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Article

Donor–Acceptor Heteroleptic Open Sandwiches

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A series of donor–acceptor heteroleptic open sandwiches with formula CpM–M′Pyl (M = B, Al, Ga; M′ = Li, Na; Cp = cyclopentadienyl; Pyl = pentadienyl) has been designed in silico using density functional theory. The most stable complexes are those containing boron as a donor atom. A molecular orbital analysis shows that the s character of the lone pair located at the group 13 element is mainly responsible for the complex stabilization. It is also found that the surrounding medium has a similar effect on these sandwiches such as in the "classical" donor–acceptor complexes, showing a decrement in the group 13 element–alkaline metal bond lengths.

I. Introduction

A very interesting recent result in organometallic chemistry has been the synthesis of decamethyldizincocene or Cp*Zn−ZnCp* [Cp* = η^5-$C_5(CH_3)_5$].[1] As demonstrated by a crystallographic study, this complex contains two eclipsed Cp*Zn fragments where the Zn−Zn bond is collinear with the C_5 symmetry axes of the Cp* rings. This discovery has triggered the interest of several groups in finding new bis-metallic sandwiches.[2−9]

A standard definition of a sandwich complex or metallocene has two features: first, it states that these compounds have a sandwiched "metal" (M) and, second, that the ligands are two "cyclopentadienyls" (η^5-C_5H_5, Cp). Consequently, a bis-metallic sandwich contains two "metals" located between two Cp rings. There are, however, a plethora of metallocenes where M is a main-group element and/or at least one Cp is substituted by other π-cloud ligands such as pentadienyl (η^5-C_5H_7, Pyl).[10] Thus, the following question immediately emerges: Can a bis-element sandwich with ligands different from Cp and Cp* exist? Recently, Timoshkin and Schaefer reported a series of main-group homoleptic sandwiches formed by donor−acceptor interactions of CpM and M′Cp (M = Li, Na, K; M′ = B, Al, Ga).[7] However, there are no reports of bis-element sandwiches with acyclic ligands such as pentadienyl. These facts are strong enough motivations to survey (via density functional theory, DFT) a series of structures with the general formula CpM−M′Pyl (M = B, Al, Ga; M′ = Li, Na), which are the first examples of donor−acceptor heteroleptic open sandwiches.

II. Computational Details

All geometry optimizations and electronic structure calculations were performed using *Gaussian 98*.[11] All structures were fully optimized using Becke's exchange (B), Lee, Yang, and Parr (LYP) correlation,[12,13] within the hybrid functional (B3LYP) approach, as implemented in Gaussian. A 6-311++G(d,p) basis set was employed for all calculations.[14,15] Every stationary point on the potential energy surface (PES) was characterized by a harmonic analysis using the same theoretical methodology as that used in the optimization. The harmonic frequencies were used to evaluate the zero-point energy correction for energy differences (scaled by 0.9806, as recommended by Scott and Radom).[16] To analyze the bonding mechanism, a natural population analysis was done.[17] The

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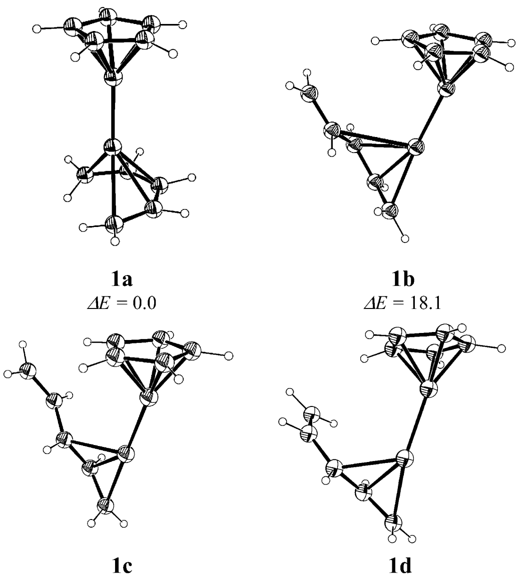
visualization of the molecular orbitals (MOs) was done with Molekel.[18] Solvent effects were estimated by using the self-consistent reaction field (SCRF) theory of Tomasi et al.,[19,20] with the cavity defined by the united-atom model.[21]

