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DFT Prediction of Multitopic *N*-Heterocyclic Carbenes Using Clar's Aromatic Sextet Theory

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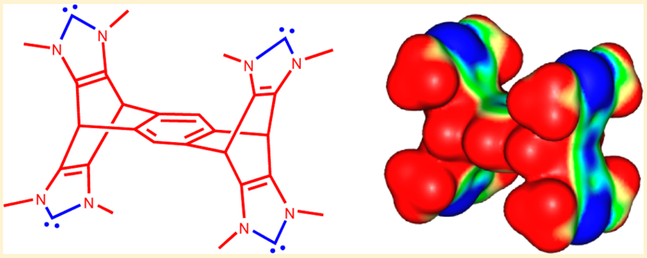
Supporting Information



ABSTRACT: Existence of several multitopic *N*-heterocyclic carbene (NHC) ligands with up to four carbene centers have been predicted on the basis of Clar's aromatic sextet theory. Assessment on stability and reactivity of NHCs was made by quantifying aromaticity, aromatic stabilization energy (E_{aroma}), strength of carbene lone pair, proton affinity, and CuCl binding energy. On NICS(0) and HOMA scales of aromaticity, several NHCs showed high aromaticity, while E_{aroma} (17.2−19.4 kcal/mol) indicated substantial stability for the *N*-heterocycle. Homodesmotic reactions suggested that heat of formation of most of the newly designed carbenes is very close to that of the existing bis-NHCs. Designing a multitopic ligand through branching via C_{sp3} linkage was very effective as it improved the stability of the carbene. Electrostatic potential minimum (V_{min}) at the carbene lone pair suggested that annelation of heterocycle to a benzenoid ring or branching through C_{sp3} linkage can only marginally influence the electron donating power of the ligand. Hence, all multitopic NHCs showed proton affinity (252.3−267.4 kcal/mol) and CuCl binding energy (62.9−66.6 kcal/mol) very close to those of 1,3-dimethylimidazolidine-2-ylidene (**1**). It has also been demonstrated that branched multitopic 3-dimensional NHCs are attractive for designing metal−organic framework with narrow (1−1.5 nm) cage/pore size.

■ INTRODUCTION

N-Heterocyclic carbenes (NHCs) are well-known for their unique reactivity and strong coordination behavior with transition metals in various oxidation states.[1−6] A large variety of stable NHCs with structural and electronic diversities have been reported for numerous applications in chemistry.[6−12] Most of the NHCs function as monodentate ligands through the utilization of the carbene lone pair, while recent research has yielded a variety of multitopic ligands that can act in bischelating, pincer, tripodal, or bridging modes of complexation[13−33] with the metal. Recently Bielawski et al. reported a Janus-type NHC (benzobis(imidazolylidene) (**3**), which was the first annelated system with two carbene centers arranged facially opposite.[32] They also synthesized a Cerberus-type annelated tritopic NHC from a triptycene derivative (**13**).[33] Compound **13** is the only known Cerberus-type tritopic NHC, while quinobis(imidazolylidene) (**15**),[16] oxanthrobis(imidazolylidene) (**16**),[34] and pyracenebis(imidazolylidene) (**17**)[35] are recent entries in the class of Janus-type bis-NHC systems. NHC-based chemistry is expected to grow from their early adolescent stage to a mature stage[5] with the synthesis of multitopic ligands, as they offer rapid advancement in homogeneous catalysis, organocatalysis, organometallic polymers, molecular electronics, metal-based drug molecules, metal−organic and covalent−organic frameworks, etc.

