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Notes

Donor−Acceptor Sandwiches of Main-Group Elements

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Summary: Main group bis-element sandwiches formed by donor−acceptor interactions of MCp and ECp (M = Li, Na, K; E = B, Al, Ga) have been studied at the B3LYP/pVDZ level of theory. The most stable are boron-containing species which are stabilized by electrostatic interactions, while other compounds are destabilized. The stability of the donor−acceptor bond decreases in the row B > Al > Ga for donors and Li > Na > K for acceptors. The Cp group enhances donor properties by 10−15 kJ mol^{-1}. We predict that these new compounds are viable synthetic targets.*

Introduction

The unexpected discovery of the bis-metallic sandwich compound Cp*ZnZnCp* (Cp* = C_5Me_5)[1a] in 2004 opened a new dimension to metallocene chemistry. In this remarkable D_{5h}-symmetric compound a pair of metal atoms is sandwiched between two Cp* rings. This unprecedented structural motif is fascinating and encourages further study. The frontiers of emerging chemistry of bis-element transition-metal[1b,2] and main-group[3] metallocenes are rapidly being explored with theoretical methods. In particular, D_{5h}-symmetric main-group bis-element sandwiches CpEECp (E = Be, Mg, Ca; Cp = C_5H_5) have been theoretically predicted to be stable molecules.[3] Formation of these group 2 dimetallocenes may be formally viewed as two interacting half-sandwich radicals (Figure 1a). On the other hand, formation of bis-element sandwiches may be formally achieved by donor−acceptor interactions between half sandwiches of group 1 and group 13 elements (Figure 1b). Group 13 element compounds in oxidation state I possess a lone pair and are known to act as donor molecules. In recent years, donor properties of monovalent group 13 compounds toward transition metals and main-group elements have been studied extensively, both experimentally[4] and theoretically.[5] Cyclopentadienyl derivatives of monovalent group 13 elements are well-known. AlCp* and GaCp* are oligomeric (tetrameric and hexameric, respectively) in the solid state but exist in the vapor phase as monomer molecules.[6,7] Group 1 metallocenes form polymeric chainlike or triple-decker-like structures in the condensed phase.[8,9] In the present report we details a theoretical study of the formation of the novel main-group donor−acceptor bis-element sandwiches CpE−MCp (E = B, Al, Ga; M = Li, Na, K). We report the structures and stability of these compounds and predict the most promising targets for synthetic work.

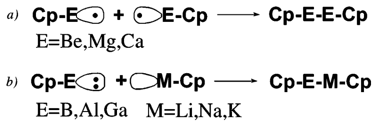

Figure 1. Formation of the main-group bis-element sandwiches: (a) by interaction of group 2 element cyclopentadienyl radicals; (b) by donor−acceptor interactions between monovalent group 13 and group 1 half-sandwiches.

Results and Discussion

The present theoretical approach is based on density functional theory in the form of the B3LYP functional (see Computational Methods). Optimized structures of the group 1 and 13 half-sandwiches are given in the Supporting Information. Our predictions are in line with the previous theoretical study by Rayón and Frenking.[5d]

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Table 1. Structural and Energetic Properties of Investigated Compounds (C_{5v} Point Group)

