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## Introduction

The concept of aromaticity has long gone beyond the classical Hückel organic structures.<sup>1,2</sup> Today, the terms  $\pi$ - and  $\sigma$ -aromaticity are well used for a variety of compounds, including complex inorganic structures.<sup>3</sup> In these cases, the delocalized bonding well describes the formation of highly symmetric stable compounds. Numerous planar boron clusters,<sup>4–7</sup> metal clusters,<sup>3,7–13</sup> and metallabenzenes<sup>14–18</sup> fit well into the concept of aromaticity. Along with  $\pi$ - and  $\sigma$ -aromaticity, multiple local  $\pi$  aromaticity is found to be a useful tool to describe complex conjugate systems such as graphene.<sup>19–21</sup> This concept has been accepted up to a point. In our work we showed that the concept of multiple local  $\sigma$ -aromaticity could be applied in chemistry. It should be noted that the analysis of completely delocalized canonical MOs cannot lead to a reliable picture of chemical bonding in such clusters,<sup>22,23</sup> since there is a mixture of electron lone pairs (an element that does not participate in chemical bonding interactions) with bonding elements of the cluster. Thus, to analyse aromaticity, firstly we need to localize all classical elements (such as 1c–2e lone pairs and 2c–2e Lewis bonds). The adaptive natural density partitioning algorithm (AdNDP) can be very useful for this purpose.

Homoatomic clusters of type  $[M_9]^{2-}$  ( $M = Si, Ge, Sn$ , and  $Pb$ ) have been investigated both experimentally and theoretically.<sup>24,25</sup> The structures of most such clusters confirm the predictions from Wade's rules.<sup>26,27</sup> Interestingly, the expectation of the geometry of  $[M_9]^{4-}$  species with  $2n+4$  ( $n = 9$ ) skeletal

## Multiple local $\sigma$ -aromaticity of nonagermanide clusters†

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Nonagermanide clusters are widely used in inorganic synthesis and are actively studied by experimentalists and theoreticians. However, chemical bonding of such versatile species is still not completely understood. In our work we deciphered a bonding pattern for various experimentally obtained nonagermanide species. We localized the electron density via the AdNDP algorithm for the model structures  $[(Ge_9)^{4-}]$ ,  $[(Ge_9\{P(NH_2)_2\}_3)]^-$ ,  $Cu[Ge_9\{P(NH_2)_2\}_3]$  and  $Cu(NHC)[Ge_9\{P(NH_2)_2\}_3]$  and obtained a simple and chemically intuitive bonding pattern which can explain the variety of active sites and the existence of both  $D_{3h}$  and  $C_{4v}$  geometries for such clusters. Moreover, the  $[Ge_9]^{4-}$  core is found to be a unique example of an inorganic Zintl cluster with multiple local  $\sigma$ -aromaticity.

electrons leads us to a *nido* nine-vertex polyhedron ( $C_{4v}$  capped square antiprism).

An isolated  $[Ge_9]^{4-}$  cluster has been experimentally obtained in the solid state in the form of alkali metal salts ( $K_4Ge_9$ ,<sup>28</sup>  $Cs_4Ge_9$  and  $Rb_4Ge_9$  (ref. 29)). The geometry of these clusters (except  $Rb_4Ge_9$ ) was found by X-ray crystallography and it was slightly distorted from the ideal  $C_{4v}$  capped square antiprism, confirming Wade's rules.<sup>24</sup> However, various DFT calculations (Table 1) suggest that the global minimum structure for  $[Ge_9]^{4-}$  is a tricapped trigonal prism ( $D_{3h}$  symmetry).<sup>23,30</sup> In turn, the  $C_{4v}$  symmetric structure has one imaginary frequency. A similar picture could be found, for instance, in a biphenyl system (twisted geometry in the gaseous phase and completely planar in the solid state).  $D_{3h}$  and  $C_{4v}$  structures transform from one to another through the diamond square process (Fig. 1).<sup>31,32</sup>

Although Wade's rules can give us a prediction of the cluster structure, we still do not have a comprehensive picture of the chemical bonding for such species. In this paper, we presented a new description of bonding in  $[Ge_9]^{4-}$  clusters, based on the local  $\sigma$ -aromaticity concept. The obtained bonding pattern explains both the presence of active sites and the existence of  $C_{4v}$  and  $D_{3h}$  geometries for these compounds.

