Insights from domain-averaged Fermi hole (DAFH) analysis and multicenter bond indices into the nature of Be(0) bonding

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Summary

The nature of the bonding interactions in the recently synthetized first stable neutral complex of so-called zero-valent beryllium (*i.e.* formally Be(0)) are investigated using the analysis of domain-averaged Fermi holes (DAFHs) and of multicenter bond indices. It is shown that both of these types of analysis, which have previously proved useful for various molecules with nontrivial bonding patterns, basically corroborate the appealing model suggested in the original study to explain the stability of the complex (except for a more realistic specification of the actual valence state of the Be atom). Nevertheless, as well as confirming the anticipated dominance of three-center two-electron π bonding in the central C−Be−C fragment, reinforced by the existence of two donor-acceptor Be−C σ bonds, a more detailed scrutiny of the multicenter bond indices also reveals somewhat unexpected features which suggest also the existence of delocalized 3c-4e σ bonding in the C−Be−C skeleton.

Keywords: Peculiarity of Be(0) bonding, DAFH analysis, Multicenter bond indices, CASSCF calculations, QTAIM

Introduction

The particular position of beryllium among the alkaline-earth elements, namely its extreme Lewis acidity as well as the high tendency for covalent bonding [1], represents an increasing challenge for both experiment and theory to reveal and to explore the richness and versatility of its chemistry. In addition to an increasing number of experimental studies that report a broad variety of beryllium-containing species [2-8], the growing interest in Be chemistry has also initiated wider applications of theoretical computational approaches that, besides avoiding exposure to highly toxic beryllium, also represent a promising approach to reveal the subtleties and peculiarities of bonding to beryllium [9-16].

Of special relevance in this respect is the impetus arising from the richness and versatility of donor-acceptor interactions in the complexes of main group elements. The relatively recent discovery of divalent C(0) compounds, the so-called carbones [17-19], where the carbon atoms do not use any valence electrons for bonding, initiated the quest for the synthesis of analogous complexes also with other main-group elements. Nevertheless, until recently, many of the reported examples of such species involved derivatives of the parent carbones [20-24] and/or of group 14 congeners [25-29]. Isoelectronic homologues of carbones with boron, $(BR)L_2$, have also been reported [30-32].

A very significant recent advance is the discovery of the first stable neutral complex of so-called zero-valent beryllium (*i.e.* formally Be(0)). The stability of this complex was ascribed in a joint experimental and theoretical study to strong three-center two-electron (3c-2e) bonding that arises from the interaction of the Be(0) center with two cyclic (alkyl)(amino)carbene (cAAC) ligands, so as to form a linear C−Be−C unit [33]. These interactions were rationalized using an appealing model that assumed, besides the existence of two donor-acceptor Be−C σ bonds, resulting from the donation of σ electron pairs from carbene-like ligands to empty orbitals of Be, also the donation of an electron pair from a doubly-occupied p_π orbital of Be to empty p_π orbitals on the adjacent C atoms of the stabilizing carbene-like ligands. Stimulated by this recent advance, we decided to subject the anticipated bonding interactions in this complex to more detailed scrutiny using the analysis of multicenter bond indices [34-36] and of domain-averaged Fermi holes [37-40]. Given that these two computational methodologies have proved to be very useful in revealing the nature of the bonding in various classes of molecules with nontrivial bonding patterns, such as multicenter bonding, hypervalence, and so on [41-44], we can anticipate that their application to this neutral complex of formally zero-valent beryllium should provide useful new insights

into its electronic structure. In order to provide reliable pictures of the bonding in the complex, both methodologies were applied at an appropriate multiconfigurational post-Hartree-Fock level of theory.

Theoretical

Analysis of domain-averaged Fermi holes

As the principles of the analysis are sufficiently described in various earlier studies [37-40] we confine ourselves here to only a brief summary of the basic principles necessary for the purpose of this study. The domain-averaged Fermi holes (DAFHs) can most straightforwardly be introduced via the selective integration over a domain Ω of a so-called pair correlation function [45], *i.e.*

$$g_\Omega(\boldsymbol{r}_1) = \rho(\boldsymbol{r}_1) \int_\Omega \rho(\boldsymbol{r}_2) d\boldsymbol{r}_2 - 2 \int_\Omega \rho(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_2 = \rho(\boldsymbol{r}_1) N_\Omega - 2 \int_\Omega \rho(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_2$$

(1)

in which $\rho(\boldsymbol{r}_1)$ and $\rho(\boldsymbol{r}_1, \boldsymbol{r}_2)$ are the ordinary spinless first-order electron density and the pair density, respectively, and N_Ω denotes the number of electrons in the domain Ω:[1]

$$N_\Omega = \int_\Omega \rho(\boldsymbol{r}) d\boldsymbol{r}$$

(2)

The DAFH analysis consists in the first step of the construction of the matrix $\boldsymbol{G}_\Omega$ that represents the domain-averaged 'hole', g_Ω, in appropriate basis. After the matrix representation of the hole $\boldsymbol{G}_\Omega$ has been constructed, the next step of the analysis consists of subjecting the eigenvalues and eigenvectors of that matrix to an isopycnic localization transformation [47], which converts the original eigenvectors into more localized functions that provide highly visual and appealing depictions of the bonding that are often close to classical chemical thinking.

The utility of the DAFH analysis for structural investigations arises because the form of the matrix $\boldsymbol{G}_\Omega$ does of course depend on the actual choice of the domain Ω. We have demonstrated in a wide range of studies that especially interesting and chemically relevant

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[1] For the sake of mathematical rigor it is also possible to reformulate the whole approach in terms of density matrices instead of densities [46]; this choice of formulation has no practical impact on the actual application of the DAFH analysis to a particular system.

information can be extracted from holes that are averaged over the individual atomic domains resulting from Bader's virial partitioning of the electron density [48], also known as the quantum theory of atoms in molecules (QTAIM). In such cases, the analysis provides information about the actual valence state of the atom in the molecule. Holes that are averaged over the more complex domains that correspond to certain functional groups, or other such pertinent molecular fragments, can also be constructed and analyzed using the union of multiple QTAIM domains. In such a case, the analysis provides information about the electron pairs that remain intact within the fragment and also about the broken or dangling valences that are created by the formal splitting of the bond that would be required to isolate the given fragment from the rest of the molecule.