compd	R(E−M)	R(E−C)	R(M−C)	$\theta_E{}^b$	$\theta_M{}^b$	E^{diss}	q_E (Δq_E)^c	q_M (Δq_M)^c	q_{CT}	μ
CpBLiCp	2.281	1.878	2.210	−7.02	1.12	92.3	−0.033 (−0.086)	0.807 (−0.133)	0.109	10.14
CpBNaCp	2.623	1.883	2.587	−6.81	2.66	82.8	−0.059 (−0.113)	0.867 (−0.086)	0.080	12.78
CpBKCp	3.164	1.903	3.000	−6.41	2.99	60.0	−0.061 (−0.115)	0.936 (−0.040)	0.039	14.95
Cp*BLiCp	2.275	1.851	2.219	−4.51	1.07	106.0	−0.064 (−0.052)	0.789 (−0.150)	0.127	10.64
Cp*BNaCp	2.612	1.855	2.597	−4.19	2.56	97.1	−0.089 (−0.077)	0.849 (−0.103)	0.098	13.43
Cp*BKCp	3.151	1.871	3.009	−3.91	2.91	71.3	−0.096 (−0.084)	0.921 (−0.055)	0.051	15.69
CpAlLiCp	2.801	2.327	2.174	−0.19	1.27	34.3	0.633 (0.016)	0.821 (−0.118)	0.082	7.56
CpAlNaCp	3.185	2.326	2.555	0.03	2.97	30.3	0.591 (−0.026)	0.886 (−0.067)	0.054	10.38
Cp*AlLiCp	2.768	2.297	2.182	2.98	1.20	42.2	0.668 (0.013)	0.818 (−0.121)	0.085	8.80
Cp*AlNaCp	3.145	2.295	2.562	3.09	2.86	39.2	0.624 (−0.030)	0.882 (−0.071)	0.059	11.70
CpGaKCp	3.748	2.417	2.966	0.69	3.35	12.2	0.534 (−0.062)	0.961 (−0.015)	0.011	11.40

[a] Bond lengths are in angstroms, angles in degrees, dissociation energies E^{diss} (without ZPVE correction) in kJ mol^{-1}, and dipole moments μ in debyes.The B3LYP/TZVP level of theory was used. [b] θ is the angle between the C−H (C−C) bond and the plane of the C_5 ring. A negative sign corresponds to inward bound hydrogen atoms or methyl groups and a positive sign to those that are outward bound. [c] q_E and q_M are atomic charges on E and M in the complex (based on the natural population analysis); Δq_E and Δq_M are changes of the atomic charges on E and M upon complex formation (based on the natural population analysis).

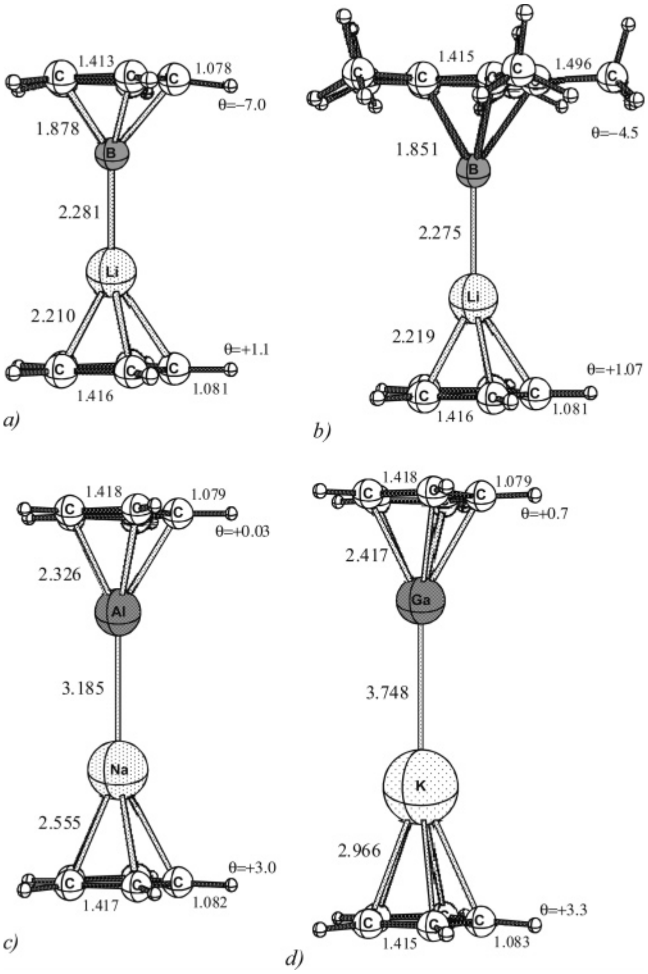

Figure 2. Optimized structures of selected donor−acceptor bis-element sandwiches (C_{5v} point group): (a) CpBLiCp; (b) Cp*BLiCp; (c) CpAlNaCp; (d) CpGaKCp. Bond distances are in angstroms and angles in degrees. θ is the angle between the C−H (C−C) bond and the plane of the C_5 ring. A negative sign corresponds to inward bound hydrogen atoms or methyl groups and a positive sign to ones that are outward bound.

