

Metal–Metal Bonds

International Edition: DOI: 10.1002/anie.201609455
German Edition: DOI: 10.1002/ange.201609455

Ultrashort Beryllium–Beryllium Distances Rivalling Those of Metal–Metal Quintuple Bonds Between Transition Metals

Caixia Yuan, Xue-Feng Zhao, Yan-Bo Wu,* and Xiaotai Wang*

Abstract: Chemical bonding is at the heart of chemistry. Recent work on high bond orders between homonuclear transition metal atoms has led to ultrashort metal–metal (TM–TM) distances defined as $d_{M-M} < 1.900 \text{ \AA}$. The present work is a computational design and characterization of novel main group species containing ultrashort metal–metal distances (1.728–1.866 Å) between two beryllium atoms in different molecular environments, including a rhombic Be_2X_2 ($X = \text{C}, \text{N}$) core, a vertical Be–Be axis in a 3D molecular star, and a horizontal Be–Be axis supported by *N*-heterocyclic carbene (NHC) ligands. The ultrashort Be–Be distances are achieved by affixing bridging atoms to attract the beryllium atoms electrostatically or covalently. Among these species are five global minima and one chemically viable diberyllium complex, which provide potential targets for experimental realization.

Being the fourth element and the second metal in the periodic table, beryllium is well-known for its applications in high-strength alloys, radiation windows, and other modern materials, because of a combination of useful physical properties.^[1] The chemistry of beryllium, however, remains underdeveloped in comparison with that of the other second row elements, especially carbon and boron. This is partly due to the high toxicity of beryllium and its compounds. In terms of atomic structure, beryllium has the smallest atomic radius of any metal and holds more valence orbitals (four) than valence electrons (two). The combination of small size and electron deficiency results in a large diversity in the structures of beryllium compounds. Indeed, contemporary research on beryllium has focused on its fundamental structural chemistry, with extensive use of advanced computational methods.

An active area of beryllium chemistry is the study of Be–Be interactions in various molecular environments, which dovetails with the field of metal–metal bonding chemistry. For example, the ground state diatomic Be_2 has long been thought to have a formal bond order of zero, with four valence electrons distributed evenly in the bonding $1\sigma_g^+$ and anti-

bonding $1\sigma_u^+$ molecular orbitals (MOs). A recent combined experimental and computational study has given new insight into the bonding in Be_2 , including a Be–Be distance of 2.454 Å and an unusual potential energy curve.^[2] In a metallic crystal of beryllium, two Be–Be distances (2.225 and 2.286 Å) have been observed,^[3] and the latter can be viewed as the threshold of putative Be–Be bonding interactions. Among the computationally established Be–Be bond distances are 2.077 Å in the cyclopentadienyl-capped diberyllium(I) complexes,^[4] and 1.945 Å in the σ -donor ligand-stabilized diberyllium(0) complexes of the $\text{NHC} \rightarrow \text{Be}=\text{Be} \leftarrow \text{NHC}$ type ($\text{NHC} = \text{N}$ -heterocyclic carbenes).^[5] The formal Be–Be double bond at 1.945 Å is the shortest homoatomic, unsupported Be–Be bond known theoretically.

Recent computational studies have shown that, aided by bridging atoms, Be–Be distances can be decreased to less than 1.945 Å. Specifically, Cui et al. reported Be–Be distances of 1.910 and 1.901 Å in the so-called molecular discs D_{7h} Be_2B_7^- and D_{8h} Be_2B_8 , which were found to be global minima.^[6] We located a global minimum with the formula $\text{C}_2\text{Be}_4\text{H}_4$ (**1** in Figure 1) that has an even shorter Be–Be distance of 1.895 Å.^[7] Remarkably, this Be–Be distance falls in the range of the so-called ultrashort metal–metal distances defined as $d_{M-M} < 1.900 \text{ \AA}$ and generally observed for transition metal TM–TM multiple bonds.^[8] To our knowledge, $\text{C}_2\text{Be}_4\text{H}_4$ (**1**) represents a rare example of a global minimum with an ultrashort metal–metal distance between two main

