

Density Functional Theory Study of Ultrashort Metal–Metal Distance in Diberyllium Complexes Bearing Carbene Ligands

Lili Sun¹

¹East China University of Technology

October 12, 2020

Abstract

Diberyllium complexes with an ultrashort metal–metal distance (USMMD, $d_{M-M} < 1.900$ Å) are fascinating for the nature of the valence electronic structure of beryllium. In this paper a family of diberyllium complexes, in which Be_2H_3^+ was coordinated by *N*-heterocyclic carbenes or mesoionic carbenes, were studied using density functional theory which generated an ultrashort Be–Be distance of 1.754–1.779 Å. Based on bonding nature and electronic structure studies, the ultrashort Be–Be distance was attributed to multiple bonding orbitals and directly orbital overlapping between the two beryllium atoms. These diberyllium complexes exhibited great stability with large HOMO-LUMO gaps and high dissociation energies, and were potential targets in future experiments.

1. Introduction

The nature of chemical bonding is a fundamental question in chemistry. Since Cotton et al. proposed the first quadruple metal–metal bond in $\text{Re}_2\text{Cl}_8^{2-}$ ^[1], great attention has been drawn to homonuclear transitional metal complexes with multiple metal–metal bond and ultrashort metal–metal distance (USMMD, $d_{M-M} < 1.900$ Å). In 2005, Power et al. reported the crystalline structure of a dichromium complex containing a quadruple Cr–Cr bond of 1.835 Å^[2,3]. This research has triggered the crystallographical study of various dichromium complexes, in which the length of a quadruple Cr–Cr bond was as short as 1.706 Å^[4–7], and characterization of a sextuple Cr–Cr bond^[8,9]. USMMD was also reported as a parameter of the homonuclear complexes composed by other transitional metals, such as manganese and molybdenum^[10,11]. Yet, how to realize USMMD in binuclear complexes of main group metals is challenging, especially in those of the s-block elements that do not have sufficient valence electrons.

Beryllium interrupts the homoatomic bonding of electron-deficient elements Li, Be and B. Previous studies showed the effective bond order (EBO) in Li_2 and B_2 was around 1, while in Be_2 it was as low as 0.2^[12], demonstrating an unusual bonding nature of beryllium dimers. Spectroscopic measurements^[13] and theoretical simulations^[14] determined the Be–Be distance in Be_2 to be 2.45 Å with bond dissociation energy (BDE) of 2.26 kcal/mol, which chemists usually consider not to be a genuine chemical bond. Electronic structure studies of Be_2 revealed that its two highest occupied molecular orbitals, HOMO and HOMO-1, were σ -antibonding and bonding, respectively, while the two lowest unoccupied molecular orbitals, LUMO and LUMO+1, were of a π -bonding nature. Such findings sparked ideas of achieving short Be–Be distances by withdrawing electrons from the antibonding HOMO of Be_2 or filling its LUMO by binding electron-donating groups. Previous calculations proved that Be_2^+ and Be_2^{2+} had shorter Be–Be distances compared with Be_2 ^[15], indicating strengthened Be–Be bonds. Brites and co-workers^[16] found the ground state of Be_2H_2 possessed a Be–Be distance of 2.09 Å with the BDE of about 75 kcal/mol, and they attributed this stronger Be–Be interaction in Be_2H_2 to electron donation from the antibonding orbital of Be_2 to the 1s orbitals of two H atoms. In 2016, Cui et al.^[15] reported that Be_2F_2 with a Be–Be distance of 2.05 Å and BDE of 76.9 kcal/mol, and they related this short distance to the σ -bonding HOMO of Be_2F_2 . Brea and Corral^[17] have

also stabilized strong Be–Be bonds by coordinating radical ligands to Be₂; however, they did not achieve shorter Be–Be distances in these diberyllium complexes.

In 2013, Couchman et al.^[18] measured Be–Be distances in a range of 1.945–1.978 Å in computationally designed NHC^R–Be–Be–NHC^R (NHC = *N*-heterocyclic carbenes, R = H, Me, and Ph) complexes; however, those complexes had small HOMO-LUMO gaps, thus possibly intrinsically unstable. As beryllium atom is highly electron deficient, it is possible that addition of bridging groups between two beryllium atoms can realize shorter Be–Be distances and enhance the stability of diberyllium complexes simultaneously. Through this strategy diberyllium complexes with ultrashort Be–Be distances were computationally and experimentally studied^[15,19–22]. Yuan et al.^[20] obtained a Be–Be distance of 1.829 Å in NHC^H–Be₂H₂–NHC^H by adding two bridging hydrogen atoms in NHC^H–Be–Be–NHC^H. Qin et al.^[21] further introduced a –CH₂– group and managed an ultrashort Be–Be distance of 1.770–1.794 Å in newly designed L–Be₂H₂CH₂–L (L = NHC^H, NH₃, PH₃) complexes. Zhao et al.^[22] found that *D*_{3h}Be₂H₃⁺ possessed a Be–Be distance below 1.700 Å, and simulated a triple bond in [L–Be₂H₃–L]⁺ (L = NH₃, PH₃, and Ne–Xe) complexes with ultrashort Be–Be distances between 1.692 Å and 1.735 Å, comparable to lengths of quintuple Cr–Cr bonds.

