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Can Donor–Acceptor Bonded Dinuclear Metallocenes Exist? A Computational Study on the Stability of CpM′−MCp (M′ = B, Al, Ga, In, Tl; M = Li, Na, K) and Its Isomers

Ning He, Hong-bin Xie, and Yi-hong Ding*

State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

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Recently, a series of dinuclear metallocenes CpM′−MCp connected by a donor–acceptor interaction M′→M have been designed. However, an important yet unresolved issue is whether the donor–acceptor bonded metallocenes can be intrinsically stable toward isomerization since such a simple combination might result in various isomeric forms. Therefore, in this paper, we investigate the stability toward isomerization of a series of donor–acceptor dinuclear metallocens CpM′−MCp (M′ = B, Al, Ga, In, Tl; M = Li, Na, K) at the DFT level. We find that the σ-type donor–acceptor sandwich form CpM′−MCp (A) can be the ground-state isomer only for M′ = B. For M′ = Al, Ga, In, Tl, the previously unconsidered π-type donor–acceptor sandwich form M′Cp−MCp (B), in which Cp in CpM′ acts as a donor and M acts as an acceptor, is more stable. Moreover, the classical isomer R_2E-ERR' is very important for the homonuclear group 13 compounds; the classical isomer CpM′Cp−M (F) in sandwich form plays only a minor role except for *cis*-CpBCp−Li, which is nearly isoenergetic with the σ-type donor–acceptor isomer CpB−LiCp. Finally, Cp*M′ (Cp* = methyl-substituted cyclopentadienyl group) will significantly stabilize the σ-type donor–acceptor isomer relative to the classical one, yet has little influence on the energy differences between the σ- and π-type donor–acceptor isomers. Therefore, our results should provide useful guides for future synthetic effort aimed at the other donor–acceptor bonded dinuclear metallocenes.

1. Introduction

The donor–acceptor (D−A) interaction concept is defined as the interaction between the occupied orbitals of the donor and the vacant orbitals of the acceptor. It is widespread in various fields ranging from radical−molecule chemistry, organic and inorganic chemistry, organometallics, to biochemistry, etc. Generally, D–A bonds are associated with weak interaction, the strength of which depends on the electron-donating ability and the electron-accepting ability. Yet, for some species, π-back-donation exists between the donor and acceptor, which results in a much stronger D–A bond.[1–3]

A recent breakthrough in organometallic chemistry was the unexpected synthesis and isolation of the dinuclear sandwich compound Cp*ZnZnCp* (Cp* = η^5-C_5Me_5) by E. Carmona and co-workers.[4] It represents the first such dinuclear metallocene and has opened a new dimension in metallocene chemistry. Carmona and co-workers' pioneering finding has led to further studies of various dinuclear metallocenes.[5–9] Of particular interest, A. Y. Timoshkin and H. F. Schaefer reported calculations on a series of novel main-group heterodinuclear metallocenes CpM′−MCp (M′ = B, Al, Ga; M = Li, Na, K)[10] at DFT levels. Taking into consideration that (i) group 13 element compounds in oxidation state +1 possess a lone pair and are well-known to act as donor molecules and (ii) group 1 element complexes in oxidation state +1 have a vacant orbital, Timoshkin and Schaefer proposed that formation of bis-element sandwich compounds would be formally achieved by the donor–acceptor interaction between half-sandwich compounds of group 1 (CpM) and 13 (CpM′) elements. This was the first introduction of the donor–acceptor interaction concept to dinuclear metallocenes. Further, G. Merino et al. investigated a series of structures of general formula CpM′−MPyl (M′ = B, Al, Ga; M = Li, Na; Pyl = pentadienyl, η^5-C_5H_7) by means of DFT.[11] P. W. Roesky and co-workers[12] were even able to synthesize a compound $[(\eta^5\text{-}C_5Me_5)_2Ln\text{-}Al(\eta^5\text{-}C_5Me_5)]$ (Ln = Eu, Yb) in moderate yield in which an Al→Ln donor–acceptor bond was involved. With the development of modern synthetic techniques, it is quite reasonable to speculate that realization of more sandwich compounds with donor–acceptor bonds is possible.