Structural information is extracted from the (transformed) numerical eigenvalues, which allow us to identify the bonds (and/or core and/or valence lone pair electrons) formed by shared electron pairs, as well as the broken or dangling valences resulting from the formal splitting of the bonds. The interpretation of these numerical data is greatly facilitated by visual inspection of the forms of the corresponding localized DAFH functions. The appealing visual insights provided by this type of analysis have proved useful in revealing the nature of the bonding interactions in many systems, ranging from the elucidation of the picture of the bonding in the equilibrium geometries of ground states molecules with nontrivial bonding patterns to the detailed monitoring of the electron reorganization that accompanies the splitting of chemical bonds [49-52].

Multicenter bond indices

Multicenter bond indices are generic families of quantities that result from the formal partitioning of density matrices and related quantities into mono-, bi-, tri- and generally k-center contributions that can be attributed certain physical or chemical meaning. The simplest situation is for the restricted Hartree-Fock (RHF) self-consistent field (SCF) approximation where the idempotency of the first-order density matrix allows the partitioning of the identity shown in Eq. 3, in which P and S denote the first-order density and the overlap matrices, respectively.

$$\frac{1}{2^{k-1}} \text{Tr}[(PS)^k] = N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \dots \sum_{A<B<C\dots<K} \Delta_{ABC\dots K}^{(k)}$$

(3)

Thus, for example, the diatomic contributions resulting from the partitioning of Eq. 3 for $k = 2$ are identical with the well-known Wiberg or Wiberg-Mayer bond indices [53,54]. Similarly,

the triatomic contributions from the partitioning of the identity for $k = 3$, as shown in Eq. 4, have found widespread use as so-called three-center bond indices [34-36] for the detection of three-center bonding interactions.

$$\Delta_{ABC}^{(3)} = \frac{3!}{2^2} \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\lambda \in C} \left[(PS)_{\mu\nu} (PS)_{\nu\lambda} (PS)_{\lambda\mu} \right]$$

(4)

where the notation $\mu \in A$ signifies that the relevant summation is restricted to the basis functions associated with atomic center A. Note that the occurrence of the factor of 3! in Eq. 4 simply reflects the fact that the symmetry-unique value of the index for a given ABC triad involves all equivalent terms arising from the permutation of the ABC labels. The usefulness of bond indices for structural investigations has stimulated more recent generalizations that allowed reformulations of the whole formalism using real-space three-dimensional partitioning into individual atomic domains [55,56].

As well as the generalization just mentioned, attention has been paid in recent years to extensions of the scope of multicenter bond indices beyond the SCF approximation. One such extension is based on a reformulation of the original formula (Eq. 3) in terms of quantities $\Delta^{(k)}(r_1, r_2 \ldots r_k)$ which are defined in an analogous fashion to the cumulants of higher-order densities [57,58]:

$$\int \Delta^{(k)}(r_1, r_2 \ldots r_k) \, dr_1 dr_2 \ldots dr_k = N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \ldots \sum_{A<B<C\ldots<K} \Delta_{ABC\ldots K}^{(k)}$$

(5)

An obvious potential disadvantage of such an approach is that the calculation of the corresponding bond indices requires the knowledge of correlated higher-order densities. Given that densities of higher than second order are not readily available, the number of studies using explicitly correlated third-order densities is rather scarce [59,60]. Instead, most of the more recent studies of correlated descriptions of multicenter bonding have tended to rely either on various approximations to higher-order densities or on the straightforward extension of Eq. 4 using the first-order density matrix calculated from natural orbitals, but with non-integer occupation numbers [61-63]:

$$\Delta_{ABC}^{(3)} = \frac{3!}{4} \sum_i \sum_j \sum_k n_i n_j n_k \langle i|j \rangle_A \langle j|k \rangle_B \langle k|i \rangle_C$$

(6)

where the notation $\langle i|j \rangle_A$ signifies that the integration in this overlap integral has been restricted so as to be only over atom A. Although the multicenter indices resulting from such an approach do not satisfy a normalization analogous to the one in Eq. 3, the ability to detect the existence of delocalized bonding interactions remains intact. Several studies dealing with the application of such "approximate" higher-order bond indices to various problems have been reported [61-65], ranging from the description of genuine three-center bonding to the quantitative characterization of aromaticity.

Despite the undeniable utility of the above straightforward approximations to multicenter bond indices, we have found it useful to adopt another strategy for improving the definition of the three-center bond index for correlated singlet systems. This new strategy was inspired directly by the earlier study of Mayer [66] who suggested, for such systems, to correct two-center Wiberg-Mayer indices using a matrix $\boldsymbol{R}$ which is defined so as to restore the exact validity of the normalization (Eq. 3). The resulting expression takes the following form, in which the matrix $\boldsymbol{R}$ has formally been substituted for the spin density matrix $\boldsymbol{P}^\mathrm{s}$ which would have appeared for cases with nonzero total spin:

$$W_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} \left[(\boldsymbol{PS})_{\mu\nu}(\boldsymbol{PS})_{\nu\mu} + (\boldsymbol{RS})_{\mu\nu}(\boldsymbol{RS})_{\nu\mu} \right]$$

(7)

For nonzero total spin, the corresponding three-center index (which we denote X_{ABC}) takes the following form:

$$
\begin{aligned}
X_{ABC} \quad &= \quad \frac{1}{8} \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\lambda \in C} \left[\begin{array}{l} (\boldsymbol{PS})_{\mu\nu}(\boldsymbol{PS})_{\nu\lambda}(\boldsymbol{PS})_{\lambda\mu} + (\boldsymbol{PS})_{\mu\nu}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\nu\lambda}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\lambda\mu} \\ +(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\mu\nu}(\boldsymbol{PS})_{\nu\lambda}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\lambda\mu} + (\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\mu\nu}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\nu\lambda}(\boldsymbol{PS})_{\lambda\mu} \end{array} \right] \\
&+ \quad \frac{1}{8} \sum_{\mu \in A} \sum_{\nu \in C} \sum_{\lambda \in B} \left[\begin{array}{l} (\boldsymbol{PS})_{\mu\nu}(\boldsymbol{PS})_{\nu\lambda}(\boldsymbol{PS})_{\lambda\mu} + (\boldsymbol{PS})_{\mu\nu}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\nu\lambda}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\lambda\mu} \\ +(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\mu\nu}(\boldsymbol{PS})_{\nu\lambda}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\lambda\mu} + (\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\mu\nu}(\boldsymbol{P}^\mathrm{s}\boldsymbol{S})_{\nu\lambda}(\boldsymbol{PS})_{\lambda\mu} \end{array} \right]
\end{aligned}
$$

(8)