It was pondered the possibility of stabilizing the *D*_{3h}Be₂H₃⁺ and meanwhile protecting its ultrashort Be–Be distance by other ligands. Compared with the long-studied NHCs ligands, mesoionic carbenes (MICs) are considered as stronger σ-donors and less good π-acceptors^[23–25]. It is unknown if there will be difference when MICs coordinate to Be₂H₃⁺. To answer this question, a family of diberyllium complexes were designed to consist of Be₂H₃⁺ and NHCs or MICs ligands, including 1,3-dimethylimidazol-2-ylidenes (NHC^{Me}₁), 1,4-dimethyl-1,2,4-triazol-5-ylidenes (NHC^{Me}₂), imidazoline-4-ylidenes (MIC₁), pyrazoline-4-ylidenes (MIC₂), 1,2,3-triazol-5-ylidenes (MIC₃) and tetrazol-5-ylidenes (MIC₄) (Figure S1 in Supporting Information), investigated by density functional theory. Calculations showed that diberyllium complexes bearing carbene ligands possessed ultrashort Be–Be distances of 1.754–1.779 Å and super strong Be–C_{carb} bonds at once, and these complexes were highly stable with large HOMO-LUMO gaps and high dissociation energies and could be potential targets in future experiments.

2. Computational Methods

A family of diberyllium complexes [L–BeH₃Be–L]⁺ (L = NHCs, MICs) were studied by the density functional theory. All structures were optimized and characterized as stationary points at B3LYP^[26–30] level of theory using 6-311+G(d,p)^[31,32] basis set and re-optimized at B3LYP/cc-pVTZ^[33,34] level unless otherwise specified. Vertical electron affinities (VEAs) and vertical detachment energies (VDEs) were calculated at B3LYP/cc-pVTZ level. Adaptive Natural Density Partitioning (AdNDP)^[35] analyses were completed at B3LYP/6-31G(d)^[36–39] level. Geometry optimizations, frequency calculations, and Natural Bond Orbital (NBO)^[40] calculations were completed by Gaussian 09 package^[41]. AdNDP analysis and Charge Decomposition Analysis (CDA)^[42–44] were performed by Multiwfn^[45]. Balsac^[46] and VMD^[47] software was used for visualization and analysis of molecular geometries and electronic structures.

3. Results and Discussion

3.1. Molecular Geometries

First of all, the chosen computational method was validated by optimizing a *D*_{2h}NHC^H–BeH₂Be–NHC^H complex. As in Figure 1, the calculated Be–Be, Be–H and Be–C_{carb} distances were 1.830 Å, 1.434 Å, and 1.676 Å, respectively, almost identical to those obtained by a CCSD(T) method^[22]. Wiberg Bond Indexes (WBIs) for Be–Be, Be–H and Be–C_{carb} bonds, and NBO charges on the –BeH₂Be– core and carbene center (C_{carb}) were closed to results obtained by higher level calculations^[22]. Overall, this chosen level of theory was reliable.

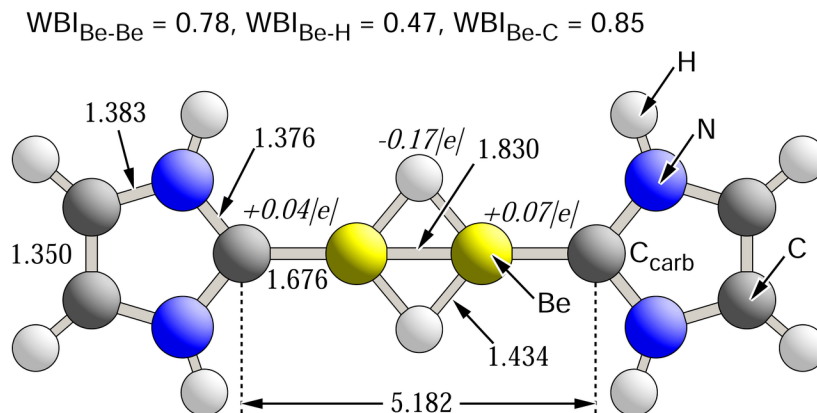


Figure 1. Selected geometrical parameters of $\text{NHC}^{\text{H}}\text{-BeH}_2\text{Be-NHC}^{\text{H}}$ complexes obtained at B3LYP/cc-pVTZ level. Unit for bond length was angstrom ($\text{\AA}$), and for angle was degree ($^\circ$). NBO charges at C_{carb} , Be, and H atoms were in italic.