## Computational methods

All structures were optimized at the PBE0/aug-cc-pvdz<sup>33,34</sup> level of theory. Frequency calculations were performed using the harmonic approximation. To understand the chemical bonding pattern, matrix representation of the first order reduced density operator in the NAO basis set was analysed by the adaptive natural density partitioning (AdNDP) algorithm<sup>35</sup> as implemented in the AdNDP 2.0 code<sup>36</sup> at the PBE0/cc-pvdz level of theory. In the AdNDP method, we followed general ideas of the NBO analysis proposed by Weinhold.<sup>37</sup> It represents a chemical

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Table 1 Relative energies with ZPE corrections (kcal mol<sup>-1</sup>) of  $D_{3h}$  and  $C_{4v}$  [ $\text{Ge}_9$ ]<sup>4-</sup> structures at various levels of theory

Structure	PBE0			B3LYP		
	LANL2DZ	Aug-cc-pvdz	Aug-cc-pvtz	LANL2DZ	Aug-cc-pvdz	Aug-cc-pvtz
$D_{3h}$ [ $\text{Ge}_9$ ] <sup>4-</sup>	0.0	0.0	0.0	0.0	0.0	0.0
$C_{4v}$ [ $\text{Ge}_9$ ] <sup>4-</sup>	0.0	1.6 <sup>a</sup>	10.2 <sup>a</sup>	0.0	0.4 <sup>a</sup>	9.1 <sup>a</sup>

<sup>a</sup> Structure is a first order stationary point.

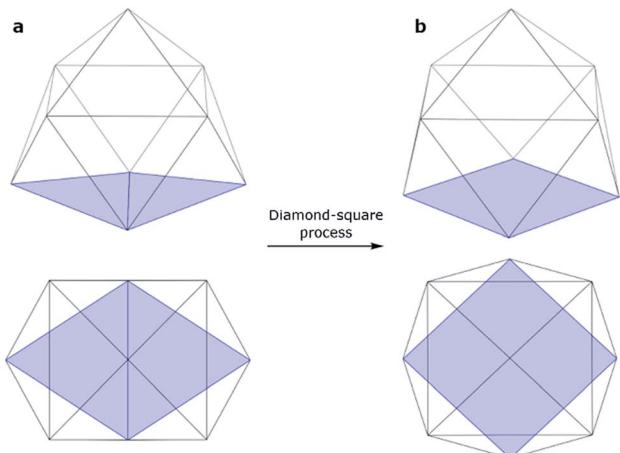


Fig. 1 Side and top views of (a) tricapped trigonal prism ( $D_{3h}$  symmetry) and (b) capped square antiprism ( $C_{4v}$  symmetry).

bonding structure in terms of  $nc$ -2e bonds following the concept of electron pairs and 2c-2e classical bonds. To assess the aromaticity of each aromatic fragment, nucleus-independent chemical shift (NICS)<sup>38,39</sup> calculations were performed at the PBE0/aug-cc-pvtz level. The ChemCraft 1.8 software was used to visualize chemical bonding patterns and geometries of the investigated compounds.

