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One-Electron Metal−Metal Bond Stabilized in Dinuclear Metallocenes: Theoretical Prediction of DBe-LiCp (D = C_5H_5 or C_5Me_5)

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Recently, stimulated by the unexpected synthesis and isolation of a bis-metallic sandwich compound Cp*ZnZnCp* (Cp* = η^5-C_5Me_5), many studies have focused on various dinuclear metallocenes involving a direct metal−metal (single or multiple) bond. However, we are not aware of any report on the metallocenes incorporating a "one-electron metal−metal bond". Herein, through the good steric and electronic stabilization effect of Cp and Cp*, we for the first time theoretically design a new type of sandwich-like compounds DBe-LiCp (D = Cp or Cp*) associated by an "unaided" one-electron metal−metal bond. Bonding characteristics of CpBe-LiCp were analyzed by natural bond orbital (NBO) theory. To shed more light on the stability of sandwich complexes, the dissociation energies (DBe-LiCp → DBe + CpLi) and extrusion energies (DBe-LiCp → DBeCp + Li) were calculated. Through calculation of thermodynamic standard entropies, we predict that these new compounds may be detected in the gaseous phase at appropriate experiment conditions.

1. Introduction

Molecular compounds featuring direct metal−metal bonds have been of fundamental interest in various areas for many decades.[1] In organometallic chemistry, a recent breakthrough is the unexpected synthesis and isolation of a bis-metallic sandwich compound Cp*ZnZnCp* (Cp* = η^5-C_5Me_5) by Resa et al.[2] In this remarkable D_{5h}-symmetric compound, a direct metal−metal bond (Zn−Zn) is sandwiched by two Cp* rings. It represents the first type of dinuclear metallocenes, and has initiated a new research field to metallocene chemistry. Up to now, Resa et al.'s pioneering finding has led to explosive studies on various dinuclear metallocenes involving a direct "normal" metal−metal (single or multiple) bond.[3−19] However, we are not aware of any report on the metallocenes incorporating a "one-electron metal−metal bond". Herein, we will theoretically show that we can go further in the dinuclear metallcene chemistry: *even a one-electron metal−metal single bond can be stabilized in sandwich-like complexes*.

Ever since Pauling's prediction of the one-electron bond in certain diatomic species such as H_2^+ and Li_2^+,[20] a great deal of work has been devoted to this unique bonding pattern. Yet, the considerable weakness of the one-electron bond relative to the normal electron-paired bond has made the synthesis of such a type of complexes very difficult. The limited experimental examples involve the gaseous complexes CH_3−IF[21] and CH_3−ICl[22] (see Scheme 1a) detected through molecular beam techniques as well as the relatively stable organophosphorus complexes[23−25] and boron complexes[26] characterized in liquid (Scheme 1b−d) or solid phase (Scheme 1e). We note that in the latter complexes, the one-electron bond is assisted by either the framework effect or other electron-paired bonds. The present paper will report a new kind of promising bis-metallic sandwich-like compound DBe-LiCp (D = Cp or Cp*), which is simply drawn together by the one-electron bond through the steric and electronic stabilization of Cp and Cp*.

TABLE 1: The Energetic Properties (kJ/mol) and the Natural Bond Orbital (NBO) Charges for CpBe-LiCp and Cp*Be-LiCp at the B3LYP/6-311+G (d,p) Level (NBO charges for CpBe, Cp*Be, and CpLi are 0.856, 0.865, and 0.915 for Be and Li atom, respectively)

	CpBe-LiCp	Cp*Be-LiCp
ΔE_{diss}	42.8	46.7
ΔE_{extr}	77.8	83.9
q_{Be}	1.012	1.025
Δq_{Be}	−0.156	−0.160
q_{Li}	0.730	0.717
Δq_{Li}	0.185	0.198