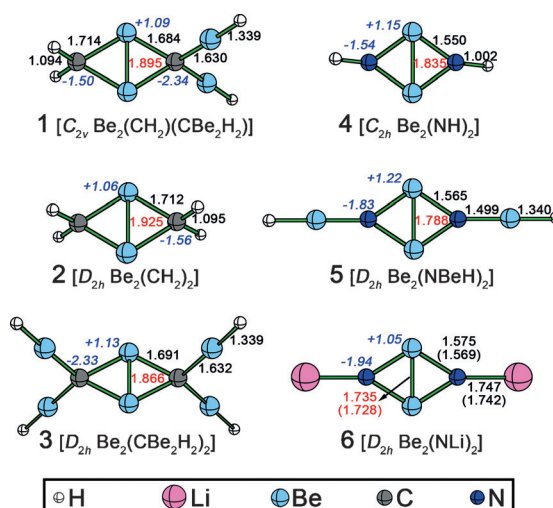


Figure 1. CCSD(T)-optimized structures of **1–6**. Be–Be distances (Å), other interatomic distances (Å), and NBO charges ($|e|$) are shown in red, black, and italic blue, respectively. CCSD(T)/aug-cc-pVQZ-optimized interatomic distances for **6** are given in parentheses.

[*] Dr. C. Yuan, X.-F. Zhao, Prof. Dr. Y.-B. Wu

The Key Lab of Energy Conversion and Storage of Shanxi Province and the Key Lab of Chemical Biology and Molecular Engineering of the Ministry of Education of China, Institute of Molecular Science Shanxi University, Taiyuan Shanxi 030006 (P.R. China)
E-mail: wyb@sxu.edu.cn

Prof. Dr. X. Wang

Department of Chemistry, University of Colorado Denver
Campus Box 194, P.O. Box 173364, Denver, CO 80217-3364 (USA)
E-mail: xiaotai.wang@ucdenver.edu

Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201609455>.

group atoms. This result inspired us to carry out the present study, which led to the computation of species containing ultrashort Be–Be distances comparable to the shortest transition metal TM–TM quintuple bonds (1.706–1.835 Å).^[8b–g]

To gain insight into what causes the ultrashort Be–Be distance in the rhombic Be₂C₂ core of **1**, we have performed a detailed bonding analysis using the adaptive natural density partitioning (AdNDP) method.^[9] The AdNDP analysis gives two sets of two-center two-electron C–Be σ -bonds within the Be₂C₂ rhombus, with occupation numbers (ONs) of 1.96 and 1.98 |e|, but it does not find direct orbital overlap between the two beryllium atoms (Figure 2). Consistently, the Wiberg bond indices (WBI) for the C–Be and Be–Be interactions, based on a natural bond orbital (NBO)^[10] calculation, are 0.73/0.64 and 0.13, respectively (Table 1), which indicate significant C–Be but negligible Be–Be covalency. Additionally, for the Be₂C₂ rhombus the NBO analysis assigns +1.09 |e| to beryllium, –1.50 |e| to the CH₂ carbon, and –2.34 |e| to the C(BeH)₂ carbon (Figure 1). These NBO charges

indicate significant electrostatic interaction between beryllium and carbon within the Be₂C₂ rhombus. In view of all these results, we rationalize that the ultrashort Be–Be distance in **1** results from the bridging carbon atoms attracting both beryllium atoms electrostatically.

To test our rationale, we have designed **2** and **3** (two derivatives of **1**), the former from eliminating the beryllium atom from each C–Be–H arm and the latter from inserting a beryllium atom into each C–H bond. Compounds **2** and **3** were optimized as energy minima, and their NBO charges were analyzed (Figure 1). As beryllium is more electropositive than hydrogen, the impacted carbon atom in **2** becomes less negatively charged (–1.56 |e|), and that in **3** becomes more negatively charged (–2.33 |e|). Thus, in comparison with **1**, the Be–C electrostatic interactions within the Be₂C₂ rhombus become weaker in **2** and stronger in **3**. As expected, the Be–Be distance changes in opposite directions, becoming longer (1.925 Å) in **2** and shorter (1.866 Å) in **3**. These results give further support for the idea that the distance between two beryllium atoms can be decreased by enhancing their electrostatic attraction for a bridging atom. Below, we apply this idea further.