III. CpB−LiPyl and Their Isomers

Some of the most intensively investigated cyclopentadienyl compounds are those containing a group 13 element in the $1+$ oxidation state.[22−24] Generally, in gas phase or solution, these compounds are monomeric,[25,26] but in the solid-state, Cp*Al and Cp*Ga form tetrameric and hexameric clusters.[24,27,28] The analysis of the electronic structure in the CpM molecules (M = B, Al, Ga) reveals that the group 13 element has a lone pair of electrons; i.e., it can act as a Lewis base.[29−31] This behavior is counterintuitive with respect to the commonly known and expected reactivity of group 13 compounds. Thus, on paper, these CpM fragments (M = B, Al, Ga) may interact with a Lewis acceptor like M′Cp or M′Pyl (M′ = Li, Na). An issue that has to be addressed in the special case of the M′Pyl ligand is the existence of other isomers.

It is well-known that LiPyl and NaPyl can adopt several conformers,[32] which has to be considered when they interact with a Lewis base, like CpM, to form a CpM−M′Pyl complex. Let us consider the simplest one: CpB−LiPyl. Starting from several conformations of the acyclic ligand, four minima were found, which are depicted in Figure 1. Not surprisingly, the most stable conformation (**1a**) has a U-shaped arrangement. Pratt and Streitwieser argued that the U-shaped structure of LiPyl is the preferential conformation because in this arrangement the electrostatic attraction between the cation and the anionic carbons is maximized.[32] Besides the U-shaped structure, the sickle-shaped (**1b**), W-shaped (**1c**), and distorted sickle-shaped (**1d**) structures were also found. The energetic order of these complexes (see Figure 1) shows that the most stable conformer corresponds to **1a**, which has the maximum coordination of the metal cation to the pentadienyl anion, η^5.



1a
ΔE = 0.0

1b
ΔE = 18.1

1c
ΔE = 13.5

1d
ΔE = 24.6

Figure 1. Optimized geometries of CpB−LiPyl isomers. Relative energies (ΔE) are given in kJ·mol^{-1}.

IV. Structures and Stabilities of CpM−M′Pyl

Guided by the previous analysis, we designed a series of new heteroleptic open sandwiches. The geometries of the ligands and complexes are shown in Figure 2. Selected structural parameters are summarized in Table 1. For comparison and in order to study the bonding mechanism prevailing in these compounds, the homoleptic sandwiches CpM−M′Cp were also studied. Inspection of Table 1 shows that the M−M′ bond lengths are similar to those found in CpM−M′Cp. In general, the structures of the Cp and Pyl moieties are similar to those of the corresponding free ligands, with slight differences due to complexation. For example, there is an increase of the M′−C1 and M′−C2 bond lengths by about 8 pm and a reduction of the M−C bonds (7−9 pm). Note that in the boron-containing complexes, homo- or heteroleptic, the hydrogens in the Cp ring are bent inward with $\theta \approx -9.0°$, while the aluminum and gallium cases have an almost planar structure, with angles slightly negative for aluminum and slightly positive for gallium. This trend is also observed in the CpM ligands and Cp*M−LiPyl complexes.