Several experimental and theoretical studies aimed at quantifying the stereoelectronic properties of NHCs as well as understanding the nature of metal−carbon bonding have contributed immensely to the development of novel ligands for catalysis.[36−47] According to structural, thermodynamic, and magnetic criteria, it has been recognized that imidazol-2-ylidene, the core constituent of a typical NHC, possesses substantial aromatic character due to the delocalization of six π electrons (sextet) within the *N*-heterocyclic ring.[48−50] For instance, the aromatic stabilization of imidazol-2-ylidene is 27.8 kcal/mol, which is comparable to that of benzene (26−37 kcal/mol).[51−54]

In the case of polycyclic aromatic hydrocarbons (PAHs), Clar's sextet theory is used to describe and compare the aromatic character. A Kekule resonance structure having the largest number of disjoint aromatic π-sextets (benzene-like moieties; Figure 1) is the most aromatic and the most suitable to describe a PAH.[55−57] For instance, tetracene, a linear polyacene having only one sextet, is less aromatic than chrysene having two sextets. Similarly, triphenylene with three aromatic sextets is more aromatic than its isomers tetracene and chrysene.

Extending Clar's sextet theory to heterocyclic five-membered NHC systems is not straightforward because this theory is centered on delocalization of a sextet of electrons within a six-membered ring. Since one NHC ring possesses one full "sextet"

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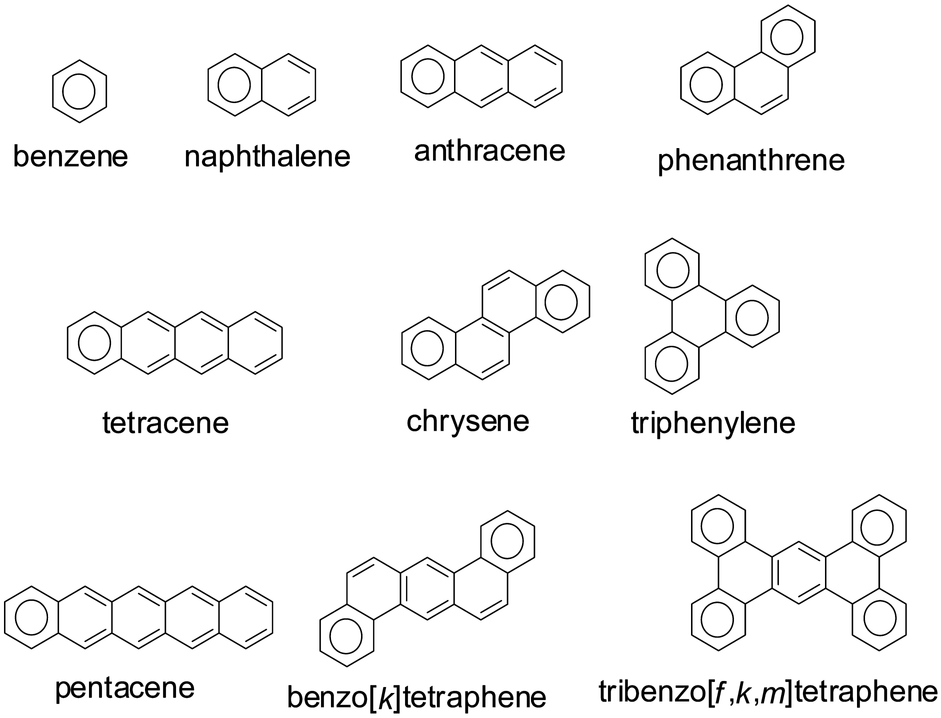


Figure 1. Clar's "sextet" structures of benzenoid hydrocarbons.