In structures **1–3**, the rhombus consists of two Be–C–Be bridges. We have considered using smaller and more electronegative nitrogen atoms to replace the bridging carbon atoms to obtain even shorter Be–Be distances. Thus, we have derived **4** from **2**, and **5** from **3** by substituting nitrogen for carbon and by satisfying the three-coordinate requirement of nitrogen (Figure 1). This leads to shorter Be–Be distances within the Be₂N₂ rhombuses of **4** and **5**, which have been found to be 1.835 and 1.788 Å, respectively, at the CCSD(T)/aug-cc-pVTZ level. Furthermore, by replacing the hydrogen atoms in Be₂(NH)₂ (**4**) with more electropositive lithium atoms, we located Be₂(NLi)₂ (**6**) with an ultrashort Be–Be distance of 1.738 Å at the CCSD(T)/aug-cc-pVTZ level, which was then refined by re-optimization at the CCSD(T)/aug-cc-pVQZ level, thereby yielding a Be–Be distance of 1.728 Å. This is close to the shortest TM–TM distance found for the Cr–Cr quintuple bond (1.706 Å) in a 2,6-dimethylpiperidine complex.^[8g]

We have performed AdNDP analyses of structures **4–6**, and the results for **6** are presented in Figure 2. Apart from four two-center two-electron N–Be σ -bonds, there is a four-center two-electron π -bond delocalized over the Be₂N₂ rhombus (orbital E), which involves N \rightarrow Be π -donation and is nonbonding for the Be–Be interaction. This is corroborated by the small WBI values (0.09–0.14 in Table 1) for the Be–Be interactions in structures **4–6**, which indicate insignificant Be–Be bonding. Nevertheless, the N–Be bonding interactions within the rhombuses of structures **4–6** are strong and result from a combination of covalent and electrostatic contributions, judged by the corresponding WBI_{N–Be} values (0.70, 0.64, and 0.77) and N/Be charge separations (–1.54/ +1.15, –1.83/ +1.22, and –1.94/ +1.05). In comparison with **4**, the rhombus of **5** contains a somewhat weaker N–Be covalent interaction (0.64 vs. 0.70) but a much stronger N–Be electrostatic interaction, and the rhombus of **6** comprises stronger N–Be interactions of both covalent and electrostatic nature. The shortening of the Be–Be distance, upon moving from **4** to **6**,

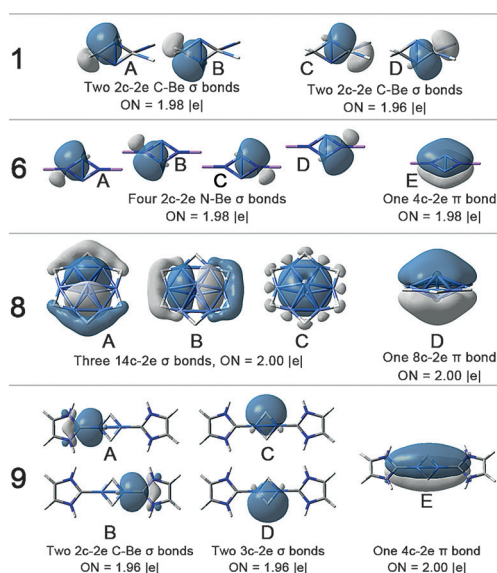


Figure 2. Selected AdNDP orbitals concerning beryllium bonding in representative species **1**, **6**, **8**, and **9**. The full sets of AdNDP MOs of **1–9** are given in Figures S1 (Supporting Information).

Table 1: The lowest vibrational frequencies (ν_{\min} in cm⁻¹); HOMO–LUMO gaps (eV); and the Wiberg bond indices (WBI) for Be–Be, Be–X, and Be–H (WBI_{Be–Be}, WBI_{Be–X}, WBI_{Be–H}) of **1–9**.

