes with both zero and negative charge are considered in this case also. Several of the anionic sandwich complexes chosen in the present study including those of Li, Na, K, Mg, and Ca have not been subjected to quantum chemical analysis before. Among all complexes studied only the anionic complexes of magnesium and calcium have a slightly

open structure, whereas all the remaining structures have optimized to typical sandwich geometries. The metal to centroid of Cp distance for all the complexes is also greater than their corresponding half-sandwich structures, though their trends are essentially similar Table S1 of Supporting Information. The structures optimized at B3LYP level are all minima on the potential energy surface albeit with varying symmetries. At MP2 level all the structures are minima with 6-31G* basis set.

Dissociation Energy. Half-Sandwich Systems. Table 2 gives the BSSE corrected dissociation energy values (DE_{ions} in kcal/mol) in the case of neutral half-sandwich complexes of Li, Na, K, Mg, and Ca with cyclopentadienyl ligand and also charged complexes of Mg and Ca at B3LYP and MP2 levels of theory (represented by mode b of Scheme 1 given in the introduction section). In the case of M-Cp complexes with alkali metal the following trend is noted for DE_{ions} (Li-Cp > Na-Cp > K-Cp). The dissociation energy of Li-Cp complex is much higher than the Na-Cp complex, with a difference of ~30–32 kcal/mol both at B3LYP and MP2 levels of theory. The difference in dissociation energy (DE_{ions}) between Na-Cp and K-Cp is lesser in magnitude being ~14–23 kcal/mol. In the case of M-Cp complexes with magnesium and calcium, a similar trend is observed for DE_{ions} (Mg-Cp > Ca-Cp) for both neutral and

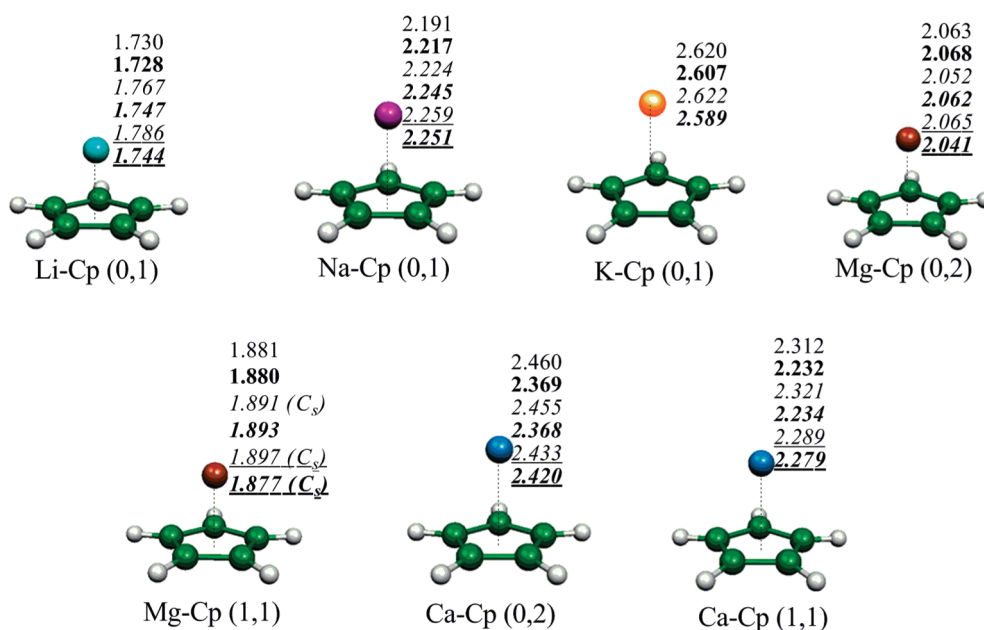


Figure 1. Optimized geometries of cyclopentadienyl metal complexes (M-Cp). All structures have C_{5v} symmetry (except those mentioned in the figure) and no imaginary frequency. The charge and multiplicity of the complexes is given in parentheses. Distance from centroid of Cp to metal in Ångstroms is represented in plain (B3LYP/6-31G*), bold (B3LYP/6-311++G**), plain-italicized (MP2/6-31G*), bold-italicized (MP2/6-311++G**), plain-italicized-underlined (MP2/cc-pVDZ), and bold-italicized-underlined (MP2/cc-pVTZ).