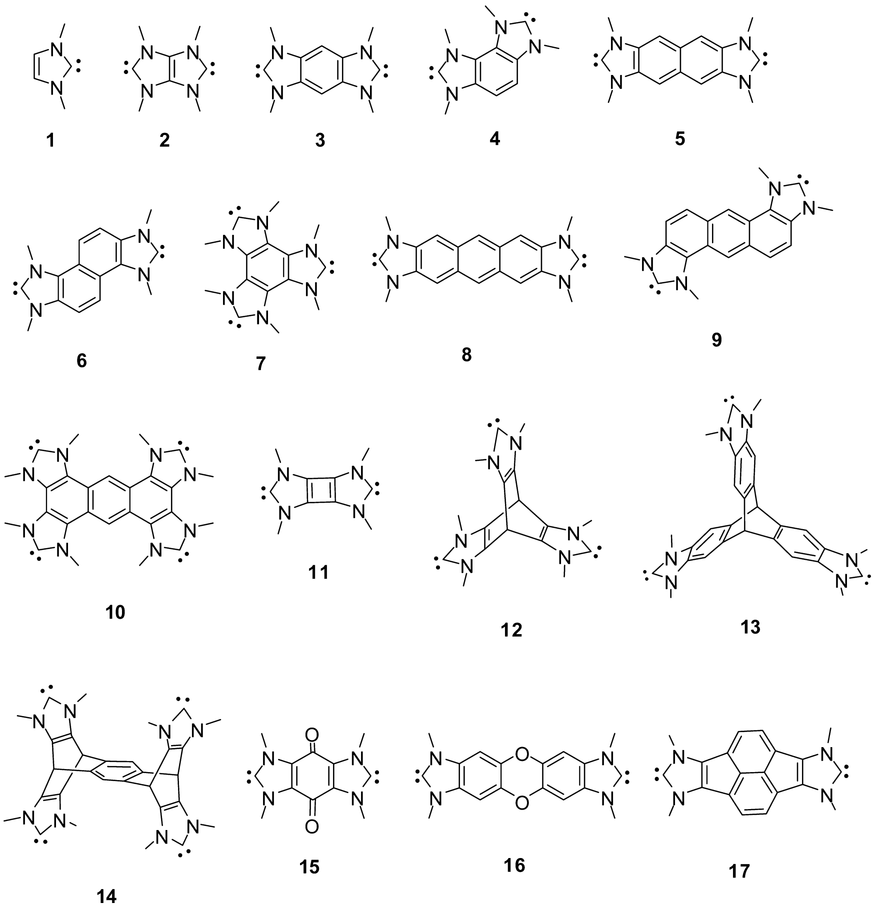


Figure 2. Proposed NHC systems along with known systems **1**, **3**, **13**, **15**, **16**, and **17**.

of electrons, the ring fusion at the CC bond may lead to the formation of a naphthalene analogue, **2**, a bisimidazolinylidene (Figure 2). Though **2** is not yet reported, the saturated analogue of **2** (tetraazabicyclooctane) is recently synthesized by

Peris and co-workers and also showed its conversion into a biscarbene iridium complex.[29] Expansion of **2** to higher analogues, *viz.*, anthracene, phenanthrene, and other PAH topologies, using only imidazole carbene moieties is impossible because the molecule has only one CC bond to make a ring fusion. In order to bypass this disadvantage and also to follow Clar's sextet theory, NHC system can be fused with benzenoid moieties to produce multiple ring multitopic structures. The Janus-type ditopic NHC synthesized by Bielawski et al. gives a good example for the application of such a strategy.[32] Hence, multitopic NHC structures that are analogues to Clar's benzenoid hydrocarbons can be designed (Figure 2). In such systems, the number of π-electrons are identical to the corresponding PAH. Structure **11** is analogues to the strained biphenylene molecule, and it can be considered as made by joining two NHCs via two formal C_{sp2}−C_{sp2} single bonds.

Ring fusions can yield only two-dimensional NHC architectures. For three-dimensional structures, the C−C bond of an NHC can be connected to C_{sp3} atoms as in **12**. The Cerberus-type architecture **13** of Bielawski et al. is the only known example of this,[33] and in this ligand the NHCs annelated to benzenoid moieties are connected to C_{sp3} atoms. A variety of multitopic NHC systems with architecture similar to that of **13** can be made by substituting its benzenoid part with various other PAH moieties. Further, we propose that molecular architecture incorporating four NHC moieties as in **14** could be feasible if two ditopic NHC moieties can be connected via an aromatic spacer moiety. By changing the spacer to different PAH moieties as well as by the use of annelated NHC systems as branches from C_{sp3} links, further expansion of this architecture is possible. This study will reveal that most of the linear, angular, two-dimensional, and three-dimensional multitopic designs of NHCs given in Figure 2 can exist as stable molecules. The assessment on the stability as well as reactivity will be made by studying the aromaticity, proton affinity, and lone pair strength of the carbene and the coordination reaction of the ligand with CuCl.