	ν_{\min}	Gap [eV]	WBI		
			Be–Be	Be–X	Be–H
1	83	3.90	0.13	0.64/0.73	
2	190	3.85	0.15	0.70	
3	53	4.50	0.12	0.65	
4	313	3.39	0.11	0.70	
5	88	3.68	0.09	0.64	
6	88	2.09	0.14	0.77	
7	143	2.84	0.76	0.39	
8	152	3.23	0.69	0.32	
9	31	1.76	0.80	0.85	0.47

appears to be an outcome of the joint influence of covalent and electrostatic N–Be bonding within the N_2Be_2 rhombus.

The ultrashort Be–Be distances in **1–6** are achieved by electrostatic interaction and without much orbital contribution to direct Be–Be bonding. We wondered whether ultrashort Be–Be distances could be attained by forming a maximum number of bonding orbitals involving the beryllium atoms. The answer is positive. With the aid of Be–Be–Be and Be–H–Be bridges, we have achieved another group of species with ultrashort Be–Be distances, including the three-dimensional molecular stars **7** and **8** with a vertical Be–Be axis, as well as the linear molecular strut **9** with a Be–Be core supported by bridging hydrogen atoms and terminal σ -donors (Figure 3). The bridging atoms (Be and H) in **7–9**, which have identical or similar electronegativity to beryllium, are chosen so as to maximize covalent bonding with beryllium.

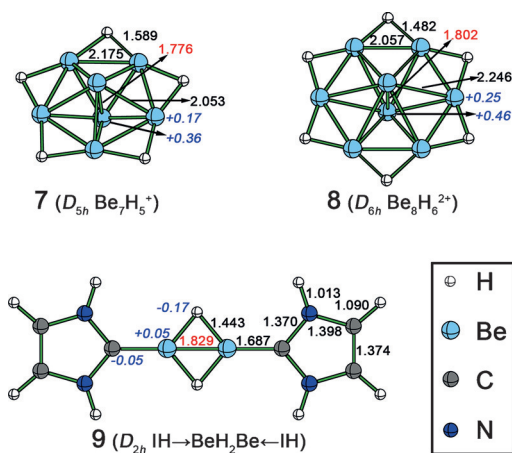


Figure 3. CCSD(T)-optimized structures of **7–9**. Be–Be distances (Å), other interatomic distances (Å), and NBO charges ($|e|$) are shown in red, black, and italic blue, respectively.

Design of the three-dimensional molecular stars **7** and **8** was inspired by our recently reported global minimum with the formula $C\text{O}Be_5H_5^+$, a two-dimensional planar star-like ring with a planar pentacoordinate carbon center.^[11] Considering that two beryllium atoms give a total of four valence electrons, as one carbon atom does, we wondered whether the carbon center in $C\text{O}Be_5H_5^+$ could be replaced by a perpendicular Be–Be axis to generate a three-dimensional molecular star. The idea was borne out by the calculation with B3LYP/aug-cc-pVTZ that gives the D_{5h} $Be_7H_5^+$ (**7**) as an energy minimum with a vertical Be–Be axis. Refinement at the CCSD(T)/aug-cc-pVTZ level shows the length of the Be–Be axis to be 1.776 Å. We note that the peripheral Be–Be distance in **7** is lengthened to 2.175 Å from 1.945 Å in $C\text{O}Be_5H_5^+$. The elongation suggests steric strain occurring in **7** that apparently stems from the small size of the five-membered peripheral Be_5H_5 ring. Thus, we substituted the six-membered Be_6H_6 ring for the Be_5H_5 ring in **7**, and increased the net charge to +2 to maintain the same number of skeletal electrons as in **7**. This rational design has resulted in a new three-dimensional molecular star, namely the D_{6h} $Be_8H_6^{2+}$ (**8**). At the B3LYP/aug-cc-pVTZ level, **8** is an energy

minimum with a ν_{\min} value of 152 cm^{-1} , and re-optimization with CCSD(T)/aug-cc-pVTZ gives the axial Be–Be distance at 1.802 Å, which is slightly longer than that in **7**. The peripheral Be–Be distance in **8** is decreased to 2.057 Å from 2.175 Å in **7**, indicating that geometrical strain is lessened.