2. Computational Methods

All the calculations were carried out with the Gaussian 03 program package.[27] During calculations, the default Gaussian integration grid is replaced by a finer integration grid (99 radial shell with 590 angular points per shell). The geometries of DBe-LiCp (D = Cp or Cp*) were fully optimized, using the B3LYP method[28] with 6-311+G(d,p) basis set. Harmonic vibrational frequencies were calculated at the same level to check whether the obtained structure was a minimum or a saddle point. To obtain more accurate energies, CCSD(T)/aug-cc-pVDZ and CCSD(T)/6-311+G(d,p) single point energy calculations for CpBe-LiCp are performed with B3LYP/6-311+G(d,p) geometries. To shed more light on the stability of sandwich complexes, the dissociation energies (DBe-LiCp → DBe + CpLi) and extrusion energies (DBe-LiCp → DBeCp + Li) were calculated. The counterpoise (CP) method[29] was used to correct the basis set superposition error (BSSE)[30] in the calculation of the binding energy. For CpBe-LiCp, bonding characteristics were analyzed by natural bond orbital (NBO) theory.[31] Electron density maps (shown in Figure 3) of HOMO-*n* (*n* = 0−2), especially the singly occupied molecular orbital (SOMO) of CpBe-LiCp, were plotted at the contour values ±0.03, using the MOLDEN graphics program.[32]

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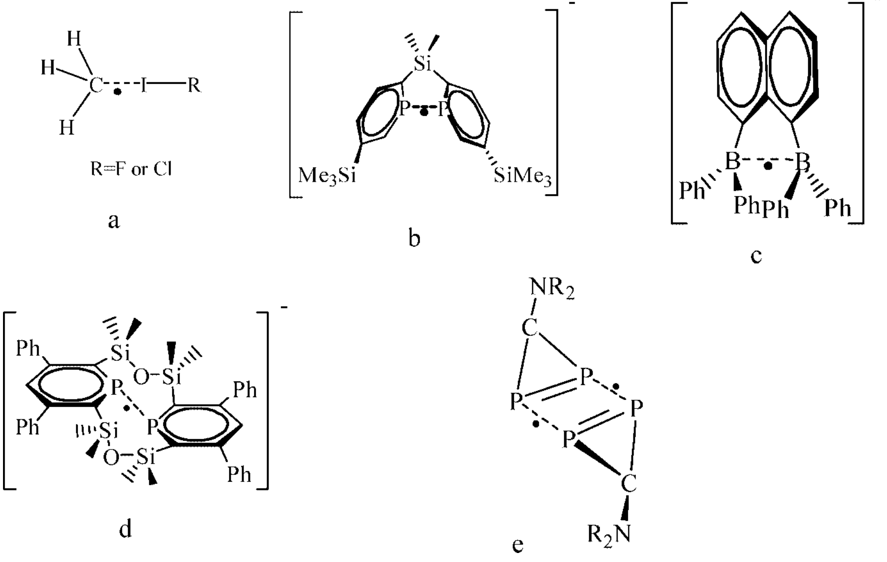
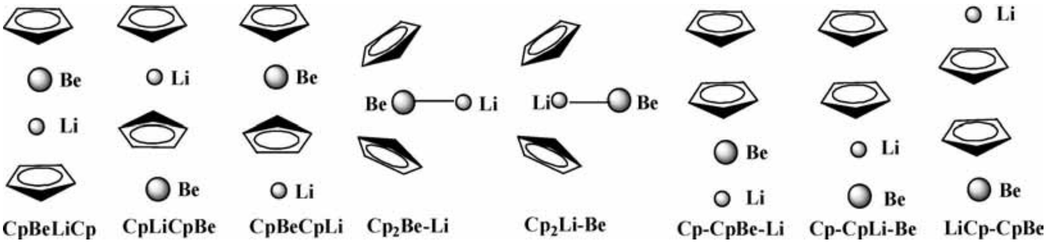
SCHEME 1: Schematic Representation of Some Experimentally Known Complexes Involving One-Electron Bonds



SCHEME 2: Illustrative Possible Isomers of CpBe-LiCp



3. Results and Discussions

By considering various possible isomers for CpBe-LiCp (see Scheme 2 and Figure 1), we predict that the sandwich form is a global minimum, which is lower about 20−90 kJ/mol in energy than the other isomers at the B3LYP/6-311+G(d,p) level. The optimized geometrical structure with the corresponding parameters, the energy properties, and the natural population analysis (NPA) of CpBe-LiCp at the B3LYP/6-311+G(d,p) level are shown in Figure 2 and Table 1. In Figure 3, the main molecular orbitals (MOs) with corresponding energies of free CpLi, CpBe, and CpBe-LiCp are demonstrated.