## Results and discussion

To understand the stability of both  $D_{3h}$  and  $C_{4v}$  isomers, we conducted AdNDP analysis of the first order reduced NAO density matrix for  $C_{4v}$  and  $D_{3h}$  [ $\text{Ge}_9$ ]<sup>4-</sup> clusters. We found that the  $C_{4v}$  structure has nine classical Lewis lone pairs on germanium atoms with occupation numbers (ONs) 1.91–1.90 |e|. The remaining electron density forms eleven delocalized  $\sigma$ -bonds with ON = 2.00–1.90 |e| (Fig. 2). These delocalized  $\sigma$ -type fragments bind three areas of the germanium cluster. The first area is the cap of the square antiprism (Fig. 2b–d) and consists of three 5c-2e bonds with ON = 2.00–1.95 |e|. The shape of these elements as well as the number of electrons (6 electrons fit the 4n+2 Hückel's rule) indicates  $\sigma$ -aromaticity in the  $\text{Ge}_5$  cap fragment. Next three 8c-2e  $\sigma$ -bonds with ON = 2.00 |e| bind the bottom square fragment (Fig. 2e–g). The contribution of this  $\text{Ge}_4$  fragment into the 8c-2e bonds is ~99.0% for the bond shown in Fig. 2e and ~81.9% for bonds shown in Fig. 2f and g. The whole  $\text{Ge}_8$  square antiprism

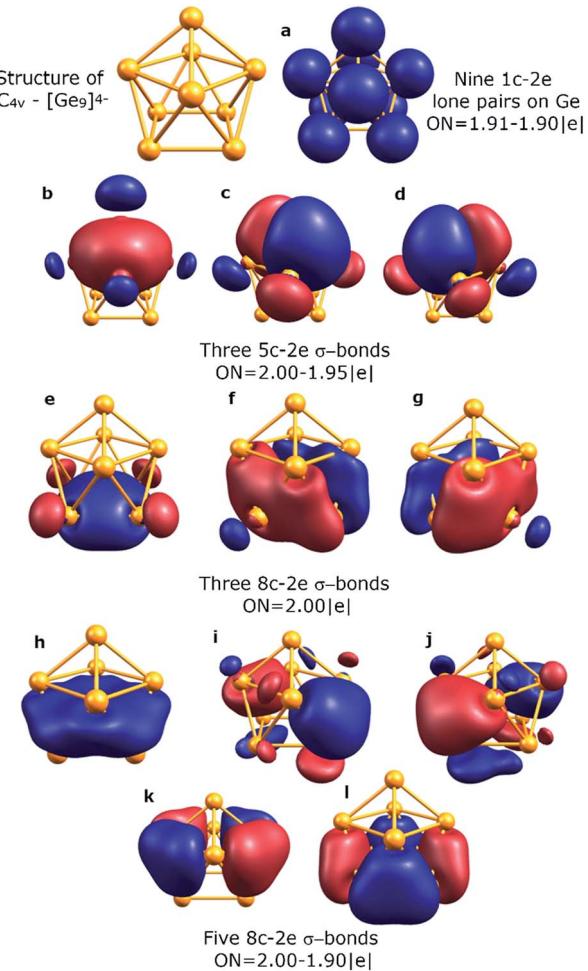


Fig. 2 Overall chemical bonding picture obtained for the  $C_{4v}$  capped square antiprism [ $\text{Ge}_9$ ]<sup>4-</sup> cluster. ON denotes the occupation number (equal to 2.00 |e| in an ideal case). Lines between atoms help in visualization and do not represent 2c-2e bonds here and elsewhere.

fragment is bound by five 8c-2e  $\sigma$ -bonds with ON = 2.00–1.90 |e|. The shapes of 8c-2e and 5c-2e bonds (one bond without a nodal plane, two bonds with one nodal plane, etc.) and 4n+2 electrons ( $n = 1, 2$ ) on each area render these fragments  $\sigma$ -aromatic. Therefore, the stability of the  $C_{4v}$  structure can be explained by the existence of three  $\sigma$ -aromatic areas: the  $\text{Ge}_5$  cap fragment,  $\text{Ge}_4$  bottom square fragment and  $\text{Ge}_8$  square antiprism fragment.