Figure 2 shows four AdNDP-generated orbitals ($ON = 2.00 |e|$) concerning the Be–Be axis in **8**, three of them being fully delocalized 14-center two-electron σ -bonding orbitals (**A–C**) and one being an eight-center two-electron π -antibonding orbital (**D**). The net result is two bonding orbitals, suggesting a virtual double bond between the axial beryllium atoms. The WBI values for the Be–Be axial bonds in **7** and **8** are 0.76 and 0.69, respectively, indicating significant covalent character. As shown in Figure 3, the electrostatic interactions between an axial beryllium atom and a peripheral (bridging) beryllium atom in **7** and **8** are somewhat repulsive ($+0.36 |e| / +0.17 |e|$ for **7** and $+0.46 |e| / +0.25 |e|$ for **8**). Thus, it is covalent bonding that causes the ultrashort axial Be–Be distances in **7** and **8**. Such covalency is negligible between the rhombus-diagonal beryllium atoms in structures **1–6**; the ultrashort distances between those beryllium atoms are achieved by electrostatic attractions with the bridging atoms (see above). Pertinently, such axial Be–Be covalency, as that observed in **7** and **8**, is not found in the Be–Be axis of either of the Be_2B_8 and $Be_2B_7^-$ structures reported by Cui et al., where three σ -bonding orbitals are counterbalanced by three π -antibonding orbitals, resulting in approximately zero bonding interactions as reflected by the small WBI values for the Be–Be axis (0.14 in Be_2B_8 and 0.12 in $Be_2B_7^-$).

Design of the molecular strut **9** was inspired by our recent computational studies on nanomolecules containing the $-BeH_2Be-$ hydrogen-bridged bonds (HBBs).^[7,12] The Be–Be distances in such HBBs range from 1.950 to 1.994 Å, which are comparable to that of the Be–Be double bonds in the calculated complexes of the type $NHC \rightarrow Be=Be \leftarrow NHC$ (1.945 to 1.978 Å).^[5] We envisioned that a combination of hydrogen bridging and σ -donor stabilization could lead to an unprecedented bonding situation between two beryllium atoms in the $NHC \rightarrow BeH_2Be \leftarrow NHC$ setting. As a validation, we calculated $IH \rightarrow BeH_2Be \leftarrow IH$ in D_{2h} symmetry using imidazol-2-ylidene (IH), the simplest NHC, as a model that allowed optimization at the high CCSD(T) level of theory. Geometry optimization and frequency calculations at the B3LYP level demonstrate **9** to be an energy minimum, and re-optimization at the CCSD(T) level reveals a Be–Be distance of 1.829 Å, which is significantly shorter than the shortest Be–Be double bond (1.945 Å) in the $NHC \rightarrow Be=Be \leftarrow NHC$ complexes.

As shown in Figure 2, AdNDP analyses reveal a total of five orbitals in $IH \rightarrow BeH_2Be \leftarrow IH$ (**9**) that are pertinent to the beryllium atoms, including two two-center two-electron C–Be σ -orbitals (**A** and **B**), two three-center two-electron Be–H–Be σ -orbitals (**C** and **D**), and one four-center two-electron C–Be–Be–C π -orbital (**E**). With respect to the Be–Be core, three of these orbitals (**C**, **D**, and **E**) are bonding (the other two nonbonding), thereby forming a virtual triple bond that leads to the shortening of the Be–Be distance. Although the electrostatic interaction between a beryllium atom and a bridging hydrogen atom in **9** is attractive (Figure 3), it is

extremely small in magnitude ($+0.05|e|/-0.17|e|$) and therefore is insignificant. Thus, the ultrashort Be–Be distance in **9** results from enhanced Be–H–Be covalent interactions.