Using the same correction matrix $\boldsymbol{R}$ for a correlated singlet system instead of the spin density matrix $\boldsymbol{P}^\mathrm{s}$, and then switching from the Mulliken-like partitioning in the atomic orbital basis to the use of QTAIM domains, one finally arrives at Eq. 9 which takes an especially simple form when it is expressed in the basis of the orthonormal natural molecular orbitals φ_i with corresponding occupations n_i:

$$X_{ABC} = \frac{1}{4} \sum_i \sum_j \sum_k \left(\begin{array}{l} n_i n_j n_k + n_i R_{jj} R_{kk} \\ +R_{ii} n_j R_{kk} + R_{ii} R_{jj} n_k \end{array} \right) \langle \phi_i | \phi_k \rangle_A \langle \phi_i | \phi_j \rangle_B \langle \phi_j | \phi_k \rangle_C$$

(9)

with $R_{ii} = [n_i(2-n_i)]^{\frac{1}{2}}$. For the sake of straightforward comparison with the original indices $\Delta_{ABC}^{(3)}$, as defined in Eq. 4, it is again convenient to profit from the invariance of the indices to permutations of the labels and to introduce a unique value $X(A,B,C) = 3! \, X_{ABC}$ for a given triad *ABC*. Although the values of this corrected index do not restore the exact normalization to the number of electrons *N*, they do often come close and they certainly represent an improvement over those defined by Eq. 6. We use values of $X(A,B,C)$, together with those of the original index $\Delta_{ABC}^{(3)}$ (Eq. 4) to characterize the possible three-center bonding in the Be(0) complex under investigation. Note that it is possible for a planar system to partition these values, as well as those of W_{AB} (Eq. 7), into separate σ and π components.

In addition to $X(A,B,C)$ and $\Delta_{ABC}^{(3)}$, it proved useful to adopt yet another alternative strategy for the description of multicenter bonding. This approach was inspired by the previous study by Cioslowski and Mixon [67] who introduced the so-called covalent bond order C_{AB} which they defined as follows:

$$C_{AB} = \sum_i (\nu_i)^2 \langle \Lambda_i | \Lambda_i \rangle_A \langle \Lambda_i | \Lambda_i \rangle_B$$

(10)

in which the localized natural orbitals (LNOs) Λ_i, with associated populations ν_i, are those which result from an application of the isopycnic transformation [47] to the canonical natural orbitals. This expression for C_{AB} (Eq. 10) does of course correspond to a simple summation over the index *i*, which labels the individual LNOs. As a consequence, an interesting advantage of the Cioslowski covalent bond order is that it can be used to complement the obvious splitting of Wiberg-Mayer-type bond indices into σ and π components (for a planar system) with the more detailed insights that emerge from the straightforward unambiguous partitioning of C_{AB} into contributions associated with individual LNOs (regardless of whether or not the system is planar). Attracted by this possibility, we suggest a rather trivial generalization of Eq. 10 so as to deal with three-center bonding:

$$K_{ABC} = \sum_i (\nu_i)^3 \langle \Lambda_i | \Lambda_i \rangle_A \langle \Lambda_i | \Lambda_i \rangle_B \langle \Lambda_i | \Lambda_i \rangle_C$$

(11)

Although it is again useful to profit from the invariance of the index in Eqn. 11 to permutations of the *ABC* labels, thereby introducing a symmetry-unique index $K(A,B,C) = 3! \, K_{ABC}$, we focus in the present work on the *relative* contributions from the terms that involve different LNOs, rather than on the total numerical values.

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Computations

The authors of the recent study that reported the synthesis of the first neutral complexes of formally zero-valent beryllium [33] also carried out various theoretical studies, including an application of the powerful combination of energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV) [68-70] to analyze the nature of the bonding interactions. Such analysis demonstrated that the surprising stability of these complexes can be ascribed primarily to unusually strong multiple bonding whose main component consists of three-center two-electron (3c-2e) π bonding across the central C−Be−C fragment. Because of our previous experience with the analysis of the picture of the bonding in other molecules with nontrivial bonding patterns (including multicenter bonding), we decided to subject the electronic structure of such a complex to systematic scrutiny using the visual insights offered by the analysis of domain-averaged Fermi holes and the additional support provided by numerical values of multicenter bond indices.

In order to provide a realistic picture of the bonding, we decided to apply these methodologies at a sufficiently realistic multiconfigurational correlated level of theory. The [Be(^{Me}L)$_2$] complex, where ^{Me}L stands for 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidine-2-ylidene, is too large for such a treatment but we can profit from the trimming down of the full structure to that of a smaller model cAAC complex, [Be(cAAC^{Model})$_2$] (**1a**) (Scheme 1), as was suggested in the original study [33]. It did, though, prove useful for most of our calculations to simplify (**1a**) to an even more compact model (**1b**) (Scheme 1) in which we replaced the ring systems by terminating NH_2 and CH_3 groups. This replacement was done *without* further geometry optimization, so as to maintain as closely as possible the local coordination at the heavy atoms in the vicinity of the central Be atom. In practice, a CH_2 group attached to N was replaced by an H atom shifted along the original NH−CH_2 axis so as to be at the same distance as is the N−H bond length in (**1a**). The same strategy was then used for the construction of each terminal CH_3 group, with the only difference being that the new C−H bond length was set equal to the average of the bond lengths of the two pre-existing C−H bonds inherited from (**1a**).
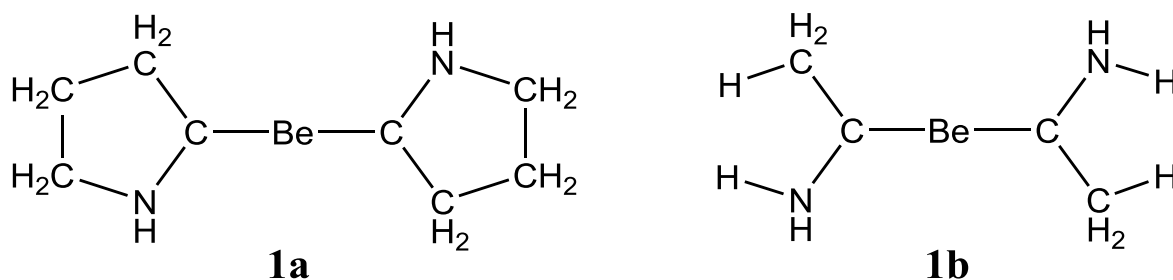
Scheme 1: Structures of the model complexes.