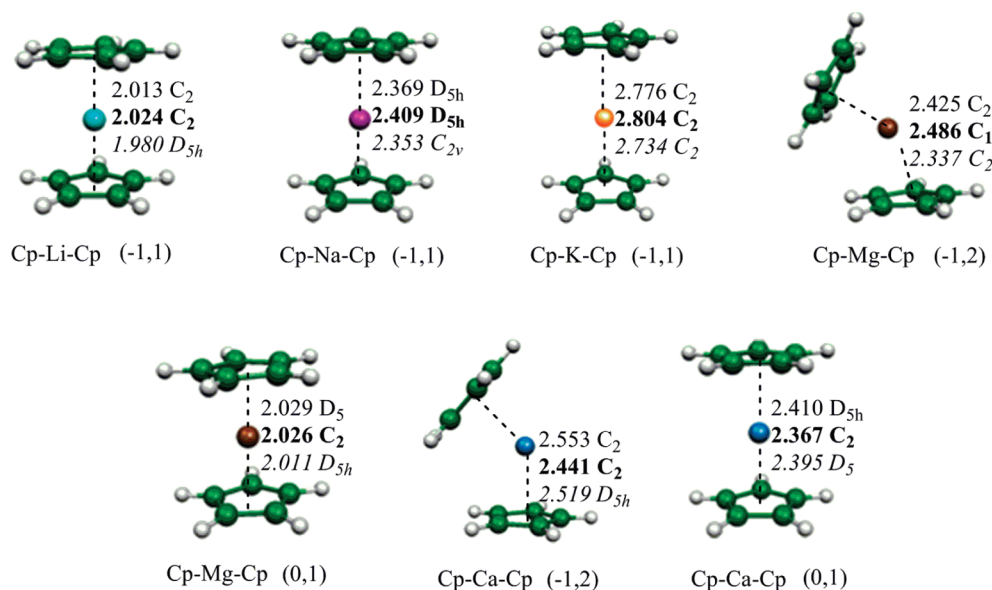


Figure 2. Optimized geometries of cyclopentadienyl and metal sandwich complexes (Cp-M-Cp). Charge and multiplicity of complexes are indicated in parentheses. Distance from centroid of Cp to metal in Ångstroms is represented in plain (B3LYP/6-31G*), bold (B3LYP/6-311++G**), and plain-italicized (MP2/6-31G*). Point group symmetry of all complexes is also indicated.

TABLE 2: Comparison of BSSE-Corrected Dissociation Energies (DE_{ions} , DE_{rad} in kcal/mol) in Gas Phase for Metal Cyclopentadiene Half-Sandwich Complexes (M-Cp) Optimized at B3LYP/6-31G*, B3LYP/6-311++G, MP2/6-31G*, MP2/6-311++G**, MP2/cc-pVDZ, and MP2/cc-pVTZ Levels of Theory^{a,b}**

		B3LYP				MP2								
complex	C,M	6-31G*		6-311++G**		6-31G*		6-311++G**		cc-pVDZ		cc-pVTZ		A
		a	b	a	b	a	b	a	b	a	b	a	b	
Li-Cp	0,1	178.7	73.3	170.2	81.5	174.1	80.0	165.3	92.7	169.9	87.3	169.1	95.2	86.0
Na-Cp	0,1	146.5	45.9	138.2	54.0	142.2	57.6	133.7	70.2	138.5	64.9	136.0	71.2	60.8
K-Cp	0,1	123.5	43.9	121.8	59.0	122.4	56.9	121.8	74.6	NA	NA	NA	NA	59.9
Mg-Cp	0,2	183.1	29.0	172.8	35.4	184.5	48.0	173.8	58.2	178.8	53.2	180.5	67.3	-
Mg-Cp	1,1	385.7	53.4	373.8	58.0	374.9	65.2	361.8	72.9	367.4	68.7	369.8	79.6	-
Ca-Cp	0,2	160.0	42.3	163.2	62.1	160.9	60.1	160.6	77.8	162.6	74.0	162.8	81.5	-
Ca-Cp	1,1	306.2	51.5	320.5	82.4	299.6	65.1	308.9	90.0	305.4	85.1	305.7	94.2	-