An equally interesting picture of chemical bonding was found for the  $D_{3h}$  [ $\text{Ge}_9$ ]<sup>4-</sup> cluster (Fig. 3). According to AdNDP



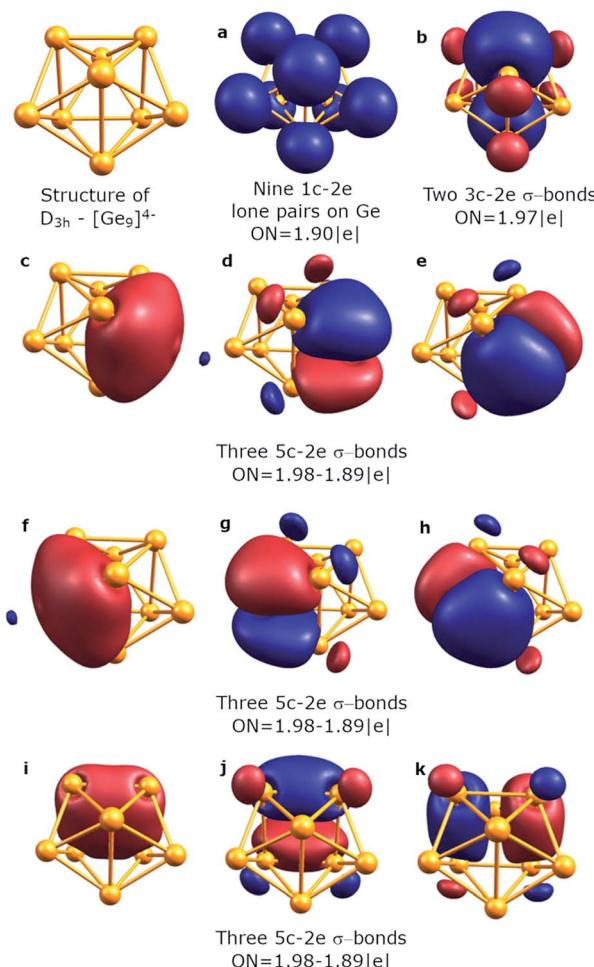


Fig. 3 Overall chemical bonding picture obtained for the  $D_{3h}$  tricapped trigonal prism  $[\text{Ge}_9]^{4-}$  cluster.

analysis, the 40 valence electrons in  $[\text{Ge}_9]^{4-}$  can be localized into nine classical 1c-2e lone pairs on Ge atoms, two 3c-2e sigma bonds with  $\text{ON} = 1.97 \text{ |e|}$ , and nine delocalized 5c-2e bonds. These nine 5c-2e bonds with  $\text{ON} = 1.98-1.89 \text{ |e|}$  are responsible for binding interactions inside each  $\text{Ge}_5$  cap fragment (rectangular pyramids built on the sides of a trigonal prism). Three  $\sigma$ -bonds per cap constitute  $\sigma$ -aromaticity. It should be mentioned that the 3c-2e bonds could be also considered  $\sigma$ -aromatic since the number of electrons fits well in Hückel's rule ( $n = 0$ ). Thus, the chemical bonding pattern for the  $D_{3h}$   $[\text{Ge}_9]^{4-}$  cluster includes nine lone pairs, two 3c-2e  $\sigma$ -aromatic bonds and three symmetric  $\text{Ge}_5$   $\sigma$ -aromatic areas with 5c-2e  $\sigma$ -bonds, which explains the stability and the variety of active sites for such a structure.

To assess local  $\sigma$ -aromaticity in  $D_{3h}$  and  $C_{4v}$  structures, we calculated  $\text{NICS}_{zz}$  and  $\text{NICS}_{iso}$  indices at different points of the clusters (Fig. 4). The coordinates of chosen points can be found in the ESI (Table S2†). Significantly negative values of  $\text{NICS}$  indices at the centers of aromatic fragments (points 1, 3, and 4 for  $C_{4v}$  and points 1 and 4 for the  $D_{3h}$  structure) corroborate our local  $\sigma$ -aromatic description of the bonding pattern for such clusters (Table 2).

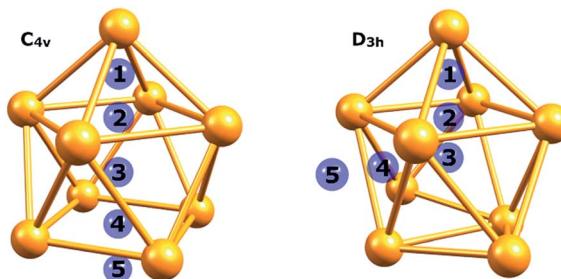


Fig. 4 Points that were chosen for the  $\text{NICS}$  indices calculation.