It was of course important to evaluate the impact of this simplification of the full [Be(^{Me}L)$_2$] complex to the compact model (**1b**). With this in mind, we performed a comparison of Mulliken-like DAFH analysis of the full [Be(^{Me}L)$_2$] complex with that for (**1b**). The wave function for the full complex was generated in a single point calculation at a geometry taken from the original study [33] and a single point calculation at the same level of theory was used for (**1b**). Comparisons of the two sets of results did not reveal any important differences for the description of the region that is common to the two systems. Furthermore, only marginal effects were observed on changing the Mulliken-like DAFH analysis of (**1b**) to the use instead of the QTAIM approach at the BP86/6-31G** level of theory. As further checks, we also looked at comparisons of Mulliken-like DAFH analysis of the [Be(cAAC^{Model})$_2$] complex (**1a**) at the BP86/def2-tzvpp level with QTAIM-based DAFH analysis of RHF descriptions of the complex (**1b**) (with various basis sets). The absence of any important differences in the picture of the bonding that emerges from any of these preliminary investigations seems to provide sufficient justification for the use here of the compact complex (**1b**) as a realistic model of the full [Be(^{Me}L)$_2$] system. As such, we felt confident to use the compact complex (**1b**) in all subsequent complete active space self-consistent field (CASSCF) multiconfigurational correlated calculations for which we performed DAFH analysis and/or calculated bond indices.

Even for the compact model (**1b**), full-valence CASSCF calculations are completely beyond the scope of our possibilities, given that they would involve all of the symmetry-allowed distributions of 38 electrons in 38 orbitals, and so it was necessary to choose a smaller active space that would provide a sufficiently realistic but still tractable description. For this purpose we exploited the possibility of identifying at the RHF/6-31G** level the Pipek-Mezey localized molecular orbitals [71] that correspond unambiguously to various C−H, N−H and C−N bonds. This allowed us initially to freeze these orbitals, together with the various 1s^2 core orbitals, in a "14-electrons in 14-orbitals" CASSCF construction. Then, in a

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subsequent step, all of the inactive orbitals were allowed to relax alongside simultaneous reoptimization of the CASSCF(14,14) active space, with the final calculations (*ca*. 1.4 million configuration state functions) carried out in C_i symmetry. Various RHF and DFT calculations were performed using the Gaussian03 program [72] and the CASSCF calculations [73,74] were carried out using the MOLPRO package [75,76]. The resulting wave functions for (**1b**) were then used, alongside the QTAIM approach, to carry out DAFH analysis and to compute the various bond index values using our own programs. The actual QTAIM analysis [48] of the various total electron densities were carried out using the AIMAll program [77].

Results and discussion

As was noted above, the authors of the recently reported synthesis of the first neutral complexes of formally zero-valent beryllium [33] attributed the stability of such complexes to the interaction of the central metal atom with the cAAC ligands. This interaction, characterized by very short Be−C bond lengths and a linear arrangement in the central C−Be−C unit, was interpreted as an indication of strong multiple Be−C bonding; such an interpretation found additional support both from experimental measurements (X-ray, NMR, cyclic voltammetry, UV-vis) and theoretical calculations (DFT and small CASSCF(4,4) constructions, as well as EDA-NOCV analysis) [33]. All of these approaches appear to support a very straightforward picture that assumes the existence of 3c-2e π bonding in the C−Be−C fragment, resulting from the donation of an electron pair from the p_π orbital of Be in the configuration $1s^2 2s^0 2p^2$ into the empty π orbitals on the carbene-like fragments, and to two donor-acceptor C−Be σ bonds, formed by the donation of an electron pair from each carbene-like moiety into suitable empty orbitals on the beryllium atom.

In order to assess the validity or otherwise of the bonding model that we have just outlined, we report below the results from applying our various methodologies at the sufficiently realistic CASSCF(14,14) level of theory. To this end, we start with an inspection of the results of the DAFH analysis for various appropriately-selected domains. Given that the various C−H, N−H and C−CH₃ bonds are mostly described by inactive orbitals, it makes most sense in the DAFH analysis of our CASSCF(14,14) wave function for (**1b**) to focus on holes corresponding to active-space G_Ω matrices.

Of special importance is, of course, the hole averaged over the domain of the isolated beryllium atom: in this case, the DAFH analysis is expected to provide information about the valence state of this atom in the molecule [78-80]. In addition, complementary information

about the picture of the bonding around the Be atom was also extracted from the analysis of the Fermi holes averaged over more complex domains formed by: *a*) the union of the active-space G_Ω matrices for an adjacent $C(CH_3)$ fragment and *b*) the union of the active-space G_Ω matrices for the NH_2 group that is attached to that $C(CH_3)$ fragment. In these cases, the analysis is expected to provide information about the broken or dangling valences of the bonds whose splitting is formally required to isolate the given fragment from the rest of the molecule, as well information about any electron pairs that are retained within that fragment.

We look first at the results of the analysis for the hole averaged over the beryllium QTAIM domain (see Fig. 1). Given that the $1s^2$ core electrons do not contribute to the construction of the active-space G_Ω matrix, the analysis results in just two degenerate pairs of eigenvalues with nontrivial values. Inspection of the associated eigenvectors shows that the pair of functions each populated by 0.14 electrons corresponds to the symmetry-equivalent dangling valences of formally broken Be−C σ bonds. Similarly, the pair of functions each populated by 0.07 electrons represent the dangling or broken valences of the formally broken Be−C π bonds.

«Fig. 1 near here»

Such interpretations are straightforwardly corroborated by the results of the DAFH analysis for the complementary $C(CH_3)$ domain. In this case, because the inactive electron pairs of the C−C and C−H bonds were not considered in the construction of the condensed-domain active-space G_Ω matrix, the DAFH analysis yielded just four eigenvalues with nontrival values (see Fig. 1). The first of these functions, populated by 1.77 electrons, is reminiscent of the dangling valence of a formally broken Be−C σ bond that was observed in the previous analysis for the Be domain, where it was populated by 0.14 electrons. Such a result is straightforwardly consistent with the existence of a more or less normal, but rather polar, donor-acceptor (2c-2e) Be−C σ bond; the populations of 1.77 and 0.14 represent the contribution of C and Be, respectively, to the unevenly shared electron pair of this bond. A more interesting situation occurs for the second, clearly π-like function (occupancy 0.95). With the isovalue chosen for all of the depictions shown in Fig. 1, this function is clearly reminiscent of one that appeared in the previous analysis for the Be domain, where it corresponded to the dangling valence of a formally broken Be−C π bond. Nevertheless the moderate overlap (0.57) of this π-like function for the $C(CH_3)$ domain with the analogous function from the other $C(CH_3)$ domain suggests that the π bonding in the C−Be−C fragment could have, at least to some degree, a three-center character. Such a notion is also supported

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by the near complementarity of the corresponding populations, $2 \times (0.95 + 0.07) \approx 2$, which is indeed consistent with the existence of a π electron pair that is spread over the entire C−Be−C fragment.