^a C and M indicates charge and multiplicity of each complex. ^b a, BSSE-corrected DE_{ions} ; b, BSSE-corrected DE_{rad} ; "NA," no basis functions are available for potassium. A indicates predicted bond dissociation energies from earlier theoretical studies at CCSD(T)/B//BP86/A³⁰ in kcal/mol.

charged complexes. The BSSE corrected dissociation energy values are lower than corresponding uncorrected values by ~ 8 –15 kcal/mol when 6-31G* basis set is used. A much lower impact of BSSE (~ 2 –5 kcal/mol) is observed when 6-311++G** basis set is employed. A difference of 6–8 kcal/mol is noticed between BSSE corrected and uncorrected values when cc-pVDZ and cc-pVTZ basis sets are employed Table S2 of Supporting Information.

The results in Table 2 also represent the dissociation energies (DE_{rad}) obtained according to mode a of Scheme 1 given in the introduction section. The dissociation energy values computed DE_{rad} , are much lower than DE_{ions} for the same metal complexes, indicating a clear preference toward dissociation of half-sandwich complex as radicals rather than as ions in gas phase. The dissociation energy values DE_{rad} , show the following trend (Li-Cp > Na-Cp > K-Cp). There is a slight variation in case of alkaline earth metal complexes with DE_{rad} (Mg-Cp < Ca-Cp) in case of neutral complexes considered, whereas DE_{rad} for Mg-Cp is greater than Ca-Cp in the case of charged complexes considered.

The decrease in the dissociation energy is in good agreement with the increase in the metal–cyclopentadiene distance for the metals Li, Na, K, Mg, and Ca, respectively, as can be seen from

the results in Table S1 of Supporting Information. The metal to centroid of Cp distance correlates well with the strength of the dissociation energy for all the complexes, with the highest dissociation energy for Li-Cp exhibiting the shortest distance of 1.730 Å at B3LYP/6-31G* level. Further, NPA charges on metal atoms obtained by performing NBO analysis reveal maximum charge transfer in case of lithium followed by sodium and potassium (Table 3).

A similar trend is also observed for both neutral and charged magnesium and calcium complexes (charge transfer for Mg > Ca complex). A comparison of Mulliken charges on the metal in complex (Table S4 of Supporting Information) reflects essentially the same trend.

Sandwich Systems. A comparison of dissociation energy (DE_{ions}) values of Cp-M-Cp complexes (Table 4) shows a decreasing trend in case of alkali metals (Cp-Li-Cp > Cp-Na-Cp > Cp-K-Cp) and alkaline earth metals (Cp-Mg-Cp > Cp-Ca-Cp both neutral and charged), which can be correlated to the extent of charge transferred from metal (Tables 3 and 4) to π system. A comparison of metal to centroid of Cp distances (Table S1 of Supporting Information) also clearly show lower distances when higher dissociation energies are observed in the

TABLE 3: Comparison of Charge on Metal in Half-Sandwich (M-Cp) and Sandwich Complexes (Cp-M-Cp) at B3LYP/6-31G*, B3LYP/6-311++G, MP2/6-31G*, MP2/6-311++G**, MP2/cc-pVDZ, and MP2/cc-pVTZ Levels of Theory based on NBO Analysis^a**