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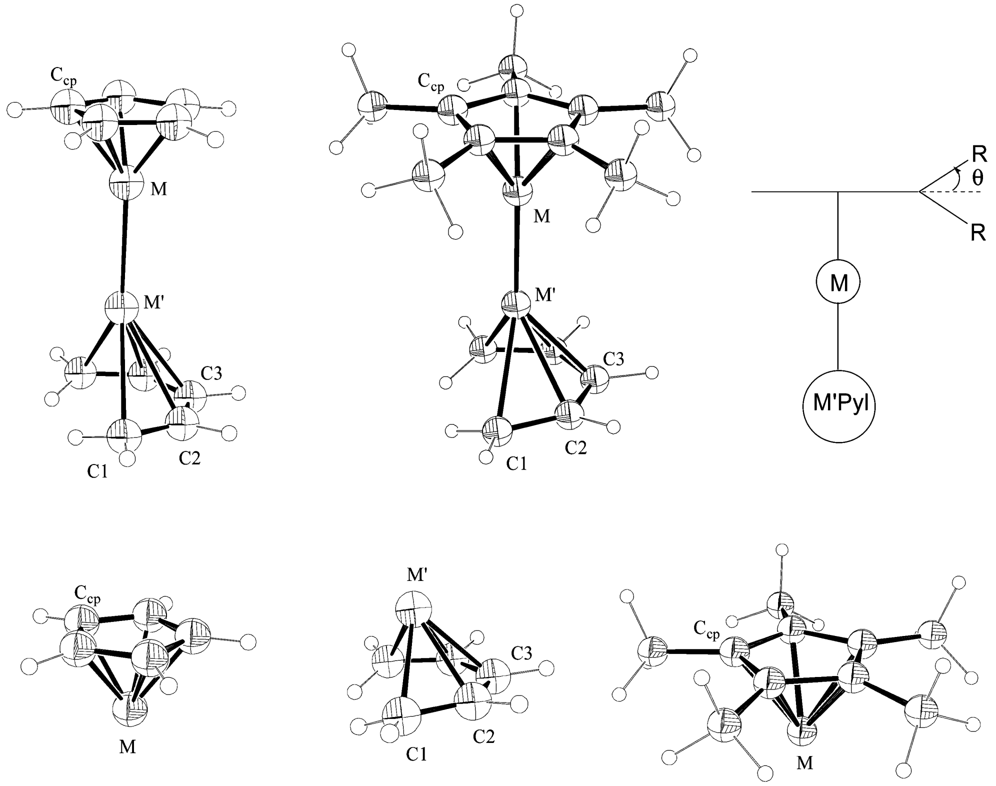

Figure 2. Geometries of the ligands and donor−acceptor complexes studied here. θ is the angle between the C−R bond (R = H, CH_3) and the plane of the C_5 ring in the inset figure.

Table 1. Selected Bond Lengths (in pm) and Dihedral Angles (in deg) of Donor−Acceptor Bis-Element Sandwiches

CpM−M′Pyl	M−M′	M′−C1	M′−C2	M′−C3	M−C	C1−C2	C2−C3	$C_{cp}-C_{cp}$	θ
CpB−LiPyl	226.0	237.4	221.6	217.2	187.7	137.7	142.1	141.6	−8.9
CpB−NaPyl	263.6	266.9	262.9	264.2	188.4	138.1	141.9	141.6	−8.5
CpAl−LiPyl	281.1	230.8	217.2	213.7	233.2	138.0	142.2	142.0	−0.3
CpAl−NaPyl	319.8	260.6	261.2	265.1	232.9	138.3	141.8	142.0	−0.2
CpGa−LiPyl	275.9	228.8	215.9	212.8	241.3	138.0	142.2	142.1	0.4
CpGa−NaPyl	316.4	258.7	260.4	265.0	241.2	138.3	141.8	142.1	0.5
CpB−LiCp	226.0	217.1			187.8	141.8		141.6	−6.0
CpB−NaCp	262.7	258.4			188.2	141.8		141.6	−5.8
CpAl−LiCp	280.5	231.4			232.7	141.9		142.0	−0.2
CpAl−NaCp	316.9	255.4			232.3	141.9		142.0	−0.1
CpGa−LiCp	274.1	212.3			240.6	141.9		142.1	0.4
CpGa−NaCp	312.7	254.4			240.4	141.9		142.1	0.5
Cp*B−LiPyl	225.6	239.9	223.3	218.2	185.2	137.8	142.1	142.6	−3.7
Cp*Al−LiPyl	279.6	231.4	217.6	214.2	230.3	137.9	142.2	143.0	2.1
Cp*Ga−LiPyl	272.8	230.2	216.8	213.6	237.9	138.0	142.2	143.0	2.8