Although the DAFH results that we have just described do appear at first sight to be mostly consistent with the conclusions of the original study [33], closer inspection indicates that there are certain differences in the details, especially in the case of the (3c-2e) π bonding. According to the original model, this multicenter π bonding resulted from the donation of an electron pair from the p_π orbital of the Be atom (in the valence state $1s^2 2s^0 2p^2$) into empty p_π orbitals on the carbene–like ligands. The actual occupations of the DAFH functions involved in this π three-center bonding do, however, suggest that the electron pair formally originally occupying the Be($2p_\pi$) orbital contributes symmetrically to such an extent into the originally empty π orbitals on the carbene-like moieties that there is only a very small residual population on Be. It is interesting in this connection to mention that the results of DAFH analysis that was carried out at the simpler RHF and BP86 levels did produce a slightly different picture of multicenter bonding that is, in some respects, closer to the anticipations of the original model [33]. The most important difference concerns the analysis of the hole averaged over the central Be domain for which, instead of two equivalent functions reminiscent of C−Be π-bonds, it yielded a single symmetric π function that is delocalized over all three atoms in the C−Be−C fragment (see Fig. 2). (The populations are 0.245 and 0.200 for RHF and BP86, respectively). As can also be seen from Fig. 2, visually rather similar delocalized π functions arose in the analysis of the condensed domain consisting of *both* of the adjacent C atoms; the corresponding populations of 1.590 and 1.636 for RHF and BP86, respectively, provide the complementary electrons that come close to completing an electron pair for the delocalized 3c-2e π bonding.

«Fig. 2 near here»

Similar differences in the description of the three-center π bonding between the RHF and BP86 descriptions, on the one side, and the correlated multiconfigurational CASSCF(14,14) description, on the other, were also observed in the forms of the LNOs. Instead of two symmetry-equivalent π functions with occupations 1.06 (Fig. 3) resulting from the isopycnic localization of the first-order correlated density matrix, the analogous localization of doubly-occupied RHF or BP86 orbitals yielded a single symmetric π function, populated by two electrons and delocalized over the whole C−Be−C fragment.

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Having discussed the dominant bonding interactions within the C−Be−C fragment, a more complete description of the bonding in (**1b**) requires also a brief demonstration of the trivial nature of the remaining bonding interactions between the $C(CH_3)$ and NH_2 fragments. These interactions are straightforwardly evident from an inspection (see Fig. 1) of the corresponding DAFH functions with occupation 0.50 from the analysis for the $C(CH_3)$ domain and of 1.49 electrons for the adjacent NH_2 domain. The close visual resemblance of these functions, together with near complementarity of the corresponding populations, suggests a straightforward link to the dangling valences of a formally broken 2c-2e C−N σ bond, in which the populations of 0.50 and 1.49 represent the contributions of C and N atoms, respectively, to the unevenly shared electron pair of this bond. In a similar fashion, the close resemblance of the fourth of the DAFH functions for the $C(CH_3)$ domain, with occupancy 0.14, and the dominant DAFH function for the adjacent NH_2 domain (population 1.74) evidently describe a slightly less than doubly occupied $N(2p_\pi)$ lone pair that is slightly deformed towards the adjacent C atom.

Taken together, except for the more realistic specification of the actual valence state of the Be atom, the picture of the bonding that emerges from the DAFH analysis is, to a considerable extent, consistent with the original model [33] that anticipated the existence of two donor-acceptor C−Be σ bonds and a delocalized 3c-2e π bonding interaction in the C−Be−C fragment. Nevertheless, despite this general agreement, a more detailed scrutiny of the bonding interactions in terms of bond indices reveals somewhat unexpected features that are associated with the multicenter bonding in the C−Be−C fragment.

In order to ascertain these features we first present in Table 1 the calculated values of $\Delta_{ABC}^{(3)}$ and $X(A,B,C)$, as defined above (Eqs. 4 and 9). (Note that the values of $\Delta_{ABC}^{(3)}$ and $X(A,B,C)$ necessarily coincide when all of the orbitals are doubly occupied, and that the normalizaton condition in Eq. 3 is also satisfied). When using the RHF or BP86 methods, the indices were calculated using the complete valence space (38 electrons), whereas the corresponding CASSCF(14,14) values were based only on the active space (14 electrons). We found that the sum of all CASSCF(14,14) X_{ABC} values for (**1b**) turns out to be 14.014, *i.e.* fairly close to 14, whereas omission of the **R**-dependent terms from Eq. 9 gave instead a grand total of 12.935.

Inspection of this Table shows that all of the various indices consistently indicate the existence of three-center bonding in the C−Be−C fragment and although, as often happens, the inclusion of electron correlation leads to a slight decrease in the corresponding values, all of the indices do still confirm a nontrivial degree of multicenter bonding character in this unit. Moreover, the positive sign of the indices is also straightforwardly consistent with the anticipated 3c-2e character of the bonding. As can also be seen from the Table, the multicenter character of the bonding is slightly enhanced when instead of trivial (C,Be,C) domains the indices are calculated for the $((CH_3)C,Be,C(CH_3))$ triad and for the (LHS,Be,RHS) triad, where LHS and RHS denote the condensed $C(CH_3)(NH_2)$ domains on opposite sides of the central Be atom.

As noted above, the original model associated the multicenter bonding in the complex solely with the existence of 3c-2e π bonding. Although the existence of such 3c-2e π bonding in the C−Be−C fragment now appears to be undeniable, based on the results we have presented, a more detailed scrutiny of various bond index values suggests, somewhat unexpectedly, that the original model could be slightly oversimplified. A first indication of the more complex nature of the three-center bonding in this complex arose because of the ability to split total values of the three-center index $K(A,B,C)$ into contributions that are associated with individual LNOs (*vide supra*). Such a partitioning shows, in the case of the (C,Be,C) triad, that each of the terms involving a π-like LNO with occupation 1.06 contributes only 32% of the total value, suggesting that only 64% of the total three-center bonding can be ascribed to the π-like character; according to this mode of analysis, the remaining 36% comes from the contributions of the two σ-like LNOs (population 1.98 each) that are associated with the σ bonding in the Be−C moieties.