complex	C,M	B3LYP		MP2			
		6-31G*	6-311++G**	6-31G*	6-311++G**	cc-pVDZ	cc-pVTZ
Li-Cp	(0,1)	0.901	0.917	0.911	0.917	0.938	0.929
Na-Cp	(0,1)	0.913	0.935	0.933	0.942	0.954	0.952
K-Cp	(0,1)	0.928	0.960	0.950	0.972	NA	NA
Mg-Cp	(0,2)	0.912	0.924	0.936	0.941	0.953	0.952
Mg-Cp	(1,1)	1.744	1.785	1.794	1.824	1.844	1.851
Ca-Cp	(0,2)	0.939	0.920	0.958	0.948	0.922	0.909
Ca-Cp	(1,1)	1.863	1.778	1.902	1.866	1.776	1.721
Cp-Li-Cp	(-1,1)	0.905	0.541	0.922	0.902		
Cp-Na-Cp	(-1,1)	0.888	0.707	0.915	0.920		
Cp-K-Cp	(-1,1)	0.894	0.796	0.923	0.933		
Cp-Mg-Cp	(-1,2)	0.898	0.790	0.929	0.929		
Cp-Mg-Cp	(0,1)	1.755	1.286	1.787	1.815		
Cp-Ca-Cp	(-1,2)	0.917	0.769	0.933	0.792		
Cp-Ca-Cp	(0,1)	1.819	1.434	1.857	1.816		

^a NA, no basis functions are available for potassium; C,M indicates charge and multiplicity of complex.

TABLE 4: Comparison of BSSE Corrected and Uncorrected Dissociation Energies (DE_{ions} in kcal/mol) for Sandwich Complexes (Cp-M-Cp) Optimized at B3LYP/6-31G*, B3LYP/6-311++G, MP2/6-31G*, and MP2/6-311++G** Levels of Theory^a**

complex	C,M	B3LYP				MP2			
		6-31G*		311++G**		6-31G*		311++G**	
		a	b	a	b	a	b	a	b
Cp-Li-Cp	-1,1	237.0	218.1	209.5	207.4	246.6	216.9	218.9	207.3
Cp-Na-Cp	-1,1	208.3	191.6	183.5	181.3	212.6	187.4	186.4	177.7
Cp-K-Cp	-1,1	183.1	165.9	162.7	161.4	188.3	165.4	170.7	163.9
Cp-Mg-Cp	-1,2	226.9	209.2	200.5	198.4	241.6	214.3	214.9	204.9
Cp-Mg-Cp	0,1	597.5	576.5	561.7	559.1	604.2	568.9	563.8	551.0
Cp-Ca-Cp	-1,2	221.8	206.5	213.6	211.7	225.8	201.6	222.9	212.4
Cp-Ca-Cp	0,1	501.8	484.7	488.5	486.9	505.3	478.3	491.2	480.9

^a a, uncorrected DE; b, BSSE-corrected DE; C,M indicates charge and multiplicity of complex.

respective complexes (Cp-Li-Cp < Cp-Na-Cp < Cp-K-Cp) and (Cp-Mg-Cp < Cp-Ca-Cp both neutral and charged).

BSSE-corrected dissociation energy in all the complexes both at B3LYP and MP2 levels of theory, shows ~4–10 kcal/mol higher DE value when 6-31G* basis set is employed compared to 6-311++G** basis set. Essentially similar trends for DE values at both B3LYP and MP2 level of theory as can be inferred from Table 4.

PCM Analysis. The dissociation energy for all the complexes studied considering the options of dissociation of complex into radicals/ions both for gas phase optimization and using water as solvent for M-Cp complexes are plotted in Figure 3. The dissociation energies and distance values are available in Table S6 of Supporting Information. This plot shows substantially high values of DE in case of gas-phase calculation when ions are involved ranging between (171 to 122 kcal/mol for neutral complexes of Li-Cp > Na-Cp > K-Cp; Mg-Cp > Ca-Cp). The corresponding DE in solvent-phase calculations for ions shows a total reversal with much lower dissociation energies ranging between (29 to 56 kcal/mol). A drastic decrease in dissociation energy DE_{ions} of the complexes is observed on comparing aqueous and gas phase, with all neutral complexes showing ~90–150 kcal/mol lesser dissociation energy and the +1 complexes of Mg and Ca having ~350–250 kcal/mol lower dissociation energy values in solvent phase. The ease of dissociation of the complex into ions rather than as radicals in solvent phase can be clearly visualized from the graph plotted by comparing the two lines labeled as DE_{ions} (gas) and DE_{ions} (water) respectively. In contrast to this the dissociation energy