Compounds **1–8** are theoretically designed small clusters, and evaluation of their thermodynamic and kinetic stabilities would give clues as to whether they could be experimentally realized. We have previously shown that **1** is a global minimum.^[7] Herein, we have explored the potential energy surfaces (PESs) of **2–8** using a stochastic search algorithm. According to the final CCSD(T)/aug-cc-pVTZ calculations, **2** and **7** are local minima, being 2.9 and 50.8 kcal mol⁻¹ above the lowest energy isomers, respectively; as such, they would not be attainable experimentally. In contrast, the other structures, namely **3–6** and **8**, are all global minima, which are respectively 2.8, 36.8, 12.5, 20.9, and 7.5 kcal mol⁻¹ more stable than the next lowest isomers (Supporting Information, Figure S2). The Be–Be distances in these global minima are all shorter than 1.900 Å, thereby qualifying as ultrashort metal–metal distances. The smallest Be–Be distance (1.728 Å) is found in **6** at the CCSD(T)/aug-cc-pVQZ level, which is the shortest distance between two main group metals in any global minimum.

We have studied the kinetic stability of the global minima (**1**, **3–6**, and **8**) with 50-picosecond Born-Oppenheimer molecular dynamic (BOMD)^[13] simulations at 298 K at the B3LYP/6-31G(d) level of theory. Structure evolution during a simulation is described by the root-mean-square derivation (RMSD) relative to the B3LYP/6-31G(d)-optimized structure. As shown in Figure S3 (Supporting Information), although the RMSD plot for **1** shows some jumps towards the end of the simulation, the corresponding metastable structures change back to **1** upon re-optimization at the B3LYP/aug-cc-pVTZ level, suggesting the overall kinetic stability of **1**. For species **3–6**, the RMSD plots display no significant jumps and only minor fluctuations with the RMSD values ranging from 0.12 to 0.81 for **3** (average = 0.43), 0.04 to 0.47 for **4** (average = 0.19), 0.09 to 0.79 for **5** (average = 0.44), and 0.04 to 0.38 for **6** (average = 0.21). These results indicate that **3–6** are kinetically stable. The RMSD plot of **8** bears similarities to that of **1**, showing some reversible jumps but no irreversible deviation.

With regard to the model structure **9**, it can be modified for synthetic purposes by replacing IH with bulky NHC ligands such as IDip (1,3-bis(2,6-diisopropyl phenyl)imidazol-2-ylidene). Note that the utilization of IDip has led to the extraordinary synthesis of complexes containing B–B double and triple bonds with the formulae IDip→BH=BH←IDip and IDip→B≡B←IDip.^[14] Computational studies and predictions of relevant boron systems contributed to these experimental achievements.^[15] Along these lines of thought, we have computed IDip→BeH₂Be←IDip (**10**, Figure 4) as an energy minimum at the B3LYP level. The Be–Be distance in **10** (1.840 Å) is comparable to the B3LYP-calculated Be–Be distance (1.829 Å) in **9**. These computational results suggest that **10** should be chemically viable and therefore provide a synthetic target for experimentalists.

In summary, we have computationally designed and characterized a series of novel beryllium compounds. The salient feature of these species is that they contain ultrashort

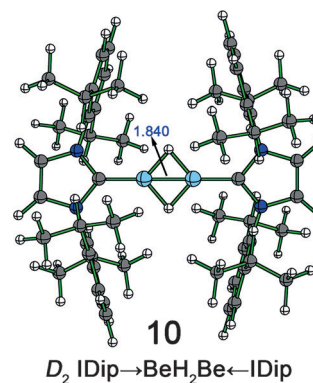


Figure 4. B3LYP-optimized structure of IDip→BeH₂Be←IDip.

Be–Be distances (1.728–1.866 Å) that rival the short bond lengths of homonuclear transition metal quintuple bonds (1.706–1.835 Å). Such ultrashort Be–Be distances are achieved by introducing appropriate bridging atoms for electrostatic or covalent interactions with the beryllium centers. The ultrashort Be–Be distances in **3–6** result from enhanced electrostatic interactions with the bridging atoms, whereas those in **7–9** arise from maximum orbital overlap via the bridging atoms. The small clusters **3–6** and **8** are found to be global minima with good kinetic stability, which makes them suitable for gas-phase detection and characterization. Compound **10** is an extension of **9**, in which the Be₂H₂ core is supported and protected by the bulky NHC ligands to make the molecule more viable for synthesis. On the whole, this theoretical study contributes to the growing field of structural chemistry of beryllium, and hopefully will encourage experimentalists to pursue and realize the interesting structures.