Independent support for this surprising result is provided by values of the three-center indices $\Delta_{ABC}^{(3)}$ and $X(A,B,C)$, for which the near planarity of the geometry of the compact model (**1b**) allows an approximate splitting of the total values into separate σ and π contributions. Such partitioning shows that alongside the expected positive contribution from the three-center π bond there is also an additional positive contribution for three-center σ bonding that reinforces the primary contribution from 3c-2e π bonding. Although there is a fairly large scatter in the relative weights of the σ and π contributions, depending on the level of theory and choice of basis set, with the σ contributions range from about 30% at the BP86/SDD level to about 10% for CASSCF(14,14)/6-31G**, the basic observation that a positive contribution for three-center σ bonding reinforces the positive contribution for 3c-2e

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π bonding remains the same. This outcome is, however, rather unusual and somewhat unexpected: the multicenter σ bonding necessarily has in this case the character of 3c-4e bonding, but such a bonding pattern is normally associated with negative values for three-center indices such as $\Delta_{ABC}^{(3)}$ [81,82]. (We note that it is important to use realistic basis sets: the contribution from the 3c-4e σ bonding becomes essentially negligible when using only a minimal basis set.)

In order to clarify this surprising feature of the 3c-4e σ bonding in (**1b**), we found it possible to modify the original simple three-center three-orbital analytical model of three-center bonding by invoking a slightly more involved Hückel-like model in which the central atom contributes to the multicenter bonding not just by one orbital, but by two. The basic features of such a model are depicted in a Scheme 2. This model, which shares various characteristics with the outcomes of our DAFH analysis, exhibits an additional flexibility that is reflected in the adjustable parameter x. The choice of the value of x affects the final value of the three-center index that gauges to some extent the "strength" of the corresponding component of the 3c-4e bonding. In the particular case of $x = 0.5$, the value of the index is +0.102, and it decreases with decreasing x. Comparison of this value with the idealized one for the 3c-2e bond index (0.375) suggests that delocalized 3c-4e σ bonding is apparently weaker in this system than the dominant 3c-2e π bonding; this result seems to be consistent with estimates based on the energy decomposition analysis of the bonding in the complex [33,83]. On the other hand, in spite of some visual resemblance of the present results with the orbital interactions anticipated from the EDA-NOCV analysis (see Fig. 2 in ref. 33), there was no obvious indication in the previous study of the delocalized multicenter σ bonding in the C−Be−C fragment that has been revealed here by detailed scrutiny of multicenter bond indices.
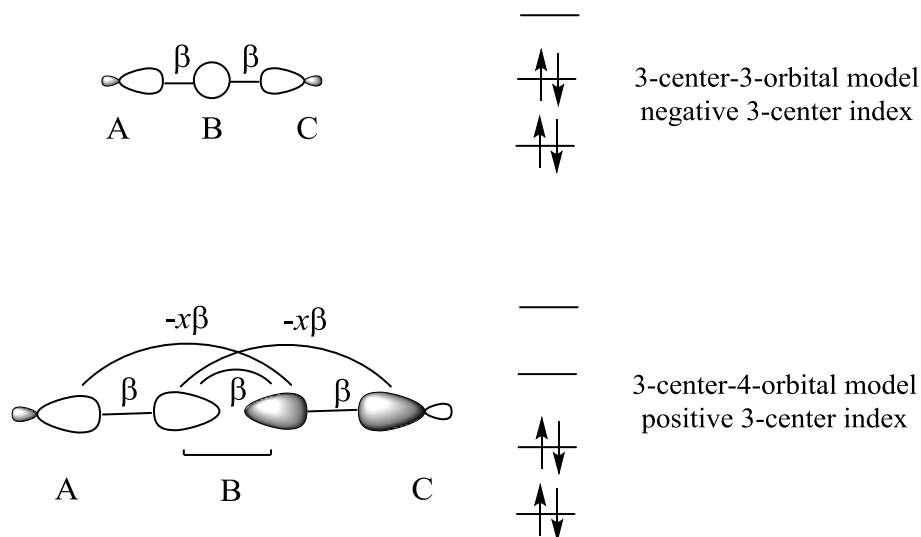
Scheme 2: Hückel-like models for 3-center bonding.

Conclusions

The recent synthesis of the first stable neutral complex of so-called zero-valent beryllium (*i.e.* formally Be(0)) represents an important step that opens up new avenues in s-block chemistry, with challenges both for experiment and for theory. Our aim in this study was to contribute to the elucidation of the bonding interactions responsible for the stability of such complexes. The authors of the original study primarily attributed the stability of these complexes to the existence of strong Be−C multiple bonding; they suggested an appealing model, supported by their EDA-NOCV calculations, that involves 3c-2e π bonding in the C−Be−C fragment, resulting from the donation of an electron pair from the $2p_\pi$ orbital of a Be atom in configuration $1s^2 2s^0 2p^2$ into an empty π orbital on each carbene-like fragment, and also two donor-acceptor C−Be σ bonds formed by the donation of an electron pair from each carbene-like moiety into suitable empty orbitals on the beryllium. Motivated by our previous experience with the analysis of the bonding interactions in molecules with nontrivial bonding patterns, we subjected the above model to detailed scrutiny using the analysis of domain-averaged Fermi holes (DAFHs) and of appropriate multicenter bond indices, both applied for QTAIM domains at the level of sufficiently realistic CASSCF multiconfigurational correlated wave functions. The results of both of these methodologies basically corroborate the anticipations of the original model [33], except for a more realistic specification of the actual valence state of the Be atom. Nevertheless, in addition to confirming the existence of delocalized 3c-2e π bonding in the central C−Be−C unit, further analysis of multicenter bond indices also revealed somewhat unexpected features of the bonding in the σ skeleton, for

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which the results appear to show the existence also of delocalized 3c-4e σ bonding in the same C−Be−C fragment.

Acknowledgment

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Fig. 1 – color for online version