Table 2  $\text{NICS}_{zz}$  and  $\text{NICS}_{iso}$  indices calculated at chosen points for  $D_{3h}$  and  $C_{4v}$   $[\text{Ge}_9]^{4-}$  clusters

Point	$C_{4v} [\text{Ge}_9]^{4-}$		$D_{3h} [\text{Ge}_9]^{4-}$	
	$\text{NICS}_{zz}$	$\text{NICS}_{iso}$	$\text{NICS}_{zz}$	$\text{NICS}_{iso}$
1	-152.42	-85.91	-62.91	-50.81
2	-102.32	-94.10	-90.53	-67.92
3	-99.76	-90.68	-90.47	-65.89
4	-97.46	-78.02	-87.71	-55.38
5	-55.43	-26.92	-68.37	-22.68

It should be noted that the described bonding pattern is not unique to germanium clusters and could be found in other isoelectronic species. To show that, we performed AdNDP analysis for  $[\text{Si}_9]^{4-}$  and  $[\text{Sn}_9]^{4-}$  clusters. The results are similar and can be found in the ESI (Fig. S4–S6†).

The described chemical bonding pattern also could be found in other synthesized germanium clusters. Various derivatized nonagermanide systems were reported,<sup>40–51</sup> including mono-, di- and tri-substituted species. Of all the series, threefold phosphine-functionalized nonagermanide clusters, synthesized in 2018 by Fässler and coworkers, are of particular interest due to their high reactivity and ease of synthesis.<sup>51</sup> In these clusters, the geometry of the core  $\text{Ge}_9$  fragment is found to be slightly distorted from that of the tricapped  $D_{3h}$  symmetric trigonal prism. In our model calculations of the  $[\text{Ge}_9\{\text{P}(\text{N}^i\text{Pr}_2)_2\}_3]^-$  cluster, we attached three  $\text{P}(\text{NH}_2)_2^+$  substituents to the three capping Ge atoms. The results are shown in Fig. 5. We found that the bonding pattern of the core  $\text{Ge}_9$  fragment remains the same as that of the  $D_{3h}[\text{Ge}_9]^{4-}$  cluster. The main difference in bonding is that three peripheral 1c-2e lone pairs on capping Ge atoms participate in the formation of new two-center classical bonds with phosphorus ( $\text{ON} = 1.97 \text{ |e|}$ ). The occupancy of the nine 5c-2e bonds, which are responsible for the local  $\sigma$ -aromaticity, remains almost the same (Fig. 5d–f). The  $-\text{P}(\text{NH}_2)_2$  substituents exhibit a classical bonding pattern with 1c-2e lone pairs on P ( $\text{ON} = 1.94 \text{ |e|}$ ) and N atoms ( $\text{ON} = 1.91 \text{ |e|}$ ) and 2c-2e  $\sigma$  N-H ( $\text{ON} = 1.99 \text{ |e|}$ ) and  $\sigma$  N-P ( $\text{ON} = 1.99 \text{ |e|}$ ) bonds (Fig. S1†).

Previously, an intriguing reactivity was found for such threefold phosphine-functionalized nonagermanide clusters.<sup>51</sup> The reaction of  $[\text{Ge}_9\{\text{P}(\text{N}^i\text{Pr}_2)_2\}_3]^-$  and  $\text{NHC}^{\text{Dipp}}\text{CuCl}$  leads to the formation of a  $(\text{NHC}^{\text{Dipp}}\text{Cu})[\text{Ge}_9\{\text{P}(\text{N}^i\text{Pr}_2)_2\}_3]$  compound,