Acknowledgements

The authors acknowledge support for this work from the National Natural Science Foundation of China (21273140 and 21471092), the Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase), the Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi, and the University of Colorado Denver. We thank Professor Hua-Jin Zhai for helpful discussions.

Keywords: low-valent beryllium clusters · metal–metal bonding · NHC complexes · ultrashort metal–metal distances

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 15651–15655
Angew. Chem. **2016**, *128*, 15880–15884

[1] R. Puchta, *Nat. Chem.* **2011**, *3*, 416.

[2] J. M. Merritt, V. E. Bondybey, M. C. Heaven, *Science* **2009**, *324*, 1548–1551.

[3] Y. W. Yang, P. Coppens, *Acta Crystallogr. Sect. A* **1978**, *34*, 61–65.

- [4] a) Y. M. Xie, H. F. Schaefer, E. D. Jemmis, *Chem. Phys. Lett.* **2005**, *402*, 414–421; b) A. Velazquez, I. Fernandez, G. Frenking, G. Merino, *Organometallics* **2007**, *26*, 4731–4736.
- [5] S. A. Couchman, N. Holzmann, G. Frenking, D. J. D. Wilson, J. L. Dutton, *Dalton Trans.* **2013**, *42*, 11375–11384.
- [6] Z.-H. Cui, W.-S. Yang, L. Zhao, Y.-H. Ding, G. Frenking, *Angew. Chem. Int. Ed.* **2016**, *55*, 7841–7846; *Angew. Chem.* **2016**, *128*, 7972–7977.
- [7] X.-F. Zhao, H. Li, C.-X. Yuan, Y.-Q. Li, Y.-B. Wu, Z.-X. Wang, *J. Comput. Chem.* **2016**, *37*, 261–269.
- [8] a) F. R. Wagner, A. Noor, R. Kempe, *Nat. Chem.* **2009**, *1*, 529–536; b) T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844–847; c) K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 14162–14163; d) C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang, Y.-C. Tsai, *Angew. Chem. Int. Ed.* **2008**, *47*, 9933–9936; *Angew. Chem.* **2008**, *120*, 10081–10084; e) Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem. Int. Ed.* **2008**, *47*, 7250–7253; *Angew. Chem.* **2008**, *120*, 7360–7363; f) A. Noor, G. Glatz, R. Mueller, M. Kaupp, S. Demeshko, R. Kempe, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1149–1152; g) A. Noor, R. Kempe, *Chem. Rec.* **2010**, *10*, 413–416; h) A. Noor, R. Kempe, *Inorg. Chim. Acta* **2015**, *424*, 75–82.
- [9] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207–5217.
- [10] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.
- [11] J.-C. Guo, G.-M. Ren, C.-Q. Miao, W.-J. Tian, Y.-B. Wu, X. Wang, *J. Phys. Chem. A* **2015**, *119*, 13101–13106.
- [12] Y. B. Wu, J. L. Jiang, R. W. Zhang, Z. X. Wang, *Chem. Eur. J.* **2010**, *16*, 1271–1280.
- [13] X. S. Li, J. M. Millam, H. B. Schlegel, *J. Chem. Phys.* **2000**, *113*, 10062–10067.
- [14] a) Y. Wang, B. Quilliam, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413; b) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420–1422.
- [15] a) A. Papakondylis, E. Miliordos, A. Mavridis, *J. Phys. Chem. A* **2004**, *108*, 4335–4340; b) L. C. Ducati, N. Takagi, G. Frenking, *J. Phys. Chem. A* **2009**, *113*, 11693–11698; c) M. P. Mitoraj, A. Michalak, *Inorg. Chem.* **2011**, *50*, 2168–2174; d) N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517–13525; e) S.-D. Li, H.-J. Zhai, L.-S. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 2573–2579.

Manuscript received: September 26, 2016
Final Article published: November 16, 2016