Symmetry-unique dominant DAFH functions for the Be domain (top row), for a $C(CH_3)$ condensed domain (rows 2 and 3) and for one of the (NH_2) condensed domains (bottom row) in (**1b**), together with the corresponding occupation numbers. (Pictures were generated using the open-source molecular visualization program Molekel [84,85].)
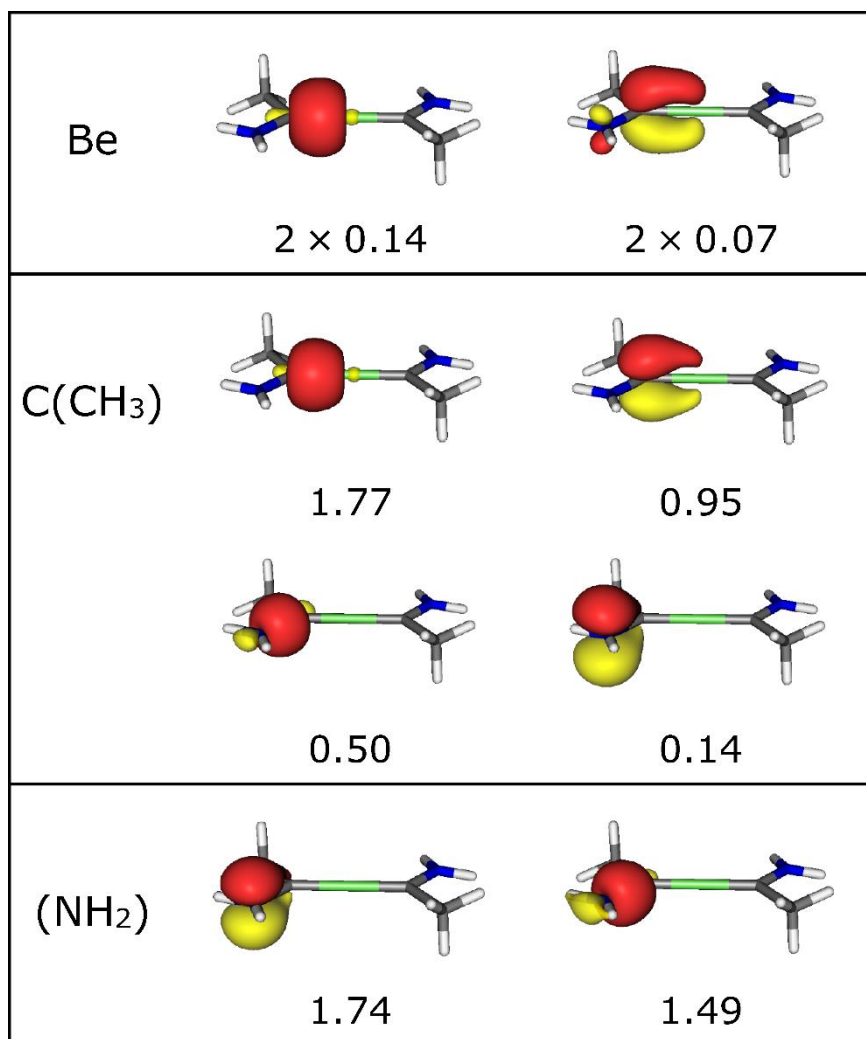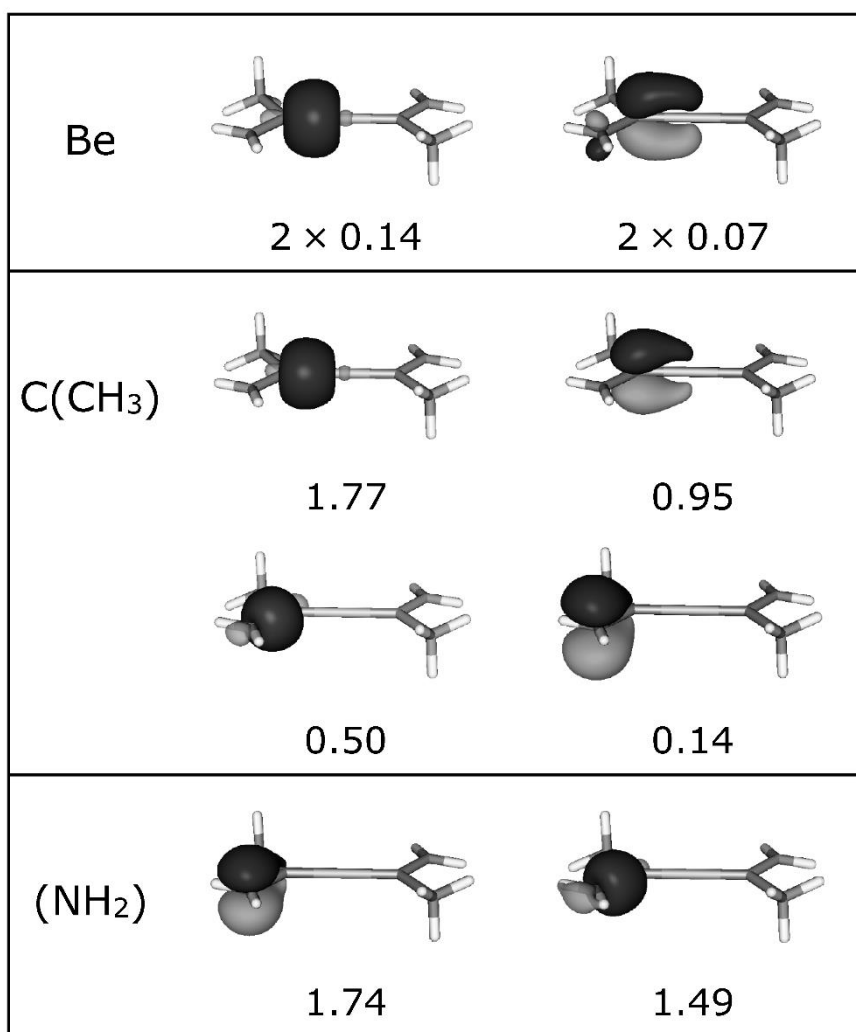
Fig. 1 –b/w for printed version

Symmetry-unique dominant DAFH functions for the Be domain (top row), for a C(CH$_3$) condensed domain (rows 2 and 3) and for one of the (NH$_2$) condensed domains (bottom row) in (**1b**), together with the corresponding occupation numbers. (Pictures were generated using the open-source molecular visualization program Molekel [84,85].)

Fig. 2 – color for online version

Dominant π-like functions (with the corresponding occupations) from DAFH analysis of (**1b**) for the holes averaged over the complementary QTAIM domains of the Be atom and of two adjacent C atoms. Calculations were performed using the BP86/6-31G** level of theory. (Pictures were generated using the ChemCraft program [86].)
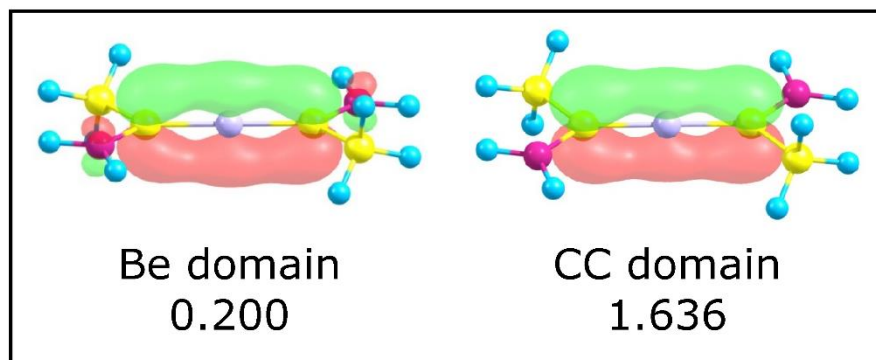