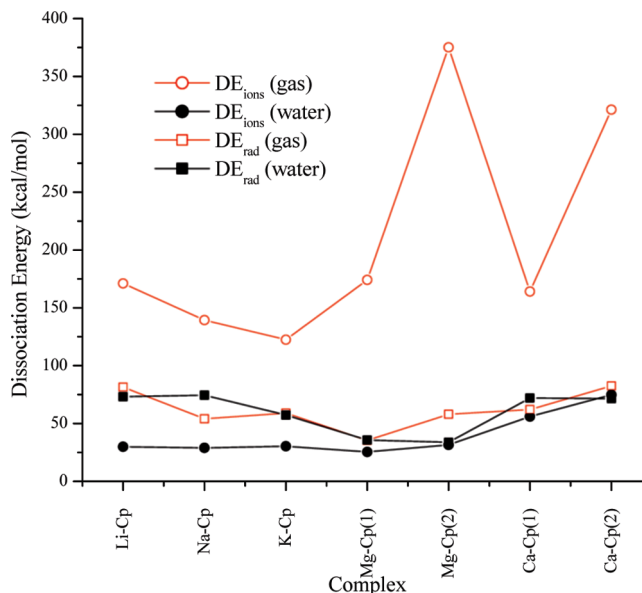


Figure 3. Graph comparing dissociation energy (DE_{ions}, DE_{rad} in kcal/mol) for metal cyclopentadiene (M-Cp) complex in gas phase and solvent phase (PCM optimization, solvent = water) at B3LYP/6-311++G** level of theory. (1) indicates neutral complex and (2) indicates complex with +1 charge for magnesium and calcium.

calculated when radicals are involved DE_{rad}, represented as DE_{rad} (gas) and DE_{rad} (water) in the graph, do not show such a drastic variation from gas (between ~81–35 kcal/mol) to solvent phase