Optimized structures of the selected donor−acceptor sandwiches are presented in Figure 2. Table 1 summarizes major structural and energetic characteristics of the donor−acceptor sandwich compounds. All sandwiches are predicted to possess C_{5v} point group structures with an eclipsed orientation of the Cp rings. Alternative staggered conformations were found to be higher in energy, but the energy difference between the two is only 0.05 kJ mol^{-1}, reflecting the very flat character of PES and essentially free rotation of the Cp rings. The same situation was reported earlier for the isoelectronic group 2 bis-metallocenes, which have been recently studied theoretically with the B3LYP/DZP method.[3] Predicted from the natural population analysis are partial charges on Be, Mg, and Ca of 0.85, 0.92, and 0.92, respectively, reflecting the ionic nature of the group 2 bis-metallocenes. It is of interest to compare the structures of group 2 bis-metallocenes with those of the isoelectronic donor−acceptor sandwiches. The E−M distances for CpBLiCp (2.281 Å) and CpAlNaCp (3.185 Å) are significantly longer compared to those for the isoelectronic metallocenes CpBeBeCp (2.057 Å) and CpMgMgCp (2.766 Å). However, the E−M bond distances in CpGaKCp (3.748 Å) and CpCaCaCp (3.740 Å) are similar. Upon complex formation, the E−C distances shorten by about 0.07−0.10 Å for B, 0.07 Å for Al, and 0.06 Å for Ga, while the M−C distances elongate by 0.03 Å for Li, 0.06 Å for Na, and 0.05 Å for K. Those structural changes are accompanied by charge transfer from the donor to the acceptor fragment. The value of the overall charge transfer q_{CT} is small and decreases on going from second-row to fourth-row complexes: from 0.11 for CpBLiCp to 0.05 for CpAlNaCp and 0.01 for CpGaKCp. Dissociation energies follow the trend found for charge transfer, decreasing from an optimistic 92 kJ mol^{-1} for CpBLiCp to a noticeable 30 kJ mol^{-1} for CpAlNaCp and to a discouraging 12 kJ mol^{-1} for CpGaKCp.

Analysis of the data in Table 1 reveals that all boron-containing complexes have fairly large dissociation energies (60−92 kJ mol^{-1}), which are 2−3 times larger compared to those of Al-containing sandwiches (30−34 kJ mol^{-1}). Gallium-containing species are only weakly bound (12 kJ mol^{-1}). Thus, the stability of the donor−acceptor bond decreases in order: for donors, B $\gg$ Al > Ga; for acceptors, Li > Na > K. Interaction of ECp with acceptor fragments was discussed by Uddin and Frenking.[5b] They showed that the electrostatic interaction between E and M takes place between the local concentration of the negative charge of E which comes from the lone pair donor electrons and the local charge depletion at M. The lower stability of Al,Ga-containing complexes may be explained in terms of longer distances, which weaken the electrostatic attraction and weaken orbital interactions of the heavier elements. The interesting feature of B-containing complexes is a peculiar charge redistribution upon complex formation. For these complexes the value of Δq_E is always negative, indicating that the negative charge is increased on the donor atom. This reflects the greater electronegativity of the boron compared to their group 1 counterparts in the complex. We should state that changes in NPA charges are very small and are possibly subject to an artifact recently described by Guerra et al.[10] A thorough analysis of the bonding situation in the complexes requires detailed additional studies and will be given in following reports.

Although the most strongly bonded cyclopentadienyl sandwich CpBLiCp has a sizable dissociation energy of 92 kJ mol^{-1}, it is of interest to form even more strongly bound complexes. In the present report, we considered improving the donor−acceptor bond strength in the sandwiches by adding electron-donating Me substituents to the Cp ring at E. Cp* is a well-known stabilizing ligand, which significantly enhances the donor properties of group 13 half-sandwiches. Substitution of Cp by Cp* increases the donor−acceptor bond energy of $C_5R_5B-BCl_3$ adducts by 30 kJ mol^{-1}.[2c] Several BCp* and AlCp* complexes have been considered in the present work (Table 1). As expected, substitution of Cp by Cp* shortens the M−E distances (by 0.03 Å) and increases dissociation energies (by 10−15 kJ mol^{-1}) and charge transfer (by 0.01−0.02).