Fig. 2 – B/W for printed version

Dominant π-like functions (with the corresponding occupations) from DAFH analysis of (**1b**) for the holes averaged over the complementary QTAIM domains of the Be atom and of two adjacent C atoms. Calculations were performed using the BP86/6-31G** level of theory. (Pictures were generated using the ChemCraft program [86].)
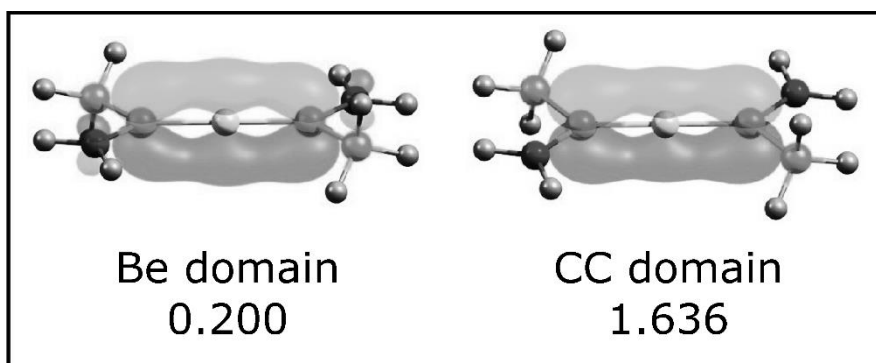
Fig. 3 – color for online version

Localized (natural) orbitals describing the central σ and π systems in (**1b**) from BP86 (top row) and from CASSCF (bottom row).

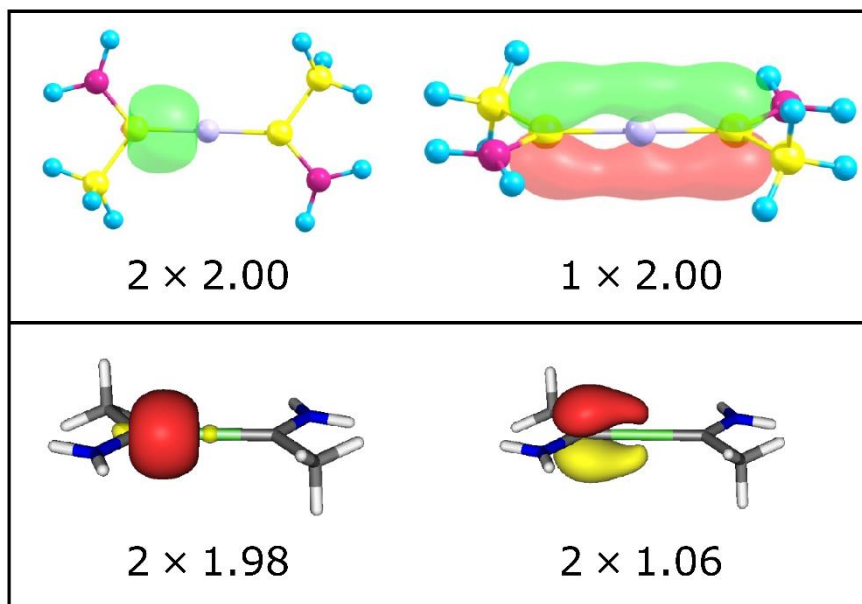|	
2 × 2.00	1 × 2.00
2 × 1.98	2 × 1.06

Fig. 3 – B/W for printed version

Localized (natural) orbitals describing the central σ and π systems in (**1b**) from BP86 (top row) and from CASSCF (bottom row).

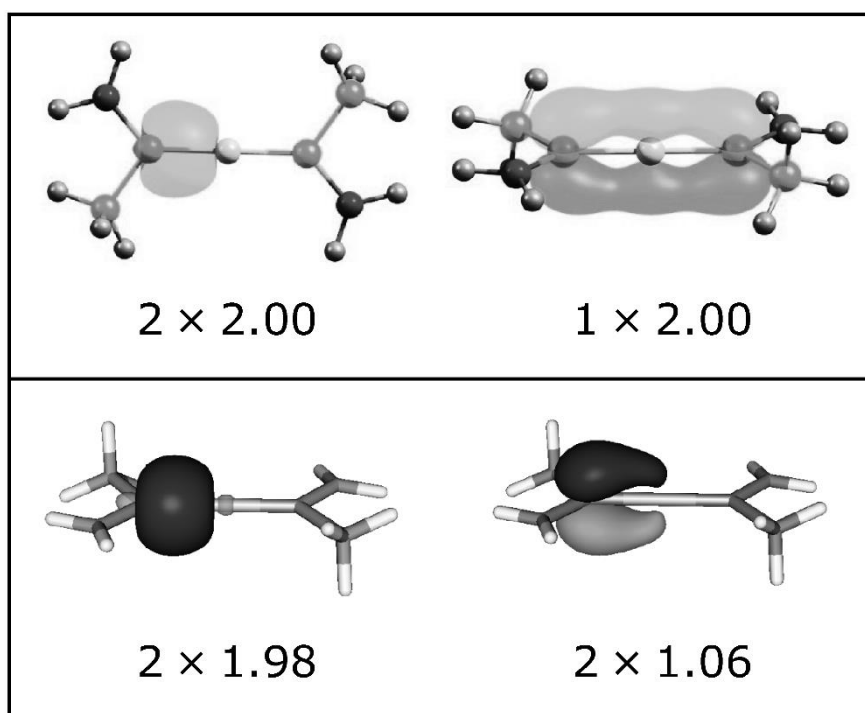|	
2 × 2.00	1 × 2.00
2 × 1.98	2 × 1.06

Table 1

Symmetry-unique values of various three-center indices for the valence space (RHF or BP86) and active-space (CASSCF) of the the compact model complex (**1b**). LHS and RHS denote the $C(CH_3)(NH_2)$ condensed domains on opposite sides of the central Be atom.

Triad			RHF	BP86	CASSCF(14,14)	
A	*B*	*C*	$\Delta^{(3)}_{ABC}$	$\Delta^{(3)}_{ABC}$	$\Delta^{(3)}_{ABC}$	$X(A,B,C)$
C	Be	C	0.199	0.153	0.088	0.107
$(CH_3)C$	Be	$C(CH_3)$	0.223	0.177	0.097	0.118
LHS	Be	RHS	0.287	0.245	0.124	0.148