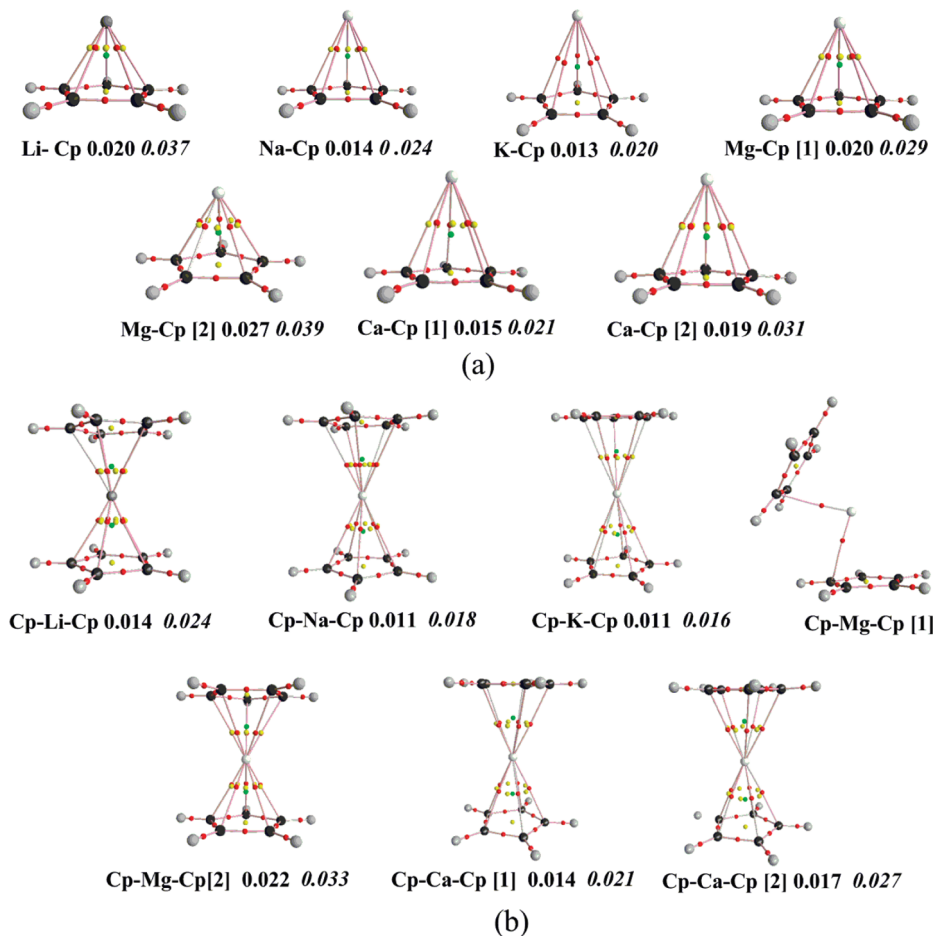


Figure 4. Electron charge density (ρ , bold in au.) and Laplacian ($\nabla^2\rho$, italics and bold in au.) at CCP (green) for (a) half-sandwich and (b) sandwich complexes of metal and cyclopentadienyl ligand at MP2/6-31G* level. In the case of (M-Cp) complexes of magnesium and calcium (1) indicates complex with 0 charge and (2) indicates complex with +1 charge. In the case of (Cp-M-Cp) complexes of magnesium and calcium (1) indicates complex with -1 charge and (2) indicates complex with 0 charge.

(between ~ 73 – 33 kcal/mol). While all metals show a clear preference to dissociate into ions in solvent phase, the Mg and Ca complexes having +1 charge on the complex show surprisingly identical preference to dissociate into M^{2+} and Cp^- or M^{+*} and Cp^* ($M = Mg, Ca$) (Figure 3). Therefore, there appears to be an equal probability in these cases for dissociation by either competing pathways. A large variation in DE_{ions} in solvent phase is noted when comparing the neutral and +1 charged complexes of Mg and Ca, and this may be traced to the differences in solvation energies of the monocationic and dicationic species of these elements. Thus a marked preference for dissociation of the complex as radicals in gas phase and as ions in solvent phase can be inferred from these PCM studies.

AIM Analysis. Half-Sandwich Systems. To evaluate the nature of cation- π interaction in M-Cp complex topological analysis of the electron density distribution within Bader's atoms in molecules theory (AIM) was performed. The nature of bonding between two monomers can be characterized by the value of electron density (ρ) and sign of Laplacian of electron density ($\nabla^2\rho$) at the bond critical point (BCP). Low ρ values along with positive $\nabla^2\rho$ values are indicative of interactions found in variety of van der Waals complexes. All the half-sandwich complexes are characterized by the presence of (3, +3) cage critical point (CCP). Figure 4a of the manuscript gives further representation of AIM results through topological graphs which include ρ and ($\nabla^2\rho$) values in au. at the CCPs shown in green color. A clear linear correlation exists between the ρ value and dissociation energy of the M-Cp complex, where the highest

ρ value is observed in the case of Li-Cp ($\rho = 0.020$ au.) followed by Na and K complexes ($\rho = 0.014, 0.013$ au., respectively). In the case of centroid of Cp to metal distance, the least distance is seen with regard to Li-Cp (1.767 Å) followed by Na and K complexes (2.224 and 2.622 Å).

Sandwich Systems. Topological graphs along with the magnitude and sign of electron density (ρ , in au.) and Laplacian ($\nabla^2\rho$ in au.) at the CCPs for the sandwich complexes are also indicated in Figure 4b. With the exception of negatively charged open Cp-Mg-Cp complex the CCPs (3, +3) have been identified for all other complexes and a linear relationship between higher dissociation energy and ρ value can be inferred from these points. The ρ value and corresponding Laplacian are slightly lower in the sandwich complexes compared to corresponding half-sandwich complexes.