The work by Timoshkin and Schaefer[10] and by Roesky and co-workers[12] promisingly points to the possible existence of heterodinuclear metallocenes CpM′−MCp featuring a donor–acceptor bond. Then, a key question arises: *Are CpM′−MCp molecules intrinsically stable*? Generally speaking, when two

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* Corresponding author. E-mail: yhdd@mail.jlu.edu.cn. Fax: +86-431-88498026.

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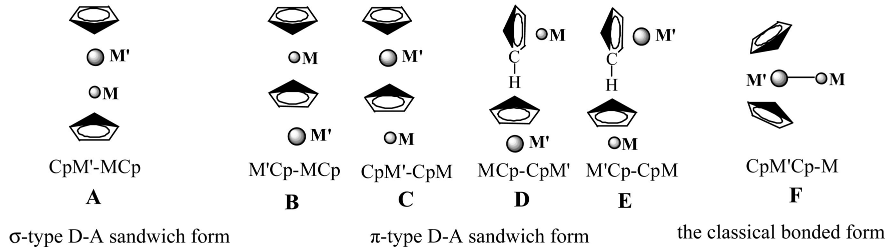
Scheme 1. CpM′−MCp and Its Major Isomeric Forms (M′ is a group 13 element and M is a group 1 element)



half-sandwich complexes CpM (M = Li, Na, K) and CpM′ (M′ = B, Al, Ga, In, Tl), which have been studied in detail by V. M. Rayón and G. Frenking,[13] approach each other, various isomeric forms may be involved from a combinational viewpoint, including the σ-type D–A bonded form (CpM′−MCp (A)), the π-type D–A bonded form (M′Cp−MCp (B), CpM′−CpM (C), MCp−CpM′ (D), and M′Cp−CpM (E)), and the classical CpM′Cp−M (F) (see Scheme 1). We are aware that (1) π-aromatic units like Cp^- can act as effective donors as in multideckered sandwich complexes CpLiCpLi···[14] (2) for the homonuclear group 13 compounds, the classical isomer $R_2E-E'RR'$ may be more stable than the donor–acceptor form $R_3E-E'R'$ for some substituents, as was theoretically shown by Frenking and co-workers;[1] and (3) the CH···π interaction has been observed in benzene dimers,[15] and thus it is of interest to explore the isomer in which one Cp ligand uses its CH bond to interact with the π-donor of the other Cp. Therefore, whether the σ-type D–A bonded CpM′−MCp (A) is the ground-state isomer or not is completely in question. A thermodynamically stabilized compound is always an appealing goal to experimental synthesis. The stability to isomerization of the donor–acceptor bonded dinuclear metallocene compounds CpM′−MCp (A) must be considered. This will be discussed in detail in this paper.

2. Computational Methods

All calculations were performed using the Gaussian 03 program package.[16] The geometries of all structures were fully optimized using the B3LYP method with the 6-311+G(d,p) basis set except for In and Tl (LANL2DZ pseudo-basis set was used). Harmonic vibrational frequencies were calculated at the same level to check whether the obtained structure was a minimum or a saddle point. For B-containing species, the transition states between the corresponding classical and the σ-type D–A isomers were located at the B3LYP/6-311+G(d,p) level. Connections of the transition states between designated local minima have been confirmed by intrinsic reaction coordinate (IRC) calculations. Also, in order to obtain more accurate energies, CCSD(T)/6-311+G(d,p) single-point energy calculations are performed for four structures (CpB−LiCp, *cis*-CpBCp−Li, CpAl−LiCp, and AlCp−LiCp) using the B3LYP/6-311+G(d,p) geometries, because they have close relative energies at the B3LYP/6-311+G(d,p) level.

3. Results and Discussion

The geometries of CpB−LiCp and CpAl−NaCp and their major isomers are shown in Figure 1. Optimized structures of the other isomers, with major geometric parameters and symmetry, are presented in the Supporting Information. Table 1 summarizes the energies of all assembled compounds, relative energies, referring to the energies of the corresponding σ-type D–A sandwich isomer CpM′−MCp (A), and dissociation energies.

3.1. σ-type D–A Sandwich Form CpM′−MCp (A). Analysis of the data in Table 1 reveals that the known σ-type D–A sandwich form CpM′−MCp (A) can be the ground-state isomer only for the donor M′ = B. For other donors M′, the stability of σ-type D–A sandwich bonded isomers decreases significantly and the π-type D–A sandwich form M′Cp−MCp (B) becomes the ground state, which will be discussed in detail in section 3.2.