The optimized structure of CpBe-LiCp is predicted to possess a C_5 point group with the rotation of one Cp ring. Different from the traditional dinuclear sandwich compounds,[2,9] the C_{5v} symmetric structure of CpBe-LiCp is not a minimum point with one imaginary frequency. To understand the bonding situation of the CpBe-LiCp complex, the natural population analysis (NPA) is performed. When the CpLi complex associates with the CpBe radical, the Li in CpLi becomes less positive, and the CpBe subunit becomes positive. There is electron transfer (0.156) from Be to Li (listed in Table 1). In view of molecular orbitals (listed in Figure 3), the single s electron of the CpBe radical approaches the Li atom of CpLi to act as an electron donor, and the Li atom in CpLi plays the role of an electron acceptor. Thus, in complex CpBe-LiCp, HOMO-2, which is associated with the Be−Li bond, is only occupied by one s electron. The singly occupied molecular orbital (SOMO) of CpBe-LiCp certifies the existence of the one-electron Be−Li bond. The calculated Wiberg bond index (WBI) (0.1499)[33] and atom−atom overlap-weighted NAO bond order (0.2398) also both support the above description. Meanwhile, as can be seen from Figure 3, for CpBe-LiCp, two doubly occupied MOs higher in energy than the singly occupied s orbital (SOMO) come from the CpLi moiety, which indicates that MOs of CpBe-LiCp are essentially slightly perturbed superposition of the MOs of the individual fragments. Therefore, the bond of Be−Li in CpBe-LiCp is kind of a weak interaction. In addition, the bond length of Be−Li (2.734 Å) in CpBe-LiCp is longer than the single bond of Be−Li (2.607 Å),[34] but clearly shorter than the sum (3.45 Å) of the van der Waals radii of Be (1.40 Å) and Li (2.05 Å).[35] This can provide another proof for the existence of a one-electron bond between Be and Li.

To obtain more accurate energies, the single-point energy calculations are performed for the one-electron bonded cyclopentadienyl sandwich complex CpBe-LiCp (listed in Table 2 and the Supporting Information). To investigate the basis sets effects, single-point energy calculations are carried out for two relatively small complexes with three different basis sets. As seen from Table 3, the ΔE_{diss} values calculated with three different basis sets are at the same order of magnitude. Moreover, compared with the results at the expensive level CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(d,p), the other two basis sets give a relatively conservative estimation. Therefore, the single-point energy calculations at CCSD(T)/aug-cc-pVDZ//B3LYP/6-311+G(d,p) and CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) can give reasonable and reliable results for our systems. Furthermore, since this kind of complex with one-electron Be−Li bonding may be susceptible to a multireference effect,[36] we calculated the value of $||t1||$ in the CCSD treatment with the 6-311+G(d,p) basis set. According to ref 36, a value of $||t1||$ higher than 0.02 indicates that the degree of multireference character is large enough to cast serious doubt on the reliability of single reference correlation treatments. Our calculated very small $||t1||$ value of 0.0096 for CpBe-LiCp clearly