RVS Analysis. Half-Sandwich Systems. RVS analysis developed by Stevens and Fink as implemented in the GAMESS package was carried out on M-Cp complexes. Accordingly total energy of a complex can be divided into the individual contributions from the coulomb and exchange energy (CEX), polarization energy (POL), and charge transfer energy (CT). To analyze the interaction in M-Cp using RVS analysis we have partitioned the complex into M^+ and Cp^- in case of alkali metals, whereas the alkaline earth metal complexes are partitioned as M^{2+} and Cp^- . The contribution of CEX to the interaction energy of all the half-sandwich complexes is several times higher than the other components as evident from Figure 5a. In the case of the three M-Cp complexes of alkali metals

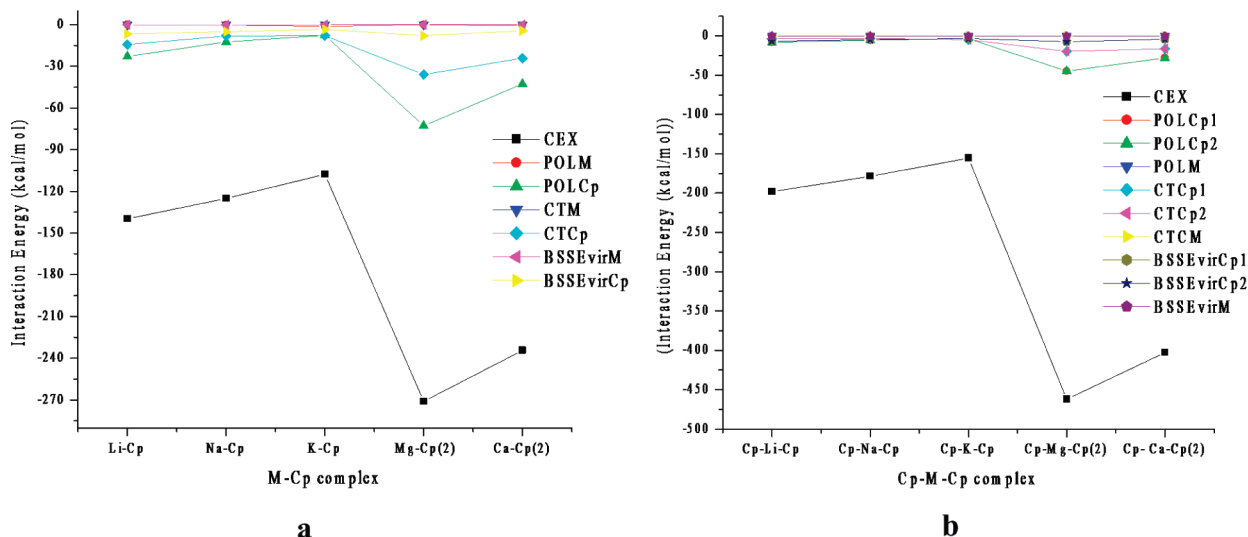


Figure 5. Graph plotted for results of RVS analysis at HF/6-31G* level for (a) M-Cp and (b) Cp-M-Cp complexes. All energies are in kcal/mol. In the case of (M-Cp) complexes for magnesium and calcium (2) indicates complex with +1 charge. In the case of (Cp-M-Cp) complexes for magnesium and calcium (2) indicates complex with 0 charge.