Boron-containing σ-type donor–acceptor complexes have fairly large dissociation energies (21–12 kcal/mol) at the B3LYP/6-311+G(d,p) level, much larger than those of the Al-containing σ-type donor–acceptor species (4–7 kcal/mol). Ga-, In-, or Tl-containing species are even more weakly bound (1–4 kcal/mol). In addition, for structures CpB−LiCp, CpB−NaCp, and CpB−KCp the dissociation energies are 21.20, 19.20, and 12.36 kcal/mol, respectively. Thus, the stability of the σ-type D–A sandwich isomers decreases in the order B >> Al > Ga > In > Tl as donors and Li > Na > K as acceptors, which is consistent with the earlier conclusions by Timoshkin and Schaefer[10] at the B3LYP/TZVP level. Uddin and Frenking have studied the interaction of CpM′ with acceptor fragments.[3] They showed that the electrostatic interaction between M′ and M takes place between the local concentration of the negative charge of M′ that comes from the lone pair donor electrons and the local charge depletion at M. Therefore, the reason for the lower stability of other M′-containing complexes (Al, Ga, In, and Tl) may be attributed to the longer interatomic distance between M′ and M, which weakens the electrostatic attraction and weakens the orbital interaction of the heavier elements.

3.2. π-Type D–A Sandwich Forms (M′Cp−MCp (B), CpM′−CpM (C), MCp−CpM′ (D), and M′Cp−CpM (E)). As in multidecked CpLiCpLi···, π-aromatic units like Cp^- can act as effective donors. When two half-sandwich complexes CpM and CpM′ approach each other, the combination types, such as M′Cp−MCp (B) and CpM′−CpM (C), cannot be ignored. Therefore, it is necessary to study the stability of π-type D–A sandwich forms M′Cp−MCp (B) and CpM′−CpM (C), in which Cp acts as a π-donor and M or M′ acts as an acceptor, respectively. On the basis of the optimizations, we found some

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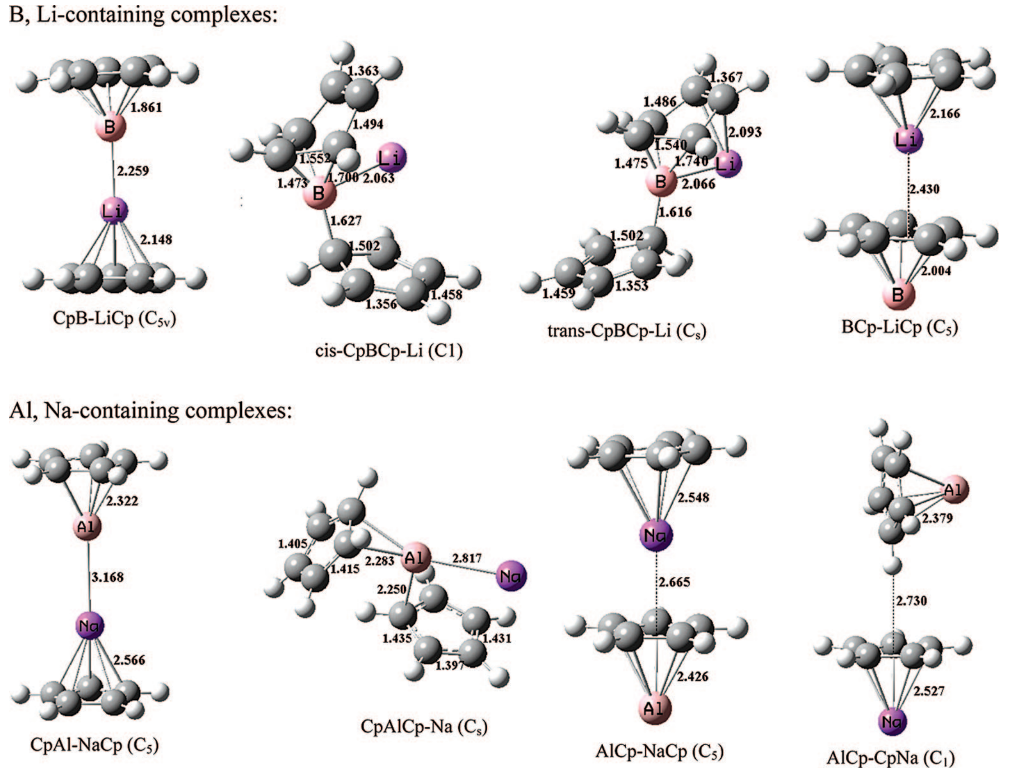

Figure 1. Geometries of CpB−LiCp and CpAl−NaCp and their major isomers were optimized at the B3LYP method with the 6-311+G(d,p) basis set. The symmetries are given in square brackets.