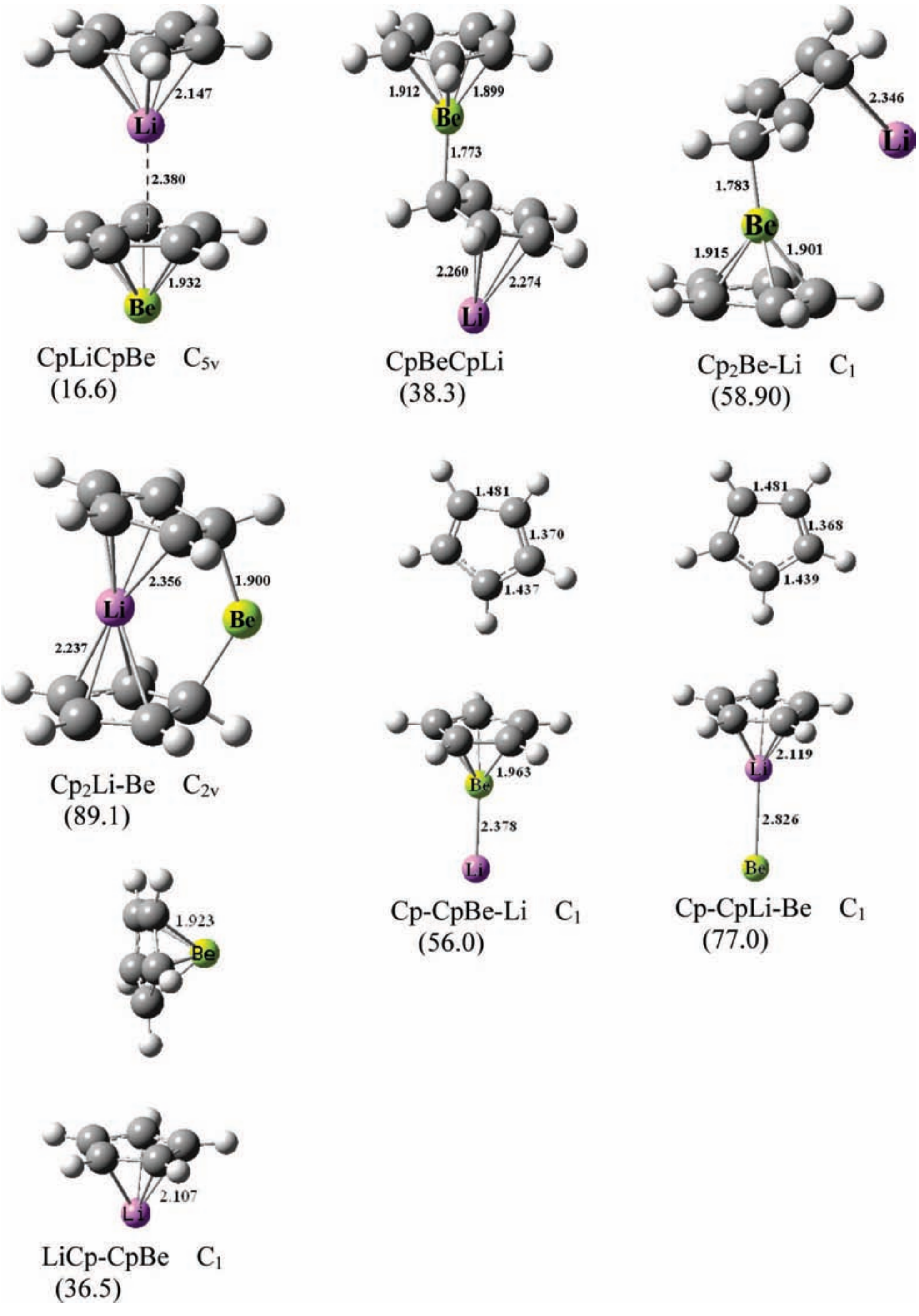


Figure 1. The geometries of possible isomers for sandwich CpBe-LiCp at the B3LYP/6-311+G(d,p) level. The relative energies compared to CpBe-LiCp are given in parentheses (energies in kJ/mol, bond distances in Å).

indicates the negligible degree of multireference character and the reliability of single reference correlation treatments for CpBe-LiCp.

Surely the goal to form even more strongly bound complex is still considerably attractive. Cp* is a well-known stabilizing ligand,[9] especially for donor properties. So, in the present paper, we substitute Cp by Cp* at the donor side to improve the one-electron bond strength (Cp*Be-LiCp). The calculated results are shown in Figure 2 and Table 1. As expected, substitution of Cp by Cp* shortens the Be−Li distances by 0.004 Å, and increases dissociation energies by 4 kJ/mol and extrusion energies by 6 kJ/mol at the B3LYP/6-311+G(d,p) level. At the same time, using the natural population analysis (NPA), we can obviously observe an increased electron transfer (0.160) from Be to Li after substitution. However, compared with the dissociation energy (259 kJ/mol) of the famous Cp*Zn-ZnCp* complex, which is the only known example of this class of CpM-M′Cp compounds, the complex Cp*Be-LiCp may be relatively easy to dissociate. Thus, the preparative condition of hypothetical complex Cp*Be-LiCp must be more rigorous than that of Cp*Zn-ZnCp*.