Figure 2 showed the optimized structures of diberyllium complexes $[\text{L-BeH}_3\text{Be-L}]^+$ ($\text{L} = \text{NHCs}$ and MICs), in which the $\text{-BeH}_3\text{Be-}$ core was coordinated by two carbene ligands. The molecular geometries of all complexes were in C_2 symmetry. The Be-Be distance varied from 1.754 $\text{\AA}$ to 1.779 $\text{\AA}$, much shorter than those in $\text{NHC}^{\text{H}}\text{-Be-Be-NHC}^{\text{H}}$ ^[18] and $\text{NHC}^{\text{H}}\text{-BeXBBe-NHC}^{\text{H}}$ ($\text{X} = \text{H}_2, \text{H}_2\text{CH}_2$)^[20,22]. In particular, A and G had the shortest Be-Be distance of 1.754 $\text{\AA}$ among all complexes, while E had the longest Be-Be bond (1.779 $\text{\AA}$). The individual average length of six Be-H bonds in complexes A~G varied from 1.478 $\text{\AA}$ to 1.488 $\text{\AA}$, slightly longer than in a free Be_2H_3^+ (1.453 $\text{\AA}$, Figure S2), suggesting the Be-H bond in $\text{-BeH}_3\text{Be-}$ core got weakened by carbene ligands coordinated to it. The calculated Be- C_{carb} bond length, ranging from 1.732 $\text{\AA}$ to 1.745 $\text{\AA}$, was compatible to experimental values^[48]. Among all complexes E owned the shortest Be- C_{carb} bond, followed by D and F, demonstrating stronger Be- C_{carb} bonds. Compared with corresponding free carbenes, the $\angle\text{X-C}_{\text{carb}}\text{-Y}$ ($\text{X}, \text{Y} = \text{C}, \text{N}$) in diberyllium complexes increased by $2.4^\circ\text{-}3.0^\circ$ with a maximum bond length change of ± 0.02 $\text{\AA}$. C-N bond lengths of the complexes ranged from 1.293 $\text{\AA}$ to 1.397 $\text{\AA}$, between the lengths of C-N single and double bonds (1.476 $\text{\AA}$ and 1.291 $\text{\AA}$, respectively^[49]), and C-C bond lengths varied from 1.353 $\text{\AA}$ to 1.398 $\text{\AA}$, between the lengths of C-C single and double bonds (1.510 $\text{\AA}$ and 1.336 $\text{\AA}$, respectively^[50]), suggesting high conjugation of the carbene ligands in these diberyllium complexes.

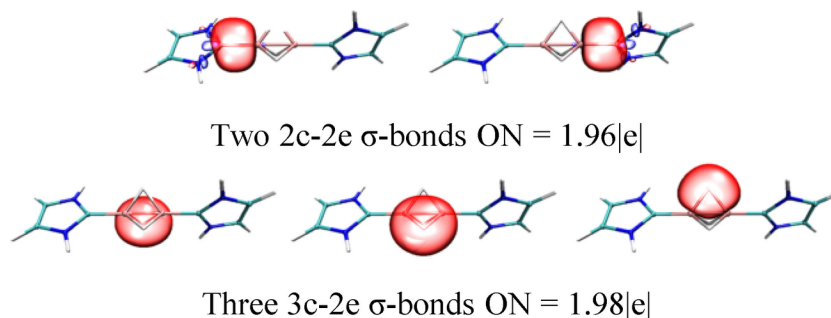
Figure 2. Optimized structures and selected geometrical parameters of diberyllium complexes A~G. Bond length unit: angstrom ($\text{\AA}$), angle unit: degree ($^\circ$). For each complex, length with a bar was an average value of six Be-H bonds.

3.2. Chemical Bonding Analysis

AdNDP analysis^[35] was conducted for complexes A, E and G that had extremums of the Be-Be distance to have a better understanding of chemical bonding. Based on an electron-pair bonding model, the AdNDP describes the electronic structure of a molecule in terms of n center-two electrons (n c-2e) orbitals or bonds, covering both Lewis bonding elements and delocalized bonding elements. In this work two equivalent schemes were used to generate AdNDP orbitals: a small n -value for delocalized bonding elements in Scheme 1, and a large n in Scheme 2. Using Schemes 1 and 2, AdNDP analysis generated identical 1c-2e lone pair electrons and 2c-2e σ -orbitals, and meanwhile, found two Be- C_{carb} 2c-2e σ -orbitals in all three complexes. In A and G, the occupation number (ON) is 1.96|e| for both two Be- C_{carb} 2c-2e σ -orbitals (Figure 3 and S3). The short Be- C_{carb} bond (1.732 $\text{\AA}$) in E suggested strong covalent interaction between Be and C_{carb} atoms, while E had a smaller ON of 1.93|e| for Be- C_{carb} 2c-2e σ -orbitals, which demonstrated these bonds were influenced not only by covalent interaction but also by electrostatic interaction. For the delocalized bonding elements AdNDP generated three Be-H-Be σ -orbitals with an ON of 1.98|e| for the three complexes employing Scheme

1, and Scheme 2 provided one Be-H₃-Be 5c-2e σ -orbital with an ON of 1.98|e| and two 5c-2e Be-H₃-Be π -orbitals with ONs of 1.99|e| and 1.98|e| (Figure 3). The three 5c-2e orbitals can be considered as a virtual triple bond^[22]. Schemes 1 and 2 were equivalent as combination of three 3c-2e σ -orbitals afforded the 5c-2e σ -orbital, and combination of two 3c-2e σ -orbitals afforded the 5c-2e π -orbitals.

Scheme 1



Scheme 2

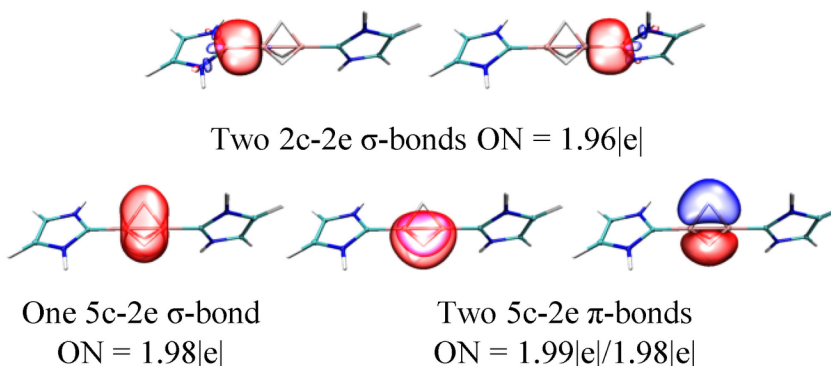


Figure 3. The AdNDP-generated nc -2e orbitals relating to beryllium atoms employing Schemes 1 and 2. Similar AdNDP-orbitals for E and G were presented in Figure S3.