the percentage contribution of CEX energy term to the interaction energy shows an increasing trend with Li-Cp (78.93%), Na-Cp (85.76%), and K-Cp (86.47%), respectively. The percentage contribution of CEX energy term to the interaction energy for alkaline earth metal complexes also reflects a similar trend with Mg-Cp (71.37%) and Ca-Cp (77.59%), respectively. CEX is followed by POL and CT contributions of cyclopentadienyl ligand. The contribution of POL and CT from the metal fragment toward interaction energy of the complex is minimal (0.01–0.9%). However a marginally larger contribution from cyclopentadienyl ligand via POL rather than CT component is noticed for all complexes (Table S6a of Supporting Information). An exception is observed in the single case of the K-Cp complex where the contributions of POL and CT to the energy are indeed very similar (−7.70 and −7.92 kcal/mol, respectively). The percentage wise contribution of POL and CT from cyclopentadienyl ligand to M-Cp interaction energy is as follows, Li-Cp (12.94%, 8.11%), Na-Cp (8.49%, 5.58%), K-Cp (6.18%, 6.36%), Mg-Cp (19.17%, 9.44%), and Ca-Cp (14.12%, 8%). Frenking et al. have partitioned the energy contributions of interactions involving M-Cp complexes of Li, Na, K, using the ADF program package employing the BP86 functionals.³⁰ They report a contribution of 80–90% from the electrostatic term to the interaction energy on the basis of ADF partitioning results. Our analysis reiterates a similar contribution from CEX ranging from 78 to 87%. The real novelty in the results of our study however lies in partitioning of the orbital relaxation effect into polarization and charge transfer components from the two fragments to clearly delineate the higher contribution of the polarization term compared to charge transfer of cyclopentadienyl ligand. Thus RVS energy decomposition analysis results of M-Cp complexes seem to support the classification of the metal ligand bonding in alkali/alkaline-metal metallocenes as mainly ionic.

Sandwich Systems. The Cp-M-Cp complexes are partitioned into M^+ and two Cp^- fragments in case of alkali metal complexes and into M^{2+} and two Cp^- fragments in the case of alkaline earth metal complexes. The contribution of CEX dominates over both POL and CT components (Figure 5b, Table S6b of Supporting Information). We observe a relatively higher contribution from cyclopentadiene via POL rather than CT in these complexes. This is essentially similar to the pattern of

energy decomposition noted for half-sandwich complexes. The percentage contribution of CEX energy term to the interaction energy for all the metal sandwich complexes is as follows Cp-Li-Cp (89.54%), Cp-Na-Cp (91.40%), Cp-K-Cp (90.43%), Cp-Mg-Cp (78.21%), and Cp-Ca-Cp (81.96%), respectively. The contribution to the interaction energy from the CEX term is higher in sandwich complexes than their corresponding half-sandwich complexes. A parallel decrease in POL and CT contributions to the interaction energy in sandwich complexes is noted compared to half-sandwich complexes. The percentage wise contribution of POL and CT from cyclopentadienyl ligands to the interaction energy of Cp-M-Cp is as follows, Cp-Li-Cp (7.40%, 3.05%), Cp-Na-Cp (5.34%, 3.21%), Cp-K-Cp (3.91%, 5.60%), Cp-Mg-Cp (15.15%, 6.64%), Cp-Ca-Cp (11.37%, 6.65%). Unlike the K-Cp complex where POL and CT terms from cyclopentadienyl ligand are highly similar (~7.8 kcal/mol), the Cp-K-Cp complex shows a larger contribution from both the cyclopentadienyl ligands through the CT term (−9.62 kcal/mol) rather than POL term (−6.72 kcal/mol).

Conclusions

Quantum chemical calculations are performed on M-Cp and Cp-M-Cp complexes of cyclopentadienyl ligand and selected alkali and alkaline earth metals. The twin dissociation pathways of M-Cp complexes and the effect of solvent on them were analyzed. The complexes dissociate into radicals in the gas phase, while the preference for dissociation into ions enhances upon solvation. The electron density values at CCPs confirm the nature of cation- π bonding between the metal atom and the π cloud of cyclopentadienyl group. RVS analysis indicates that the major contributions to the cation- π interaction come from the coulomb exchange term. The splitting of orbital relaxation effects into polarization and charge transfer energy reveals a larger impact from polarization of cyclopentadienyl ligand.

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Supporting Information Available: Tables of dissociation energies, coordinates of B3LYP/6-31G*-optimized geometries of all complexes considered in the study, tables of Mulliken charges on metals, metal-Cp distances, and tabulation of RVS results. This material is available free of charge via Internet at <http://pubs.acs.org>.

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