Compared with the bis-nuclear sandwiches CpE-MCp (E = B, Al, Ga; M = Li, Na, K) associated by one two-electron donor−acceptor bond,[9] of which the dissociation energies are

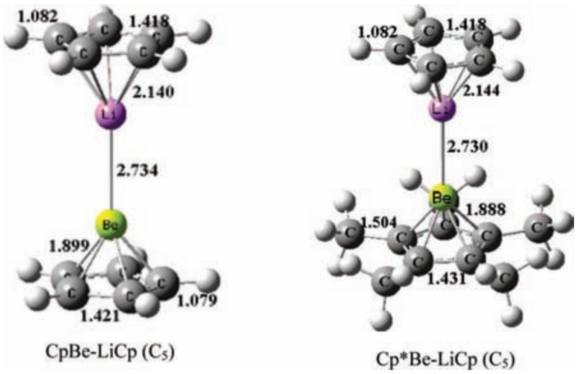


Figure 2. The geometric structures for CpBe-LiCp and Cp*Be-LiCp at the B3LYP/6-311+G (d,p) level (bond distances are in Å).

TABLE 2: The Dissociation Energies and Extraction Energies (kJ/mol) for CpBe-LiCp at Two Different Basis Sets

	CCSD(T)/aug-cc-pVDZ//B3LYP/6-311+G(d,p)	CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p)
ΔE_{diss}	57.6	57.3
ΔE_{extr}	66.0	69.4

TABLE 3: The Dissociation Energies ($\Delta E_{\mathrm{disso}}$, kJ/mol) of Two Different Complexes at Different Calculated Basis Sets

	CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(d,p)	CCSD(T)/aug-cc-pVDZ//B3LYP/6-311+G(d,p)	CCSD(T)/6−311+G(d,p)//B3LYP/6-311+G(d,p)
Cp-Li	363.2	343.8	348.0
Cp-BeH	494.8	473.1	483.3

TABLE 4: Calculated Gibbs Energy Changes (298 K, 1 atm) for the Decomposition of CpBe-LiCp and Cp*Be-LiCp

	$\Delta G°_{298}$, kJ/mol
CpBe-LiCp → CpBe + CpLi	26.4
CpBe-LiCp → CpBeCp + Li	52.6
Cp*Be-LiCp → Cp*Be + CpLi	44.1
Cp*Be-LiCp → Cp*BeCp + Li	60.2

10−40 kJ/mol except of CpB-MCp complexes, the one-electron Be−Li bond in the hypothetical complex DBe-LiCp (D = C_5H_5 or C_5Me_5) is relatively unexpected strong. Therefore, it is of great interest to see whether the one-electron Be−Li bond would be stable or not when Cp and Cp* are substituted by normal ligands such as H, CH_3, and Cl. Our preliminary calculations (see the Supporting Information) indicate that such a one-electron bonded structure either is not a minimum isomer or kinetically undergoes easy extrusion to the more stable product DBeD′ + Li. Therefore, we can intuitively conclude that the existence of the one-electron bonded compound DBe-LiCp is due to the inclusion of the stabilizing ligand Cp/Cp*, which is famous for its good steric and electronic stabilization effect. Here, the electronic effect of Cp/Cp* should play a major role. In DBe-LiCp (D = Cp, Cp*), the Be- and Li-atoms are surrounded by 8 and 7 bonding electrons (both occupy 4 bonding orbitals), respectively. Thus, both Be- and Li-atoms in the sandwich-like one-electron structure DBe-LiCp are effectively stabilized through the octet rule. To further study the one-electron bond in dinuclear metallocenes, we also preliminarily calculated a series of dinuclear metallocenes with the formula CpM-M′Cp (M = Be, Mg, Ca; M′ = Li, Na, K) at the B3LYP/6-31G(d,p) level. However, we unfortunately found that this kind of one-electron bonded structure either is not a minimum isomer or kinetically undergoes easy extrusion to CpMCp + M′.