To characterize the covalent and electrostatic interaction in the diberyllium complexes, WBIs and NBO charges were analyzed. As listed in Table 1, the total WBI of every C_{carb} atom (WBI_{C_{carb}}) in the complexes was significantly larger than those of the corresponding free carbenes, so as to support the formation of Be-C_{carb} σ -bonds. The total WBI of every beryllium atom (WBI_{Be}) varied from 2.72 to 2.77, and beryllium atom had a valence of two. The exceeding numbers (0.72–0.77) came from the electron donation of carbene center, suggesting Be-C_{carb} σ -bonds are dative. Among all complexes E had the smallest WBI_{Be-C_{carb}} value of 0.67, suggesting the weakest covalent interaction between Be and C_{carb} atoms, which agreed with the results of AdNDP analysis, while complexes A~E had a larger WBI_{Be-C_{carb}} value of 0.70, indicating strong covalent interactions.

Table 1. The Wiberg Bond Indexes (WBIs) of selected interatomic interaction (Be-Be, Be-H, and Be-C_{carb}) and atoms (Be, H and C_{carb}), and selected NBO charges (q , in |e|) for D_{3h} Be₂H₃⁺ and complexes A~G. For the complexes, WBIs presented for Be-H interaction and H atoms were average values, as is NBO charges on the H atoms (q_H).

	WBI	WBI	WBI	WBI	WBI	WBI	q	q	q
	Be–Be	Be–H	Be–C _{carb}	Be	H	C _{carb} ^a	Be	H	C _{carb}
Be ₂ H ₃ ⁺	0.46	0.47	–	1.87	0.95	–	+0.84	-0.23	–
A	0.58	0.48	0.70	2.77	0.99	3.61 (2.85)	+0.21	-0.11	+0.15
B	0.56	0.48	0.70	2.77	0.99	3.62 (2.86)	+0.21	-0.12	+0.14
C	0.57	0.48	0.70	2.77	0.99	3.62 (2.86)	+0.21	-0.12	+0.14
D	0.55	0.47	0.69	2.74	0.99	3.67 (3.02)	+0.23	-0.13	-0.17
E	0.55	0.47	0.67	2.72	0.99	3.74 (3.24)	+0.25	-0.14	-0.44
F	0.56	0.48	0.68	2.74	0.99	3.68 (3.02)	+0.24	-0.13	-0.16
G	0.57	0.48	0.68	2.75	0.99	3.63 (2.91)	+0.23	-0.12	+0.09

^a NBO charges at C_{carb} atoms for free carbenes were in parentheses.

Electrostatic interaction between beryllium and its neighboring carbene center was characterized by NBO charges. As in Table 1, the NBO charges on each beryllium atom (q_{Be}) in the complexes varied from +0.21|e| to +0.25|e|, considerably smaller than q_{Be} in the free Be₂H₃⁺ (+0.84|e|), which could be attributed to the electron-donation from carbenes to the –BeH₃Be– core. Among all complexes the carbene center of E was the most negatively charged ($q_{\text{C}_{\text{carb}}} = -0.44|e|$), and strong electrostatic attraction between Be and C_{carb} atoms would strengthen this weak covalent interaction to create a short Be–C_{carb} bond (1.732 Å). The C_{carb} atom was less negatively charged in D and F, and as a result, the electrostatic attraction between Be and C_{carb} atoms decreased. In A[~]C and G, the carbene center was positively charged, and the covalent interaction between Be and C_{carb} atoms got cancelled by electrostatic repulsion. With the same WBI_{Be–C_{carb}} value (0.68), F possesses Be–C_{carb} bond length of 1.735 Å because of the favorable electrostatic attraction between Be and C_{carb} atoms, while G had a longer bond length (1.745 Å) caused by electrostatic repulsion. A[~]C had a larger WBI_{Be–C_{carb}} value (0.70) than others; however, the strong covalent interaction between Be and C_{carb} atoms was neutralized by the interatomic electrostatic repulsion, resulting in a Be–C_{carb} bond length of 1.741–1.745 Å.

The WBI_{Be–Be} values for all complexes were 0.55–0.58, reflecting orbital overlapping between the two Be atoms. For complex E with the smallest WBI_{Be–Be} (0.55), weak Be–Be orbital overlapping matched the small ON of Be–H–Be 3c-2e σ-bonds calculated by the AdNDP analysis, while A and G with large WBI_{Be–Be} had a much shorter Be–Be distance of 1.754 Å. The average values of WBI_{Be–H} of all complexes were between 0.47 and 0.48, and the total WBI value of individual H atom was close to 1, reflecting that bridging H atoms linked two Be atoms in –BeH₃Be– core to form multiple bonding orbitals.