π-type D–A sandwich complexes did not exist. The failure of locating CpB−CpM indicates that it is unfavorable to form a π-type D–A bond CpB$\leftarrow$CpM. This can be explained by the octet rule;[17] that is, the B atom in the CpB fragment is associated with eight bonding electrons and is already coordinatively saturated. In particular, the starting geometry for optimization of CpAl−CpM is always transformed to the structure AlCp−CpM, in which Cp in AlCp is perpendicular to the C_5-symmetry of the Cp ring in CpM. For structures AlCp−CpM, the C−H bond in AlCp pointing to Cp in CpM acts as an acceptor, while Cp in CpM acts as a donor. This kind of π-type D–A bond exists extensively in aromatic compounds such as benzene.[15] However, in our papers, the isomers AlCp−CpM with discouraging or low dissociation energies (1–2 kcal/mol) show that the π-type D–A bonded isomers AlCp−CpM are destabilized as well.

Comparing the energy characters of all isomers, we find that the structures M′Cp−MCp (B) become the most stable isomers as M′ is Al, Ga, In, and Tl. Opposite of σ-type D–A sandwich complexes, Tl-containing π-type D–A complexes have relatively large dissociation energies (11–15 kcal/mol), which are higher compared to those of Ga- and In-containing species (10–11 kcal/mol). Al-containing species are only weakly bound (6–8 kcal/mol). In addition, taking structure TlCp−MCp (M = Li, Na, K) as an example, the dissociation energies are 12.63, 14.82, and 11.03 kcal/mol, respectively. Thus, the stability of the π-type D–A form M′Cp−MCp (B) increases in the order CpAl < CpGa < CpIn < CpTl as π-donors and K < Li < Na as acceptors. Schaefer and co-workers have predicted that σ-type D–A complexes Cp*M′−MCp (A) formed by two half-sandwiches Cp*M′ (Al, Ga) and CpM, with dissociation energies of about 10 kcal/mol, could exist at low temperatures.[10] However on the basis of our calculations, the isomers M′Cp−MCp (B) (M′ = Al, Ga, In, and Tl), which have lower relative energies and relatively high dissociation energies corresponding to σ-type D–A complexes, may be the main products during the synthesis.

Another kind of π-type D–A sandwich forms CpM′−CpM (C) not only have high relative energies but also have very low dissociation energies. Therefore, the existence of compounds CpM′−CpM (C) can be ignored. The lowest stability of CpM′−CpM (C), in which M′ acts as an acceptor, may be explained in terms of electrostatic repulsion between lone pair electrons in M′ and π-electrons in Cp of CpM.

3.3. Classical Bonded Form CpM′Cp−M (F). As pointed out by Frenking and co-workers,[1] for the homodinuclear group 13 compounds, the classical isomer $R_2E{-}E'RR'$ may be more stable than the donor–acceptor form $R_3E{-}E'R'$ for some substituents. Therefore, it is highly desirable to consider the competition from the classical isomeric form CpM′Cp−M (F). For boron-containing complexes, two kinds of isomers (*cis* and *trans*) were obtained, while for Al-containing complexes, the case is rather different: CpAlCp−M (M = Na, K) has only one kind of classical form; however, the classical form for CpAlCp−Li cannot be obtained although many attempts were made. In addition, when M′ is Ga, In, and Tl, almost all classical isomers, except for the compound CpGaCp−Na, are transformed to the σ-type D–A sandwich form CpM′−AlCp (M′ = Ga, In) and π-type D–A sandwich form CpM′−CpM (C) (M′ = Tl) after optimization. From the viewpoint of thermodynamics, almost all classical isomers CpM′Cp−M (F) in sandwich form are of negligible importance except for the *cis*-classical isomer CpBCp−Li, which has a high dissociation energy (21.08 kcal/mol) and a low relative energy (0.13 kcal/mol) at B3LYP/6-311+G(d,p). At the more expensive CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level, *cis*-CpBCp−Li is nearly isoenergetic to the σ-type D–A isomer CpB−LiCp. So, whether both of them can be distinctly characterized in experiments or if they can just coexist in a mixture is an interesting issue. To answer this question, one needs to have the kinetic information for the