COMPUTATIONAL DETAILS

The M06L/6-311++G(d,p) level DFT method[58] as implemented in Gaussian09[59] was used for geometry optimization for all of the systems except the large metal−organic frameworks. Frequency calculations were performed to ensure that all of the optimized structures correspond to true energy minima containing only positive vibrational frequencies. For the design of large metal−organic complexes, the M06L/6-31G(d) method was used.[60] However, because of computational limitations, frequency analysis was not done for these complexes. The interaction energy was calculated using the supermolecule approach, which is defined as the difference between the total energy of the complex and the sum of the isolated monomers. The computed interaction energies were corrected for basis set super position error (BSSE) using the counterpoise technique of Boys and Bernardi.[61] Nucleus independent chemical shift (NICS)[62] at the center of the five-membered ring (NICS(0)) was calculated at the M06L/6-311++G(d,p) level through the gauge including atomic orbital (GIAO) method.[63,64] A negative value for NICS(0) indicates aromatic character of a molecule, while values close to zero suggest nonaromatic behavior and positive values suggest antiaromaticity. Further, aromaticity of the five-membered rings were measured using the HOMA index (harmonic oscillator model of aromaticity), which is a popular geometry-based measure of aromaticity. HOMA is calculated using eq 1.

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum (R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \qquad (1)$$

where R_{opt} for CC and CN are 1.388 Å and 1.334 Å, respectively. The α value is 257.7 for CC bond and 93.52 for CN bond. R_{ij} is the bond length in the molecule, and n is the number of bonds.[65] For a perfect aromatic molecule, HOMA will be 1 while values close to zero indicate nonaromatic character. First proton affinity of all of the designed ligands were measured at M06L/6-311++G(d,p) level DFT by calculating the enthalpy released during the protonation of the ligand. For all of the ligand systems described herein, methyl group is used as the typical N-substituent.

RESULTS AND DISCUSSION

Hydrogenation of the carbene carbon can remove aromatic conjugation in the NHC ring. On the basis of this, homodesmotic reaction of the type given in Scheme 1 is designed for all of the NHCs. Since the number, nature, and type of bonds are conserved in the reaction except the aromatic conjugation (in Scheme 1, only **1** is aromatic), the energy of the reaction will give a good quantitative estimate of the aromatic stabilization (E_{aroma}) of an NHC. E_{aroma} of 25.7 kcal/mol is estimated for **1**, which is very close to the value 27.8 kcal/mol reported by Boehme and Frenking[49] for imidazol-2-ylidene. E_{aroma} values (Table 1) show that **1** is the most stabilized NHC while the Janus-type (**3**) and Cerberus-type (**13**) have E_{aroma} of 18.7 and 19.2 kcal/mol, respectively. For other known systems, *viz.*, **15**, **16**, and **17**, E_{aroma} is 18.4, 18.8, and 22.2 kcal/mol, respectively. Hence we expect that NHCs showing E_{aroma} around 18 kcal/mol could be stabilized due to aromaticity. Thus **2**, **4**, **6**, **9**, **10**, **12**, and **14** may exist as stable multitopic carbenes; **5**, **7**, **8**, and **11** also could be stable as they show

Scheme 1. Homodesmotic Reaction To Measure Aromatization Energy

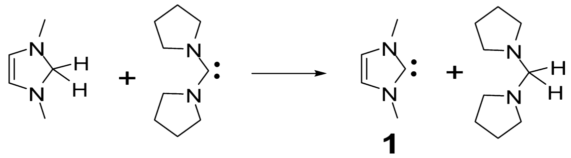
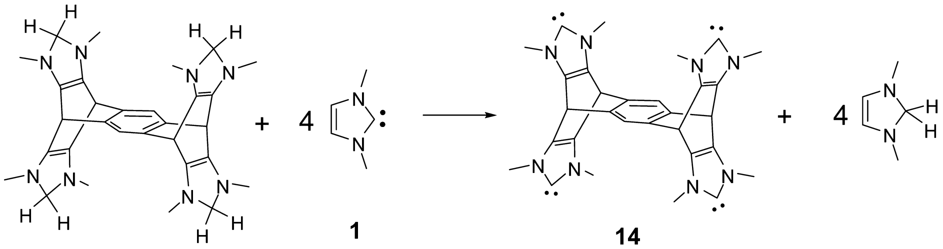