3.3. Orbital Analysis

Charge decomposition analysis (CDA)^[42–44] was conducted to understand the interaction between the –BeH₃Be– core and carbene ligands. The CDA constructed molecular orbitals (MOs) of a complex in terms of a linear combination of the donor and acceptor fragmental orbitals (FOs). Selected MOs of A that related to beryllium atoms and decomposition of these MOs into FOs of Be₂H₃⁺ and (NHC^H)₂ were presented in Figure 4a and 4b, respectively. The low-lying HOMO-30 and HOMO-29 of A represented Be–Be σ- bonding and antibonding orbitals, respectively, and were obviously contributed by 1s orbitals of two Be atoms, corresponding to FO1 and FO2 of Be₂H₃⁺ (Figure S4). As HOMO-30 and HOMO-29 were far below other selected MOs of A, they were not included in Figure 4b for brevity. HOMO-8 were the Be–H₃–Be σ-bonding orbital contributed by the FO3 of Be₂H₃⁺. HOMO-7 and HOMO-6 pictured Be–C_{carb} σ-bonding orbitals, which were attributed to the electron donation from carbene ligands to the unoccupied FO6 and FO7 of Be₂H₃⁺, respectively. HOMO-3~HOMO of A were two sets of π-orbitals, representing Be–H–Be π-bonding, and generated by the combination of FO4/FO5 of Be₂H₃⁺ and π-orbitals of (NHC^H)₂ fragments (FO33 and FO34). The two lowest unoccupied MOs (LUMO and LUMO+1) of A that represented the Be–C_{carb} π-bonding were established by two degenerated Be–Be π-antibonding orbitals (FO8 and FO9 of Be₂H₃⁺) and π-orbitals of carbene ligands (FO41 and FO42 of (NHC^H)₂). Similar pattern was found in the occupied

MOs of other complexes as well, related to the FOs of Be_2H_3^+ (E and G as examples in Figure S4); however, LUMO/LUMO+1 of E and G were pure π -orbitals of carbene ligands and irrelevant to FO8 and FO9 of Be_2H_3^+ .

There was a link between the occupied MOs and the AdNDP-generated orbitals of A. As in Figures 3 and 4, the two $\text{Be}-\text{C}_{\text{carb}} 2\text{c}-2\text{e}$ σ -orbitals were combined to generate HOMO-7 and HOMO-6, and HOMO-8 was related to the $5\text{c}-2\text{e}$ $\text{Be}-\text{H}_3-\text{Be}$ σ -orbital generated employing Scheme 2, while HOMO-3~HOMO corresponded to the $5\text{c}-2\text{e}$ $\text{Be}-\text{H}_3-\text{Be}$ π -orbitals. HOMO-8 and HOMO-3~HOMO can also be achieved by combination of $\text{Be}-\text{H}-\text{Be}$ $3\text{c}-2\text{e}$ σ -orbitals based on Scheme 1. The connection between MOs and AdNDP-generated orbitals for A also demonstrated that removing electrons would destroy the multiple bonding orbitals in the $-\text{BeH}_3\text{Be}-$ core, and large detachment energies were critical to retain an ultrashort $\text{Be}-\text{Be}$ distance.

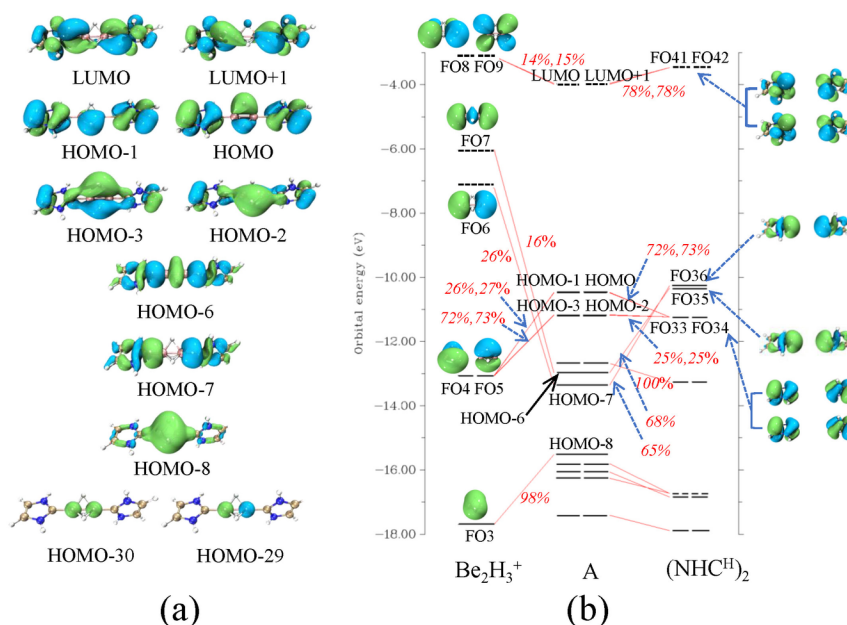


Figure 4. (a) Selected molecular orbitals (MOs) bounding to Be atoms for complex A, and (b) charge decomposition analysis (CDA) for these MOs. Orbital energy level unit: eV. Fragmental orbitals (FOs) of Be_2H_3^+ and $(\text{NHC}^{\text{H}})_2$ were shifted by +2.0 eV and -5.0 eV, respectively. Occupied and unoccupied MOs/FOs were drawn in solid and dash lines, respectively, in which the one and three gaps were double and quadruple degenerate, respectively. Criterion for degeneration was set at 0.10 eV. Contributions from FOs to MOs of A were in red and italic. FO37–FO40 of $(\text{NHC}^{\text{H}})_2$ were not presented as their contributions to MOs of A were less than 10%. Decomposition of the low-lying HOMO-30 and HOMO-29 of A was not shown as these two MOs are pure FOs of Be_2H_3^+ and far below other selected MOs.