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Table 1. Energies, Relative Energies, and Dissociation Energies for CpM′−MCp (A) and Its Major Isomers

	energies, au	relative energies, kcal/mol	dissociation energies, kcal/mol
B-Containing Compounds			
CpB−LiCp	−419.48989	0.00	21.20
	(−418.28799)[b]	(0.00)	
cis-CpBCp−Li	−419.48969	0.13	21.08
	(−418.28795)[b]	(0.025)	
trans-CpBCp−Li	−419.48110	5.52	15.69
BCp−LiCp	−419.46507	15.57	5.63
CpB−CpLi	—[a]	—	—
CpB−NaCp	−574.23989	0.00	19.20
cis-CpBCp−Na	−574.22962	6.44	13.55
trans-CpBCp−Na	−574.23087	5.66	14.34
BCp−NaCp	−574.21776	13.89	6.11
CpB−CpNa	—	—	—
CpB−KCp	−1011.87433	0.00	12.36
cis-CpBCp−K	−1011.86327	6.94	5.42
trans-CpBCp−K	−1011.86549	5.55	6.81
BCp−KCp	−1011.85969	9.19	3.17
CpB−CpK	—	—	—
Al-Containing Compounds			
CpAl−LiCp	−637.18552	0.00	7.57
	(−635.59042)[b]	(0.00)	7.57
CpAlCp−Li	—	—	—
AlCp−LiCp	−637.18640	−0.55	8.12
	(−635.59759)[b]	(−4.50)	
AlCp−CpLi	−637.17547	6.31	1.26
CpAl−NaCp	−791.93770	0.00	7.75
CpAl−CpNa	−791.91216	16.03	−8.28
AlCp−NaCp	−791.94038	−1.68	9.43
AlCp−CpNa	−791.92825	5.93	1.82
CpAl−KCp	−1229.57874	0.00	4.25
CpAlCp−-K	−1229.55104	17.38	−13.13
AlCp−KCp	−1229.58153	−1.75	6.0
AlCp−CpK	−1229.57533	2.14	2.11
Ga-Containing Compounds			
CpGa−LiCp	−2319.60857	0.00	4.95
CpGaCp−Li	—	—	—
GaCp−LiCp	−2319.61500	−4.03	8.99
CpGa−CpLi	−2319.60118	4.64	0.31
CpGa−NaCp	−2474.35990	0.00	4.60
CpGaCp−Na	−2474.33434	16.04	−11.44
GaCp−NaCp	−2474.36933	−5.92	10.52
CpGa−CpNa	−2474.35451	3.38	1.22
CpGa−KCp	−2912.00252	0.00	2.09
CpGaCp−K	—	—	—
GaCp−KCp	−2912.01038	−4.93	7.02
CpGa−CpK	−2912.00174	0.49	1.60
In-Containing Compounds			
CpIn−LiCp	−396.62313	0.00	3.76
CpInCp−Li	—	—	—
InCp−LiCp	−396.63333	−6.40	10.16
CpIn−CpLi	−396.61851	2.90	0.86
CpIn−NaCp	−551.37506	0.00	3.78
CpInCp−Na	—	—	—
InCp−NaCp	−551.38799	−8.11	11.90
CpIn−CpNa	−551.37200	1.92	1.86
CpIn−KCp	−989.01804	0.0	1.50
CpInCp−K	—	—	—
InCp−KCp	−989.02890	−6.81	8.31
CpIn−CpK	−989.01995	−1.20	2.70
Tl-Containing Compounds			
CpTl−LiCp	−446.36366	0.00	−0.09
CpTlCp−Li	—	—	—
TlCp−LiCp	−446.38392	−12.71	12.63
CpTl−CpLi	−446.37039	−4.22	4.14
CpTl−NaCp	−601.11529	0.00<	−0.25
CpTlCp−Na	—	—	—
TlCp−NaCp	−601.13931	−15.07	14.82
CpTl−CpNa	−601.12569	−6.53	6.28
CpTl−KCp	—	—	—
CpTl--CpK	—	—	—
TlCp−KCp	−1038.77989	0.00	11.03
CpTl−CpK	−1038.77405	3.66	7.37