CpM	M′Pyl	M−M′	M′−C1	M′−C2	M′−C3	M−C	C1−C2	C2−C3	$C_{cp}-C_{cp}$	θ
CpB						196.7			141.4	−5.1
CpAl						239.7			141.8	−0.1
CpGa						248.3			141.9	0.6
Cp*B						191.7			142.4	−3.2
Cp*Al						235.8			142.7	2.1
Cp*Ga						244.6			142.8	2.8
	LiPyl		225.0	213.5	211.3		138.2	142.3		
	NaPyl		254.5	260.4	267.1		138.5	141.6		
	LiCp		210.4				142.0			
	NaCp		252.6				142.0			

Let us focus on the ligand rotations and bond dissociation energies. All of the CpM−M′Pyl complexes have a nearly eclipsed conformation with a negligible rotational barrier (less than 0.05 kJ·mol^{-1} for CpB−LiPyl), which means that the molecules have a fluxional structure. The flatness of the PES with respect to this torsional motion is also fully appreciated by the values of the smallest normal mode (see Table 2). These trends are in line with those found in homoleptic CpM−M′Cp compouds.[7]

The computed CpB−LiPyl → CpB + LiPyl bond dissociation energy (BDE) is 80 kJ·mol^{-1}, which is 3 and 5 times larger than those obtained for CpAl−LiPyl and CpGa−LiPyl, respectively (see Table 2), and indicates that the boron structure is the most stable and that the stability decreases

Table 2. Smallest Frequencies ν_1 (in cm^{-1}), BDEs (in kJ·mol^{-1}), s-Character (% s), s-Character Change Δ(% s), where Δ(% s) = (% s)(CpM−M′P) − (% s)(CpM), the Natural Population Analysis Charges q, and the Charge Transfer q_{CT}

	ν_1	BDE	% s	$-\Delta$(% s)	q_M	$q_{M'}$	q_{CT}
CpB−LiPyl	12.5	80.0	75.3	11.0	0.056	0.802	0.073
CpB−NaPyl	10.0	71.4	76.5	9.7	0.050	0.844	0.064
CpAl−LiPyl	12.3	26.6	90.2	4.0	0.629	0.765	0.092
CpAl−NaPyl	12.0	24.8	90.1	4.1	0.597	0.812	0.073
CpGa−LiPyl	15.8	16.6	93.8	2.8	0.556	0.796	0.060
CpGa−NaPyl	9.0	13.7	93.8	2.8	0.528	0.833	0.044
CpB−LiCp	13.5	83.7	75.3	11.0	0.055	0.825	0.076
CpB−NaCp	13.7	79.6	76.1	10.1	0.041	0.879	0.062
CpAl−LiCp	20.5	29.6	89.9	4.3	0.629	0.794	0.100
CpAl−NaCp	9.3	30.5	89.5	4.7	0.588	0.860	0.074
CpGa−LiCp	10.1	19.0	93.2	3.4	0.516	0.888	0.047
CpGa−NaCp	7.8	17.7	93.6	3.0	0.549	0.828	0.064

when one descends in the group 13 column. The sodium complexes have slightly smaller BDEs than the lithium analogues, but the periodic trends are the same and, again, the boron-containing complex has the largest BDE. In agreement with the experimental evidence, the substitution of hydrogens by methyl groups in the Cp ligand enhances the interaction among them. For instance, this is directly reflected in the B−Li bond length reduction and the concomitant increase of the Cp*B−LiPyl → Cp*B + LiPyl BDEs (95 kJ·mol^{-1}).

Note that the calculated BDEs (Table 2) predict that the homoleptic complexes are slightly more stable than their heteroleptic analogues. The largest energy difference corresponds to the B−Na compound with a value of 8.2 kJ·mol^{-1}, while the smallest one is 2.4 kJ·mol^{-1}, corresponding to the Ga−Li complexes. When an alkaline metal is fixed, these energy differences decrease when one descends in the group 13 column.