3.4. Stability Analysis

Complex stability was evaluated based on calculation of their HOMO-LUMO gaps and dissociation energies of losing two carbene moieties in the reaction of $[\text{L}-\text{BeH}_3\text{Be}-\text{L}]^+ \rightarrow \text{Be}_2\text{H}_3^+ + 2\text{L}$. As in Table 2, the HOMO-LUMO gaps of the seven complexes ranged from 5.58 eV to 6.75 eV, much larger than the E_{G} of $\text{NHC}^{\text{Me}}-\text{Be}-\text{Be}-\text{NHC}^{\text{Me}}$ (0.51 eV)^[18] and $\text{NHC}^{\text{H}}-\text{BeH}_2\text{Be}-\text{NHC}^{\text{H}}$ (1.78 eV)^[21], and these complexes exhibited high stability with super strong $\text{Be}-\text{C}_{\text{carb}}$ bonds dissociation energies (BDEs) of which ranged from 184.9 kcal/mol to 239.0 kcal/mol, suggesting these complexes could be potential targets in future experiments. The stability study was also confirmed by vertical detachment energies (VDEs, between 10.4

to 12.3 eV) and vertical electron affinities (VEAs, between 2.4 and 3.8 eV), which indicated that it would be difficult to remove or gain even one additional electron in these diberyllium complexes.

Table 2. The HOMO-LUMO gaps (E_G , eV), bond dissociation energies (BDEs, kcal/mol), VEAs and VDEs (eV) for A^-G .

	E_G	BDEs	VEAs	VDEs
A	6.50	193.3	2.7	11.9
B	6.43	197.6	2.6	11.4
C	6.75	184.9	3.1	12.3
D	5.89	225.3	2.4	10.5
E	5.59	239.0	2.5	10.4
F	5.86	210.8	3.1	11.3
G	5.58	194.7	3.8	12.2

4. Conclusion

In this work, a family of diberyllium complexes $[L-BeH_3Be-L]^+$ ($L = NHCs, MICs$) were computationally designed with a $-BeH_3Be-$ core supported by NHC and MIC ligands. The density functional theory studies showed these complexes possessed ultrashort Be-Be distances of 1.754–1.779 Å and super strong Be- C_{carb} bonds. Electronic structure analysis demonstrated the ultrashort Be-Be distance was attributed to the multiple bonding orbitals in the $-BeH_3Be-$ core and the direct orbital overlapping between the two Be atoms. The strong Be- C_{carb} bonds originated from the electron donation of two carbene ligands coordinated to the $-BeH_3Be-$ core, influenced by the electrostatic interaction between Be and its neighboring carbene center. These complexes were highly stable because of the large HOMO-LUMO gaps and high dissociation energies, high VDEs and low VEAs, and could be potential targets in future.

Conflict of interests: The author declares no conflict of interests.

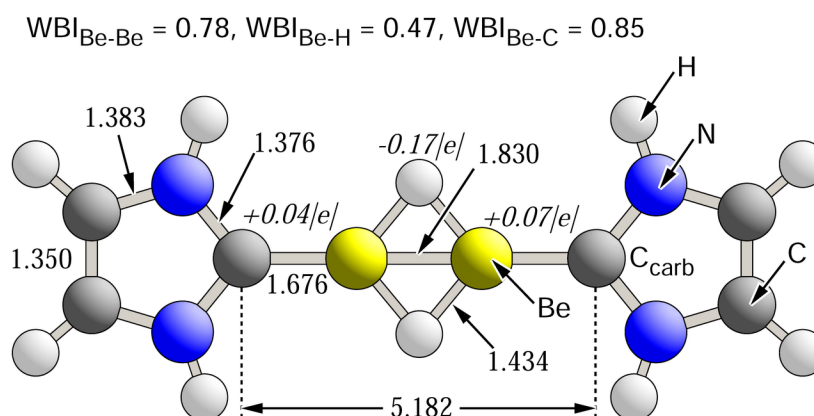
Funding Information: This study was supported by Startup Foundation of East China University of Technology (No. DHBK2019263), Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT) (No. IRT_17R20), and Department of Science and Technology of Jiangxi Province (No. 20192AEI91006).