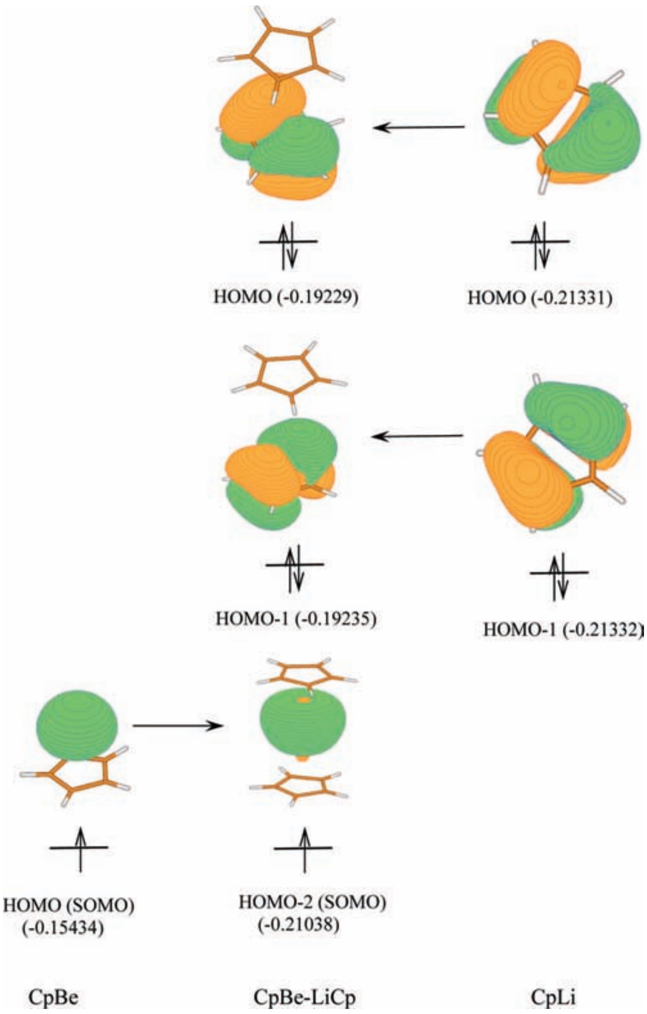


Figure 3. Electron density maps of HOMO-*n* (*n* = 0−2) for sandwich CpBe-LiCp. HOMO-2 is the single occupied molecular orbital (SOMO) for the sandwich CpBe-LiCp.

Owing to the relatively high reaction energies for decomposition processes and it being the global minimum relative to other isomers, we believe it is possible to detect the complex CpBe-LiCp bonded by a one-electron metal−metal bond under appropriate laboratory conditions. The standard thermodynamic functions are of great importance in the interpretation of the nature of the chemical interaction. So, we also consider the stability of the complex CpBe-LiCp in thermodynamics. At the B3LYP/6-311+G(d,p) level, the respective enthalpy and entropy values are 41984.18 $\mathrm{J \cdot mol^{-1}}$ and 128.68 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for the rate-determining process of CpBe-LiCp (i.e., Be−Li bond dissociation). According to the standard thermodynamic equation $\Delta H - T\Delta S > 0$ for a nonspontaneous process, the gaseous compound CpBe-LiCp might be detected below 326 K. Since the higher level CCSD(T) calculations improve the Be−Li strength, the B3LYP/6-311+G(d,p) result is expected to be a conservative estimation. Table 4 also lists the calculated Gibbs energy changes for the respective decomposition reactions of CpBe-LiCp and Cp*Be-LiCp. The values of $\Delta G°_{298}$ for the dissociation and extrusion processes are strongly positive, which indicates that the decomposition reactions do not easily occur. In addition, since the SOMO is the bonding orbital, we calculated the adiabatic electron affinity of the one-electron bonded CpBe-LiCp, which describes its ability to capture an outer electron. At the B3LYP/6-311+G(d,p) level, the distance of the Be−Li bond in anion $[\mathrm{CpBe\text{-}LiCp}]^-$ (C_5) is 2.546 Å, which is considerably shorter than the 2.734 Å value in the neutral molecule. Through the MOs analysis, we found the outer electron occupies the SOMO (HOMO-2) of CpBe-LiCp to form HOMO in [CpBe-LiCp]$^-$ (C_5) (see Supporting Information). Therefore, on the basis of the above description, the anion [CpBe-LiCp]$^-$ (C_5) is more stable than its neutral molecule CpBe-LiCp. The formation of ionic species M$^+$[CpBe-LiCp]$^-$ in the condensed phase may be more possible. Notably, compared with the experimentally characterized gaseous one-electron radical complex CH$_3$−IF[12] (see Scheme 1a) (−444.2 kJ/mol), our designed one-electron bonded CpBe-LiCp has relatively lower electron affinity (−113.3 kJ/mol). This is indicative of the high possibility of detection of the neutral CpBe-LiCp against electron attachment under appropriate experimental conditions.