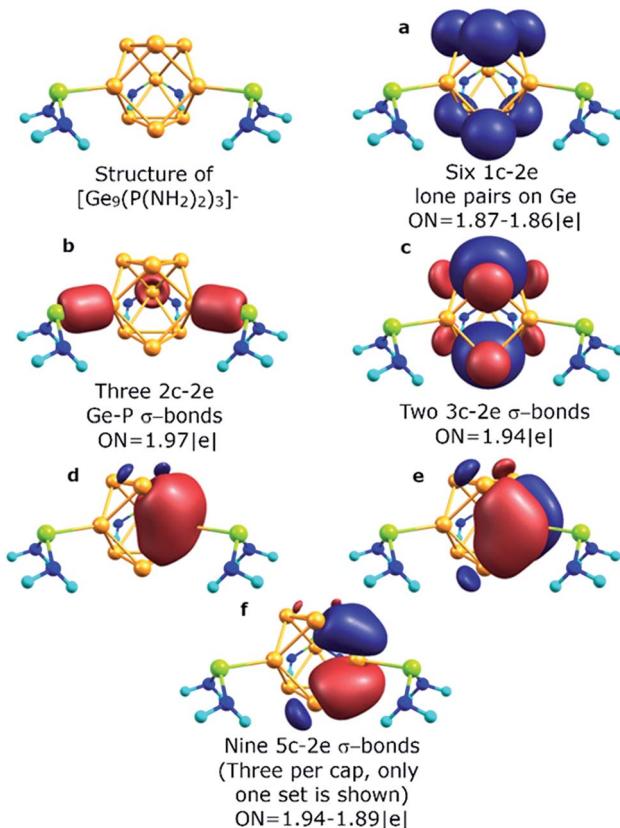


Fig. 5 Chemical bonding picture of the core  $\text{Ge}_9$  fragment obtained for the  $[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]^-$  cluster.

containing the  $D_{3h}$  symmetric  $\text{Ge}_9$  fragment. For understanding the bonding pattern within the copper containing structure, we started our analysis from the model molecule –  $(\text{Cu})[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]$ . The results are shown in Fig. S2.† We found that the Cu atom keeps five 1c-2e d-type lone pairs with an occupation number of  $1.99-1.96 \text{ |e|}$ . The bonding pattern of the  $[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]^-$  part remains almost the same, except one 3c-2e  $\sigma$ -aromatic fragment on the top of the trigonal prism that transforms into a 4c-2e  $\text{Ge}_3\text{Cu}$   $\sigma$ -bond with  $\text{ON} = 1.97 \text{ |e|}$ . The contribution of the  $\text{Ge}_3$  triangle fragment into the 4c-2e bond is found to be  $\sim 83.7\%$ . Even though this model molecule is a good object for studying bonding patterns, the optimized geometry noticeably differs from the experimentally obtained structure. For instance, the Ge–Ge distance in the upper triangle of the trigonal prism is  $3.17 \text{ \AA}$  (experimental value is  $2.87 \text{ \AA}$ ). That is why we decided to include the NHC ligand attached to the Cu atom, which models the  $\text{NHC}^{\text{Dipp}}$  ligand.

The geometry of the optimized structure with the NHC ligand attached to the Cu atom corroborates with the experimental data. So, the Ge–Ge distance in the upper triangle and the distance between capped germanium and germanium in the upper triangle of the prism is  $2.93 \text{ \AA}$  and  $2.50 \text{ \AA}$ , respectively (experimental data are  $2.87 \text{ \AA}$  and  $2.50 \text{ \AA}$ , respectively). It should be mentioned that the attachment of the second  $[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]^-$  fragment to the  $(\text{Cu})[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]$  molecule also leads to Ge–Ge distances similar to the experimental ones.