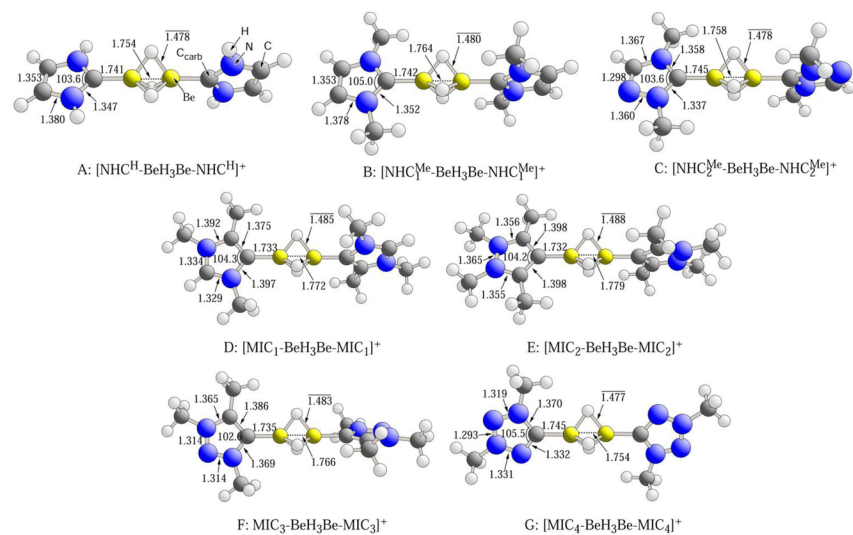
References

- [1] F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, J. S. Wood, *Science***1964** , 145 , 1305–1307.
- [2] G. Frenking, *Science* **2005** , 310 , 796–797.
- [3] T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fetting, G. J. Long, P. P. Power, *Science* **2005** , 310 , 844–847.
- [4] Y.-L. Huang, D.-Y. Lu, H.-C. Yu, J.-S. K. Yu, C.-W. Hsu, T.-S. Kuo, G.-H. Lee, Y. Wang, Y.-C. Tsai, *Angew. Chem. Int. Ed.***2012** , 51 , 7781–7785.
- [5] A. Noor, T. Bauer, T. K. Todorova, B. Weber, L. Gagliardi, R. Kempe, *Chem.-Eur. J.* **2013** , 19 , 9825–9832.
- [6] F. R. Wagner, A. Noor, R. Kempe, *Nat. Chem.***2009** , 1 , 529–536.
- [7] A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem. Int. Ed.***2008** , 47 , 7246–7249.
- [8] G. Frenking, R. Tonner, *Nature* **2007** , 446 , 276–277.
- [9] B. O. Roos, A. C. Borin, L. Gagliardi, *Angew. Chem. Int. Ed.* **2007** , 46 , 1469–1472.

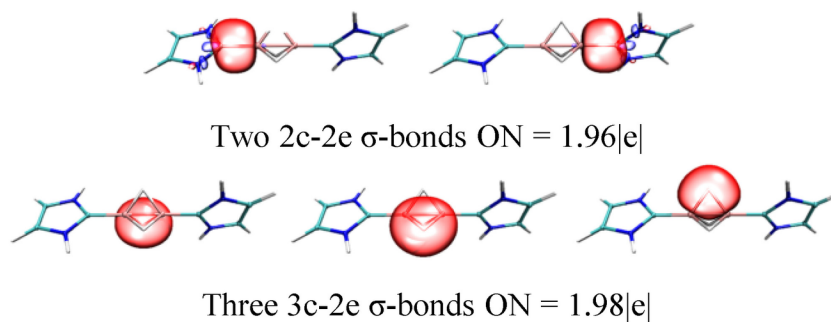
- [10] T. Alonso-Lanza, J. W. Gonzalez, F. Aguilera-Granja, A. Ayuela, *J. Phys. Chem. C* **2017** , *121* , 25554–25560.
- [11] J. Joy, E. D. Jemmis, *Chem. Commun.* **2017** , *53* , 8168–8171.
- [12] V. Bezugly, P. Wielgus, M. Kohout, F. R. Wagner, *J. Comput. Chem.* **2010** , *31* , 1504–19.
- [13] J. M. Merritt, V. E. Bondybey, M. C. Heaven, *Science* **2009** , *324* , 1548–1551.
- [14] K. Patkowski, V. Spirko, K. Szalewicz, *Science* **2009** , *326* , 1382–1384.
- [15] Z. Cui, W. Yang, L. Zhao, Y. Ding, G. Frenking, *Angew. Chem. Int. Ed.* **2016** , *55* , 7841–7846.
- [16] V. Brites, C. Leonard, *J. Phys. Chem. A* **2012** , *116* , 9484–9489.
- [17] O. Brea, I. Corral, *J. Phys. Chem. A* **2018** , *122* , 2258–2265.
- [18] S. A. Couchman, N. Holzmann, G. Frenking, D. J. D. Wilson, J. L. Dutton, *Dalton Trans.* **2013** , *42* , 11375–84.
- [19] Q. Zhang, W.-L. Li, L. Zhao, M. Chen, M. Zhou, J. Li, G. Frenking, *Chem.-Eur. J.* **2017** , *23* , 2035–2039.
- [20] C. Yuan, X.-F. Zhao, Y.-B. Wu, X. Wang, *Angew. Chem. Int. Ed.* **2016** , *55* , 15651–15655.
- [21] Z.-Z. Qin, Q. Wang, C. Yuan, Y.-T. Yang, X.-F. Zhao, D. Li, P. Liu, Y.-B. Wu, *Dalton Trans.* **2018** , *47* , 4707–4713.
- [22] X.-F. Zhao, C. Yuan, S.-D. Li, Y.-B. Wu, X. Wang, *Dalton Trans.* **2018** , *47* , 14462–14467.
- [23] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004** , *23* , 2461–2468.
- [24] F. M. Chadwick, B. F. E. Curchod, R. Scopelliti, F. F. Tirani, E. Solari, K. Severin, *Angew. Chem.-Int. Edit.* **2019** , *58* , 1764–1767.
- [25] S. C. Sau, P. K. Hota, S. K. Mandal, M. Soleilhavoup, G. Bertrand, *Chem. Soc. Rev.* **2020** , *49* , 1233–1252.
- [26] A. D. Becke, *Phys. Rev. A* **1988** , *38* , 3098–3100.
- [27] A. D. Becke, *J. Chem. Phys.* **1993** , *98* , 5648.
- [28] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988** , *37* , 785–789.
- [29] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994** , *98* , 11623–11627.
- [30] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980** , *58* , 1200.
- [31] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980** , *72* , DOI 10.1063/1.438955.
- [32] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983** , *4* , DOI 10.1002/jcc.540040303.
- [33] T. H. Dunning, *J. Chem. Phys.* **1989** , *90* , DOI 10.1063/1.456153.
- [34] B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, A. K. Wilson, *Theor. Chem. Acc.* **2011** , *128* , DOI 10.1007/s00214-010-0764-0.
- [35] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008** , *10* , 5207–5217.
- [36] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971** , *54* , DOI 10.1063/1.1674902.
- [37] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972** , *56* , DOI 10.1063/1.1677527.
- [38] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973** , *28* , DOI 10.1007/bf00533485.