The above calculated energies refer to free molecules in the gas phase. In the condensed phase, the energies of fragments need to be reconsidered. It is well-known that Li atoms easily coagulate to form Li$_n$ clusters in the solid state. For nLi → Li$_n$ ($n \to \infty$), the measured energy change is 1.66 eV (i.e., 160.4 kJ/mol) per atom.[37,38] Thus, the (CpBe-LiCp)$_n$ → (CpBeCp)$_n$ + nLi → (CpBeCp)$_n$ + Li$_n$ process becomes exothermic by 62.0n kJ/mol with respect to the formation of bulk Li$_n$. On the other hand, CpBe-LiCp and CpBe may dimerize via 2CpBe-LiCp → CpBe-BeCp + 2LiCp with exothermicity as 203.2 kJ/mol at the B3LYP/6-311+G(d,p) level, and the fragments CpLi may even undergo polymeric reactions to form (CpLi)$_n$. However, we are aware that various techniques, such as controllable temperatures,[39] high dilution,[40] and solvent effect,[41,42] have been developed to suppress these condensation processes for detection of many exotic species (including radicals). Especially for solvent effect, it is not only one of the effective methods to suppress radical polymerization, but it also has been proved to be a good way to enhance the strength of the donor−acceptor bond (Be−Li bond) by selecting appropriate solvents.[10] We hope that these schemes might help characterize the unique one-electron metal−metal bonded sandwich-like compounds CpBeLiCp and Cp*BeLiCp.

4. Conclusion

In summary, we for the first time introduce the one-electron metal−metal bond to sandwich complexes. Through the optimized geometries and NBO analysis above, the singly occupied molecular orbital (SOMO) of CpBe-LiCp certifies the existence of the one-electron Be−Li bond. Owing to the relatively high reaction energies for decomposition processes and it being the global minimum relative to other isomers, the one-electron Be−Li bond in CpBe-LiCp is relatively strong, although this kind of bond is usually considered to be much weaker than the normal electron-paired bond. Thus, the weak interaction of the one-electron metal−metal bond can be effectively enhanced in the sandwich complexes. Substitution of Cp by Cp* on the donor side can also increase the strength of the one-electron bond. Through the calculations of thermodynamic standard entropies and comparisons with the gaseous complex CH$_3$−IF, we optimistically predict that our designed new compounds may be detected in the gaseous phase below 326 K under appropriate experimental conditions. Further systematic study on this kind of dinuclear metallocenes is underway.

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Supporting Information Available: The absolute energies for all isomers and dissociation products; the computed standard entropies for CpBe-LiCp and dissociation products; the total energies, dissociation energies ΔE_{diss} and extraction energies ΔE_{extr} for RBe-LiR at the B3LYP/6-31G** level; a figure of the HOMO of [CpBe-LiCp]$^-$; and the Cartesian *xyz* coordinates for (CpBeLiCp)$^-$, CpBe-LiCp, Cp*Be-LiCp, CpBeCp, Cp*BeCp, CpLi, CpBe, and Cp*Be. This material is available free of charge via the Internet at http://pubs.acs.org.

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