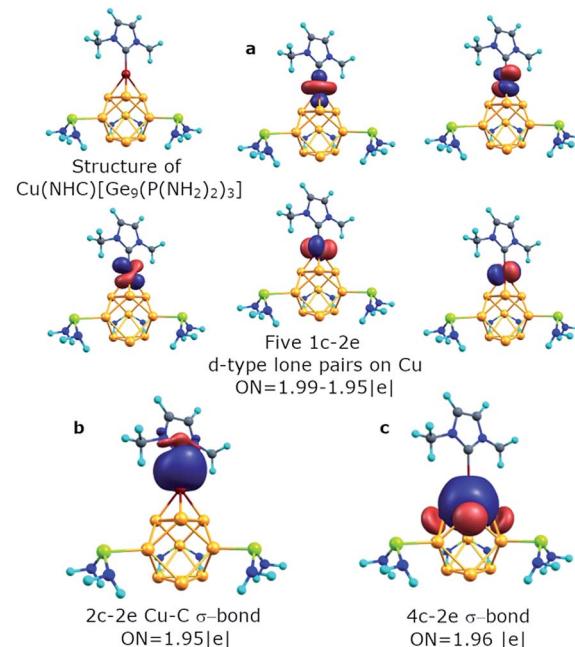


Fig. 6 Chemical bonding of the Cu atom in the  $\text{Cu}(\text{NHC})[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]^-$  cluster.

(Table S1,†  $\{[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]\text{Cu}[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]\}^-$  structure). By conducting AdNDP analysis we found that the bonding pattern of the core  $\text{Ge}_9$  fragment remains the same (Fig. S3†). It consists of six s-type 1c-2e lone pairs on Ge atoms, three local  $\sigma$ -aromatic  $\text{Ge}_5$  fragments, one 3c-2e  $\sigma$ -aromatic bond at the bottom, and one 4c-2e  $\text{CuGe}_4$   $\sigma$ -bond at the top of the prism. The binding interactions of the Cu atom are illustrated in Fig. 6. The new 2c-2e  $\sigma$  Cu–C bond with  $\text{ON} = 1.95 \text{ |e|}$  appears due to the attachment of the NHC ligand. The contribution of the carbon atom into the Cu–C bond is assessed to be  $\sim 85.3\%$ , indicating the donor–acceptor type of the sigma bond.

## Conclusions

In summary, we performed a chemical bonding analysis for five nonagermanide species. The stability of both  $D_{3h}$  and  $C_{4v}$  structures of the  $\text{Ge}_9^{4-}$  cluster could be well described *via* the concept of multiple local  $\sigma$ -aromaticity. We are not aware of such a chemical bonding in the literature. On the basis of AdNDP analysis we can separate the electron density in locally aromatic regions: the  $\text{Ge}_5$  cap,  $\text{Ge}_8$  antiprism, and  $\text{Ge}_4$  square fragments for  $C_{4v} [\text{Ge}_9]^{4-}$ , and then three  $\text{Ge}_5$  caps, and two 3c-2e triangular fragments for  $D_{3h} [\text{Ge}_9]^{4-}$ . We found a similar bonding pattern for the core  $\text{Ge}_9$  fragment for previously synthesized trisubstituted  $[\text{Ge}_9\{\text{P}(\text{NR}_2)_2\}_3]$  clusters. The  $-\text{P}(\text{NH}_2)_2$  groups are bound with the tricapped trigonal prism core *via* classical 2c-2e Ge–P  $\sigma$ -bonds.

A variety of active sites are well described with the obtained bonding picture. Thus, it was found that the copper atom in  $\text{Cu}[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]$  and  $\text{Cu}(\text{NHC})[\text{Ge}_9\{\text{P}(\text{NH}_2)_2\}_3]$  clusters interacts with the 3c-2e  $\sigma$ -bond of the  $\text{Ge}_9$  core to form a 4c-2e bond. Therefore, the described picture is indeed in good agreement



with the experimental reactivity of such compounds. The same chemical bonding was also found in isoelectronic  $[\text{Si}_9]^{4-}$  and  $[\text{Sn}_9]^{4-}$  clusters. We hope that the new obtained bonding pattern with locally  $\sigma$ -aromatic fragments could be an important step to build a coherent bonding structure of Ge-family clusters and congener species. It will also help in the development and understanding of chemical bonding for complicated cases in inorganic chemistry.

## Conflicts of interest

There are no conflicts to declare.

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