- [39] J. S. Binkley, J. A. Pople, *J. Chem. Phys.***1977** , *66* , DOI 10.1063/1.433929.
- [40] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.***1988** , *88* , 899–926.
- [41] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, *Gaussian 09*, Gaussian, Inc., Wallingford CT, **2010** .
- [42] S. Dapprich, G. Frenking, *J. Phys. Chem.* **1995** ,*99* , 9352–9362.
- [43] M. Xiao, T. Lu, *J. Adv. Phys. Chem.* **2015** ,*4* , 111–124.
- [44] T. Lu, F. Chen, *Acta Chim. Sinica* **2011** ,*69* , 2393–2406.
- [45] T. Lu, F. Chen, *J. Comput. Chem.* **2012** ,*33* , 580–592.
- [46] K. Hermann, *Balsac Visualization and Analysis Software* , FHI, Berlin, **2020** .
- [47] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graph.***1996** , *14* , 33–38.
- [48] M. Bayram, D. Naglav, C. Wölper, S. Schulz, *Organometallics* **2016** , *35* , 2378–2383.
- [49] I. N. Kolesnikova, A. N. Rykov, I. F. Shishkov, V. A. Tafeenko, L. A. Aslanov, *Phys. Chem. Chem. Phys.* **2017** , *19* , 4618–4626.
- [50] V. G. Tsirelson, R. P. Ozerov, *J. Mol. Struct.-Theochem.***1992** , *255* , 335–392.

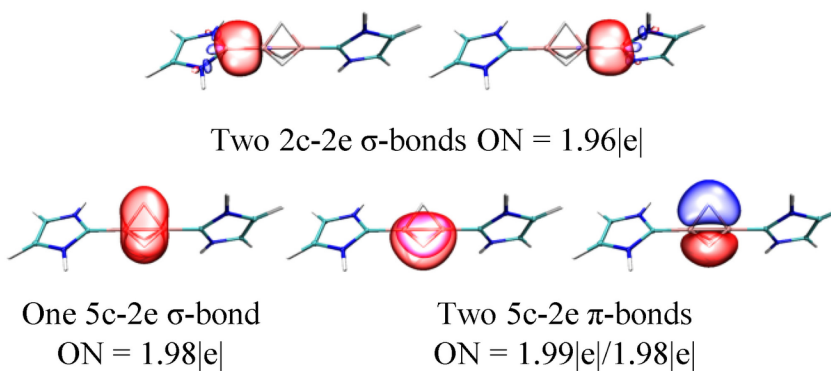


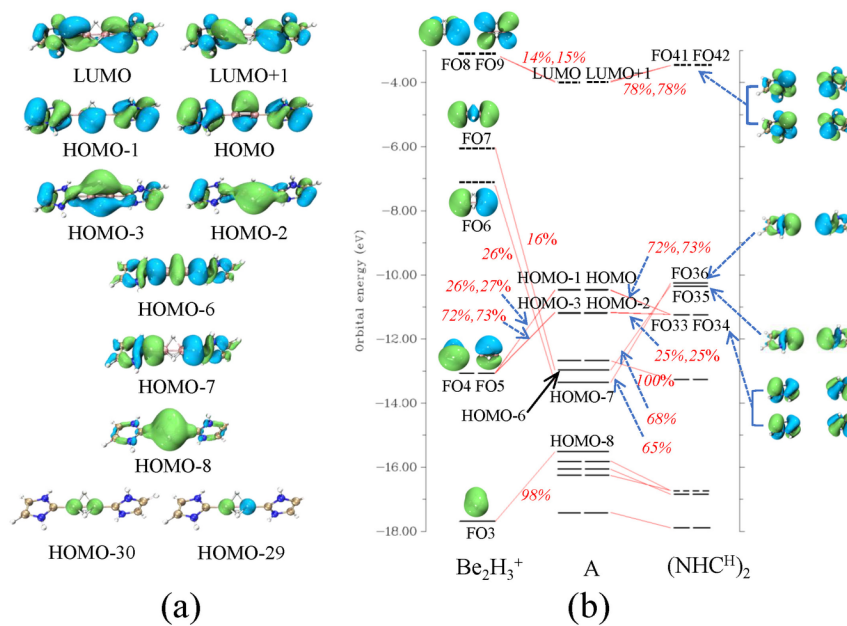


Scheme 1



Scheme 2





Hosted file

Table 1.pdf available at <https://authorea.com/users/366663/articles/486337-density-functional-theory-study-of-ultrashort-metal-metal-distance-in-diberyllium-complexes-bearing-carbene-ligands>

Hosted file

Table 2.pdf available at <https://authorea.com/users/366663/articles/486337-density-functional-theory-study-of-ultrashort-metal-metal-distance-in-diberyllium-complexes-bearing-carbene-ligands>