V. Bonding Analysis of CpM−M′Pyl and CpM−M′Cp

To gain a better understanding of the bonding mechanism in these bis-element open sandwiches, a MO analysis was done. Figure 3 shows a Walsh diagram for the dissociation pathway CpB−LiPyl → CpB + LiPyl. The highest occupied MO (HOMO; MO−A of Figure 3) and MO−C have mainly a pentadienyl character. As a result of the interaction, the HOMO is destabilized. In contrast, the energy of MO−B goes markedly down when the two fragments approach. This MO has mainly a boron lone-pair character, with an antibonding combination of the π-C_5H_5 framework. From the Walsh diagram, it is clear that the changes in the MOs lying below MO−C are less pronounced. From this fact and perturbation theory arguments, it follows that one can attribute the stabilization of the complex to the lowering in energy of bonding MO−B. The results of our analysis are not restricted to heteroleptic open sandwiches, but it is also valid for any donor−acceptor sandwich.

It should be mentioned that the lone pair in the CpB and CpAl complexes is the HOMO. However, in CpGa the lone pair is the MO below the HOMO, where this latter orbital is degenerate and it is related to the interaction between Cp and the p orbitals of gallium parallel to the Cp ring (see the

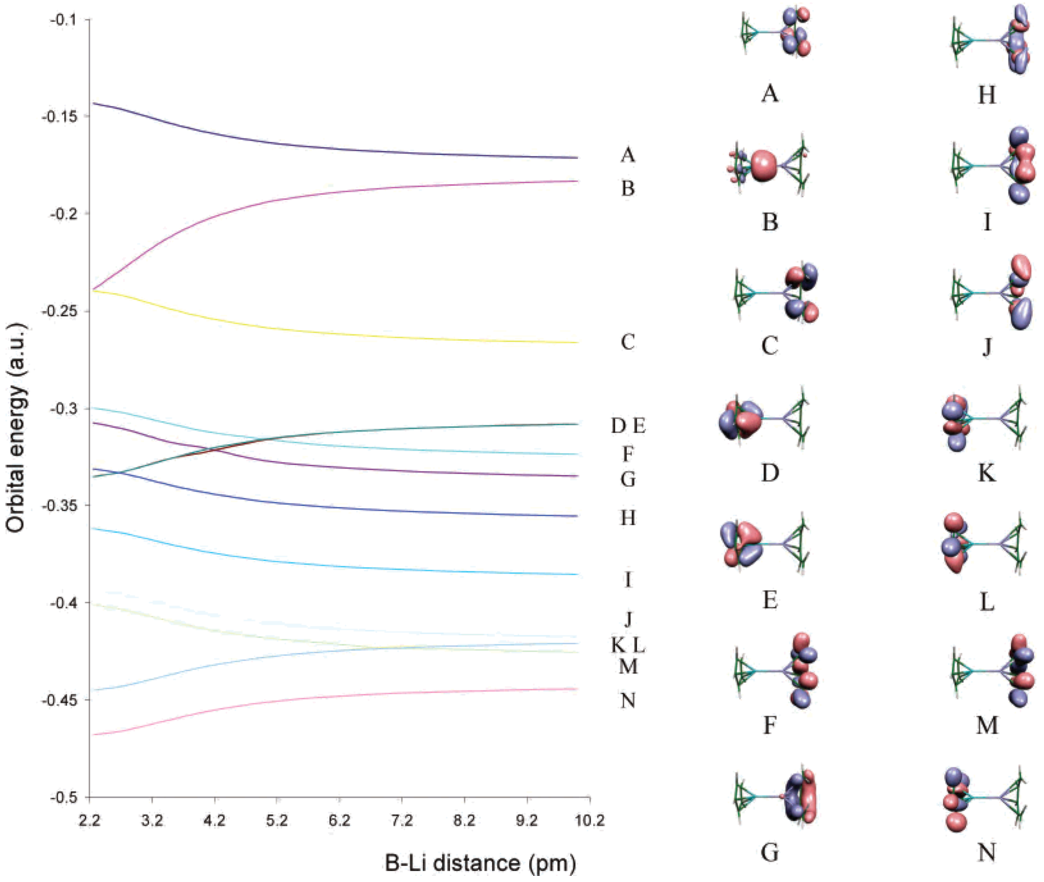

Figure 3. Walsh diagram for the dissociation pathway CpB−LiPyl → CpB + LiPyl.