[a] This kind of compound does not exist. [b] The CCSD(T)/6-311+G(d,p) single-point energy calculations are performed at the B3LYP/6-311+G(d,p) level.

isomerization between them. If they are separated by a high energy barrier from each other, they could be identified independently under different conditions. Yet, if only a small interconversion barrier exists between them, it is highly possible to have their coexistence in a mixture. Thus, we have studied the stability in kinetics for *cis*-CpBCp−Li and CpB−LiCp. The result shows that the transformation energy barrier between them is 21.74 kcal/mol, which implies that *cis*-CpBCp−Li and CpB−LiCp can be independently synthesized under different experimental conditions. Therefore, in practice, although CpB−LiCp has the strongest B→Li D–A bond, it is important to pick appropriate reaction conditions in the synthesis. We also consider transformation of other B-containing species between σ-type D–A complexes and the classical isomers. The kinetic information is shown in Figure 2. About a 20 kcal/mol energy barrier between the classical and σ-type D–A isomers indicates that at low temperature the classical isomers are kinetically stable, but become unstable at high temperatures.

3.4. Synthetic Implications. From the discussion above, although the most strongly bonded cyclopentadienyl sandwiches CpB−MCp have sizable dissociation energies, the classical bonded isomers, especially *cis*-CpBCp−Li, would affect the purity of the products. In addition, when M′ is a heavy element (Al, Ga, In, and Tl), the most stable isomers are the π-type D–A bonded sandwich compounds with relatively low dissociation energies, which are only possibly synthesized at low temperatures. Thus, in the present report, we considered improving the donor–acceptor bond strength in the sandwich compounds by adding electron-donating Me substituents to the Cp, because Cp* is a well-known stabilizing ligand. Several Cp*M′ (M′ = B, Al, Ga) complexes have been considered in the present work (results are listed in the Supporting Information). As expected, substitution of Cp by Cp* shortens the B−M distances (about 0.01 Å) and increases dissociation energies (about 3 kcal/mol). However, owing to increasing steric repulsion and electrostatic effects, the stabilities of classical boned isomers CpBCp*−M decrease intensely. Therefore, it is fortunate that the reaction between Cp*B and CpM will predominantly lead to the formation of the σ-type D–A bonded complex Cp*B−MCp. However, for heavy elements M′ = Al, Ga, the relative energies of σ-type D–A bonded complexes to the π-type donor–acceptor isomers are little changed. The isomers M′Cp*−MCp (B) are still the most stable isomers. Different from Cp*B−MCp, the stability of M′Cp*−MCp (B) does not obviously increase after substitution of Cp by Cp*. This may be explained as follows: because of the gradually shortened distance M′Cp*−MCp (B) (by 0.10–0.06 Å), the steric repulsion and electrostatic effects between Cp* and Cp are enhanced, which reduces the stability of M′Cp*−MCp (B). We also studied the stabilities of sandwich compounds by substitution of Cp by Cp* at M. Through the calculations, we found Cp* can enhance the electron-donating properties (σ or π) of only group 13 half-sandwiches, while for electron-accepting properties of group 1 half-sandwiches Cp* has no effect. Especially for CpB−LiCp*, the stability is reversed after the substitution on the acceptor side (CpLi). The relative energy of classical bonded *cis*-CpBCp*−Li (with high dissociation energies, 26.00 kcal/mol) is more stable (about 5 kcal/mol) than that of σ-type D–A sandwich isomers (CpB−LiCp*). Thus, for B,Li-containing complexes, both the σ-type D–A isomer and the *cis*-classical isomer can be selectively formed by choosing different substituents at different parts (donor or acceptor side). Also, we can improve the donor–acceptor bond strength in the