Table 1. Aromatic Properties, MESP Minimum (V_{min}), Proton Affinity (PA), and CuCl Binding Energy (E_{CuCl}) for NHCs[a]

NHC	E_{aroma}	NICS(0)	HOMA	E_{hd}	V_{min}	PA	E_{CuCl}
1	25.7	−11.8	0.523	0.0	−82.3	259.3	66.1
2	17.3	−9.1	0.441	13.7	−76.5	260.5	65.6
3	18.7	−9.9	0.700	11.8	−77.1	261.6	65.8
4	17.2	−10.3	0.694	17.3	−75.3	260.2	65.5
5	14.3	−8.7	0.613	19.3	−75.7	261.9	65.6
6	18.2	−10.8	0.794	13.6	−76.4	262.9	65.8
7	14.0	−10.4	0.611	36.5	−72.9	260.1	64.5
8	12.2	−8.1	0.507	24.1	−74.7	262.3	65.5
9	19.4	−10.8	0.798	12.1	−76.7	264.4	65.8
10	17.8	−10.3	0.771	33.1	−72.4	262.6	65.0
11	13.9	−5.7	0.580	19.0	−75.4	260.7	65.3
12	21.6	−9.1	0.542	10.9	−78.3	264.9	66.1
13	19.2	−10.1	0.768	17.4	−77.6	264.2	66.0
14	21.3	−10.0	0.466	15.6	−78.9	267.4	66.6
15	18.4	−9.3	0.796	13.2	−68.5	252.3	62.9
16	18.8	−9.3	0.779	18.4	−75.9	262.9	65.5
17	22.2	−2.3	0.796	7.7	−77.9	266.6	66.2

[a] E_{aroma}, V_{min}, PA, E_{hd} and E_{CuCl} in kcal/mol.

Scheme 2. Homodesmotic Reaction for Comparing the Stability of a Multi-topic NHC with 1



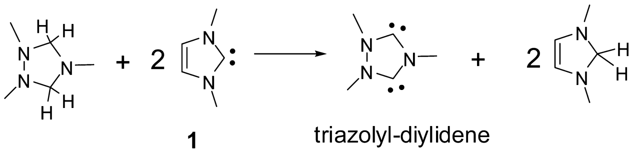
appreciable E_{aroma} values (>12 kcal/mol). In general, angular systems are more stable than linear systems (**5** and **6**; **8** and **9**), which is in accordance with the Clars' sextet theory. However, this trend in stability is not observed for **3** and **4** because the latter experiences significant steric effect from *N*-methyl substituents. Clar's theory is also obeyed in the case of linear polyacene analogues **3**, **5**, and **8** as they show a decrease in E_{aroma} with increase in the length of the molecule. Naphthalene analogue **2** is an exception to this trend because, compared to other systems, it experiences large strain effect from two fused five-membered rings.

The aromaticity index NICS(0) is negative for all of the systems, suggesting that they all possess aromatic character. The most negative NICS(0) is observed for **1** (−11.8), while the rest except **11** and **17** show values close to that of **1** (−8.1 to −10.8). HOMA values close to 0.80 is observed for **6**, **9**, **10**, **13**, **15**, **16**, and **17**, and the remaining systems show HOMA values in the range 0.44−0.70. In fact, most of the annelated NHCs with benzenoid moieties and heterocycles show HOMA values higher than **1**. Both NICS(0) and HOMA suggest that in polyacene analogues (**3**, **5**, and **8**) the aromatic character decreases, while all of the angular structures (**4**, **6**, and **9**) possess high aromatic character. The NHC analogue of tribenzo[*f*,*k*,*m*]tetraphene with four carbene centers (**10**) is particularly noteworthy for its high aromatic stabilization energy (17.8 kcal/mol) and high aromatic character (NICS(0) = −10.3; HOMA = 0.771). The NICS(0), HOMA, and E_{aroma} data clearly suggest that annelation via benzenoid moieties, branching via saturated carbon atoms, and ring fusion via heterocycles are not significantly affecting the aromatic character of the NHC unit. In fact, the data clearly suggest that annelation is good for improving the aromatic character of multitopic NHC systems.