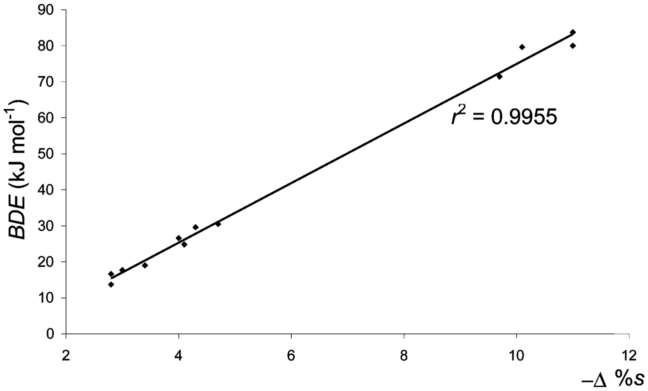

Figure 4. Correlation ($r^2 = 0.9955$) of the BDE versus the s-character change (−Δ% s) of donor−acceptor sandwiches.

Supporting Information). This fact explains why the interaction of CpGa with a Lewis acceptor is weaker than that observed for the CpB and CpAl cases.

It is well-known that the basicity of a molecule possessing a lone pair increases when the s character of the lone-pair hybrid orbital decreases. The s-character values of the lone pair located at the group 13 element (% s) obtained by the natural population analysis are listed in Table 2. In the free ligands, the lone-pair orbital has a predominant s character (86.2, 94.2, and 96.6% for B, Al, and Ga, respectively). When these fragments enter into a complex with the Lewis acid M′Pyl, a reduction of the s character is observed. A linear correlation is obtained ($r^2 = 0.9955$) by plotting the s-character change [−Δ(% s)] against the BDE (see Table 2 and Figure 4), indicating that one of the important factors controlling the complexation is the change in the s character of the lone pair, which is a subtle change of around 11%.

One may be tempted to calculate the charge transfer (q_{CT}; see Table 1) from the donor to the acceptor using the NBO atomic charges, but the small values obtained (see Table 2) prevent one from drawing a definite conclusion.[33]

VI. Solvent Effects

The origin of the solid−gas structural differences in the weak donor−acceptor complexes has been addressed in several studies.[34−37] For instance, BH_3NH_3 has a shorter B−N bond length in the solid-state (158 pm)[38] than in the gas phase (165.7 pm).[39] Previous works have suggested that the electrostatic interactions in the solid state, mainly the dipole−dipole, are primarily responsible for this shortening of the B−N bond length. Because the bonding mechanism prevailing in the herein studied molecules is similar to the "classical" donor−acceptor complexes, it is interesting to study the effect of the surrounding medium on their structure. To estimate the effect of the dipolar field on the donor−acceptor sandwiches, the geometries of CpB−LiPyl and CpB−LiCp were optimized simulating the electric field of a surrounding solvent using the SCRF model, with water as a solvent. We found that the B−Li bond length in CpB−LiPyl and CpB−LiCp shortens by 7 and 10 pm, respectively, over the value in the gas phase (226 pm in both cases). The present results indicate that the dipole induced by the medium along the principal axis of the sandwich "pushes" the electron pair of B toward Li with a concomitant shortening and strengthening of the B−Li bond.

VII. Conclusions

In this paper, the structure of a series of donor−acceptor heteroleptic open sandwiches has been predicted via a detailed DFT study. It is found that those containing boron are the more stable ones. In fact, the computed BDE is around 80 kJ·mol^{-1}, which is 3 and 5 times larger than those calculated for aluminum and gallium complexes, respectively. The MO analysis shows that the stabilization of the complex is mainly driven by the lone-pair orbital that is located at the group 13 element, finding a linear correlation ($r^2 = 0.9955$) between the s-character change of this orbital [−Δ(% s)] and the BDE. The surrounding medium has a similar effect on these sandwiches such as in the "classical" donor−acceptor complexes, showing a decrement in the group 13 element−alkaline metal bond length. In summary, everything indicates that heteroleptic donor−acceptor open sandwiches are stable molecules. However, no examples of such complexes exist in vitro. Yet.

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Supporting Information Available: The *xyz* coordinates for donor−acceptor heteroleptic open sandwiches and the MO of CpM fragments. This material is available free of charge via the Internet at http://pubs.acs.org.

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