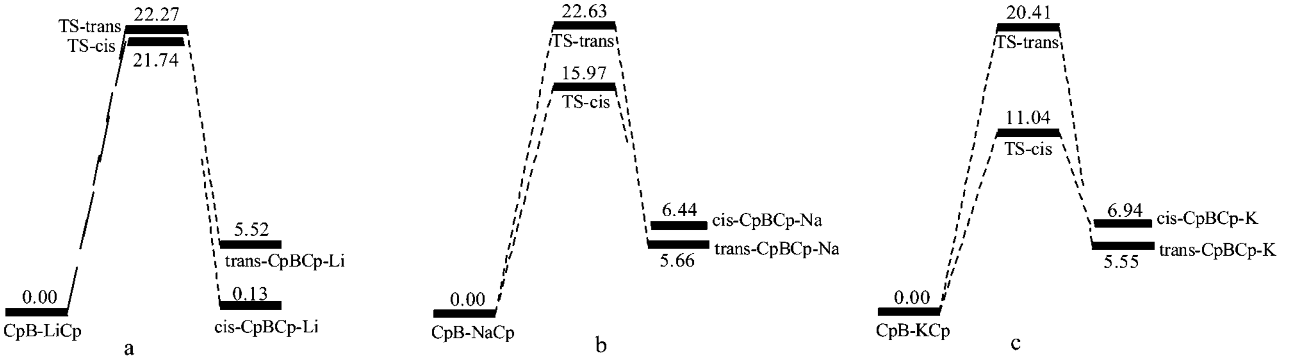

Figure 2. Kinetic information between σ-type D–A sandwiches (CpB−MCp) and the classical bonded isomers (CpBCp−M) for B-containing species (energies in kcal/mol).

sandwich compounds by selecting appropriate solvents, as done in previous work.[11]

In summary, all the computations indicate that by controlling the reaction conditions and selecting the appropriate substituents, the synthesis of the σ-type donor–acceptor sandwich compounds can be considerably hopeful for B-containing species. For other M′-containing species (M′ = Al, Ga, In, Tl), the π-type donor–acceptor sandwich compounds may be synthesized at low temperatures. Yet, we should point out that all the calculated energies reported above refer to free molecules in the gas phase. Thus, caution should be taken when one tries to apply them to the condensed phase. In the condensed phase, other factors may disturb the gas phase process. For example, it is well-known that group 1 and 13 metallocenes easily form polymeric or oligomeric structures in the solid state. So, disproportionation of target complexes into $(\text{CpM})_n$ and $(\text{CpM}')_m$ might be an alternative side reaction in the condensed phase.

4. Conclusions

In this paper, we made the first attempt to consider the stability toward isomerization of a series of donor–acceptor bonded dinuclear metallocenes CpM′−MCp (M′ = B, Al, Ga, In, Tl; M = Li, Na, K). By means of B3LYP/6-311+G(d,p) calculations, we find that the known σ-type D–A sandwich form CpM′−MCp (A) can be the ground-state isomer only for the donor M′ = B. For M′ = Al, Ga, In, Tl donors, the most stable isomer is of the previously unconsidered π-type D–A sandwich form M′Cp−MCp (B), and the stability of the π-type D–A form M′Cp−MCp (B) increases in the order CpAl < CpGa < CpIn < CpTl as π-donors and K < Li < Na as acceptors. In addition, on the basis of the calculated results, the classical isomer CpM′Cp−M (F) in sandwich forms is of negligible importance, except for *cis*-CpBCp−Li, which is nearly isoenergetic with the σ-type donor–acceptor isomer CpB−LiCp. In particular, for the donor M′ = B, a considerable barrier (around 20 kcal/mol) separates the classical and the σ-type donor–acceptor isomers. Finally, upon methyl substitution (from CpM′ to Cp*M′), the σ-type donor–acceptor isomer will be significantly stabilized relative to the classical one, yet its relative stability to the π-type donor–acceptor isomer is a little changed. For experimental verification, we predict that the σ- or π-type donor–acceptor sandwich forms as well as the kinetically stabilized classical isomer CpBCp−M should be obtainable via different combinations between the half-sandwich CpM and CpM′ (Cp*M′) in synthesis. The present work indicates that it is very necessary to investigate the isomerism of the target donor–acceptor metallocenes due to the high possibility of other isomers.

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Supporting Information Available: Figure of optimized structures of CpM′−MCp (M′ = B, Al, Ga, In, Tl; M = Li, Na, K) and its major isomers and figure of optimized structures of CpM′−MCp (M′ = B, Al, Ga; M = Li, Na, K) and its major isomers with energies, relative energies (ΔE_{rela}), and dissociation energies (ΔE_{diss}), in which one of the Cp ligands was substituted by Cp*. This material is available free of charge via the Internet at http://pubs.acs.org.

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