The possibility of the existence of group 13−group 1 element sandwiches may be traced in some experimental work. Interestingly, the off-white waxy compound AlC_5Bz_5 (Bz = $CH_2C_6H_5$), produced by the exchange reaction between AlCp* and LiC_5Bz_5 (in toluene, 50 °C, 12 days), contained small amounts of LiC_5Bz_5 as an impurity.[9] We speculate that formation of the weakly bound donor−acceptor complex $C_5Bz_5Al-LiC_5Bz_5$ may be responsible for this impurity.

Thus, it follows from our computations that donor−acceptor bis-element sandwiches are stable molecules with respect to dissociation into components. The most promising synthetic targets would be BCp*−LiC_5R_5 complexes with dissociation energies of about 100 kJ mol^{-1}. Such a donor−acceptor bond energy is expected to fully compensate for all unfavorable depolymerization/deoligomerization energies required for interactions between free components. The energy of the donor−acceptor bond decreases in the following orders: for donors, B ≫ Al > Ga; for acceptors, Li > Na > K. Complexes formed by AlCp* and GaCp* are predicted to be considerably weaker (dissociation energies are about 40 kJ mol^{-1}) but still could exist at low temperatures. Reversible decomposition of tetrameric $Al_4Cp^*_4$ into monomeric AlCp* in toluene was evidenced above 30 °C,[6] and the dissociation enthalpy was estimated as 150 ± 20 kJ mol^{-1}, which gives 38 ± 5 kJ mol^{-1} per AlCp* unit. This energy is comparable with the predicted bonding energy in Cp*Al−LiCp and Cp*Al−NaCp compounds. Since group 1 metallocenes form polymeric $(CpM)_x$ structures in the solid state, formation of CpMECp* from polymeric $(CpM)_x$ and oligomeric $(ECp^*)_n$ could still be endothermic. However, it is expected that reaction between monomeric CpM and oligomeric $(ECp^*)_n$ in solution will lead to the CpMECp* complex formation. Given the fact that both group 13 and group 1 source compounds are well-known laboratory species, the synthesis of the new members of the fascinating bis-element sandwiches is expected to be straightforward. We are optimistic that the synthesis of these novel sandwich compounds will be accomplished soon.

Computational Methods

The present theoretical approach is based on density functional theory in the form of the hybrid three-parameter B3LYP functional[11] conjoined with a TZVP basis set (TZV basis set of Ahlrichs,[12] augmented by polarization functions). The basis sets are designated (311/1) for H, (62111/1) for Li, (62111/411/1) for B,C,N, (73211/511) for Na, (73211/6111/1) for Al, (842111/6311) for K, and (842111/6311/511) for Ga.[13]

The Gaussian[14] suite of programs was used throughout. Donor and acceptor half-sandwiches, as well as their complexes, were optimized in the framework of the C_{5v} point group. All stationary points on potential energy surfaces (PES) were characterized by the evaluation of analytic second derivatives and correspond to minima on the PES. There is good agreement between our predicted B3LYP/TZVP geometries and experimental gas-phase electron diffraction structures of MCp* molecules (M = Al,[6] Ga[7]) (see the Supporting Information). In several cases, due to the flatness of the PES with respect to rotation of the Cp and Cp* groups, structures of the C_{5v} symmetry were incorrectly predicted to be nonminimum stationary points when the standard Gaussian integration grid was employed. These stationary points turned out to be minima when a finer integration grid (99 radial shell with 590 angular points per shell) was used. Atomic charges were determined using natural population analyses (NPA).[15]

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Supporting Information Available: Figures with optimized structures of donor and acceptor half-sandwiches and a table containing the total energies of the investigated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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