Though the homodesmotic reaction given in Scheme 1 is useful to assess the aromatic stabilization of the *N*-heterocycle, it cannot measure the inherent instability associated with the presence of several carbene centers in one molecule. Therefore, homodesmotic reaction of the type given in Scheme 2 is designed, which describes the formation of a multitopic ligand at the expense of monotopic ligands. Since almost every aspect of the bonding features is conserved in the reaction, the energy of the reaction (E_{hd}) will give a direct estimate of the instability of the ligand relative to **1** (Table 1). In other words, E_{hd} measures the heat of formation of NHC relative to **1**. For the known systems **3**, **13**, **15**, **16**, and **17**, E_{hd} is 11.8, 17.4, 13.2, 18.4, and 7.7 kcal/mol, respectively, meaning that systems showing E_{hd} close to 18.4 kcal/mol can be considered as stable. Therefore, **2**, **4**, **5**, **6**, **9**, **11**, **12**, and **14** having E_{hd} values in the range 10.9−19.3 kcal/mol could be stable, whereas triphenylene analogue **7**, tetracene analogue **8**, and tribenzo[*f*,*k*,*m*]-tetraphene analogue **10** having E_{hd} in the range 24.1−36.5 kcal/mol could be unstable. In the case of linear polyacene analogues, E_{hd} gradually increases, whereas stability of their angular isomers is not affected by the length of the aromatic hydrocarbon unit. The data in Table 1 also suggest that designing a multitopic ligand through branching via C_{sp3} atoms is very effective to improve the stability. This aspect is very clear about **14** as this ligand with four carbene centers has smaller E_{hd} value than the existing molecules **13** and **16**.

A 1,2,4-triazole based bis-NHC system (triazolyl-diylidene) is known in the literature and was developed by Bertand et al.[66] (Scheme 3) for the synthesis of organometallic polymers and later used by Peris et al.[67] for autotandem catalysis. The homodesmotic reaction in Scheme 3 suggests that this ligand is 29.3 kcal/mol less stable than **1**, suggesting that **8** (E_{hd} = 24.1 kcal/mol) may also exist as a stable ligand.

Scheme 3. Homodesmotic Reaction for Comparing the Stability of a Triazolyl-diylidene Ligand with 1



Recently we have shown that molecular electrostatic potential (MESP) minimum (V_{min}) at the carbene lone pair is an efficient descriptor to assess the electron-donating power of an NHC.[68] MESP distribution of the ligands depicted in Figure 3 clearly shows the electron-rich carbene lone pair region (blue region) as well as the delocalized electron distribution over the annelated rings. By calculating V_{min} for the carbene lone pair, various NHC systems can be compared for their electron-donating power. V_{min} is always located in the dark blue region of the MESP plot (Figure 3 and Table 1). **1** shows the most negative V_{min} (−82.3 kcal/mol), which suggests its strong electron-releasing power for coordination bonds. Among the known bis-NHC systems (**3**, **13**, **15**, **16**, and **17**), **17** possesses the most negative V_{min} (−77.9 kcal/mol), while **15** has the least negative V_{min} (−68.5 kcal/mol). V_{min} values of all other NHCs fall in a narrow range of −72.4 to −78.9 kcal/mol. This means that annelation through aromatic hydrocarbon moieties as well as branching through C_{sp3} carbon atoms can only slightly affect the electron-rich character of the carbene center of a multitopic NHC, and these ligands must behave as strong electron-donating ligands. However, V_{min} of **15** suggests that annelation via electron-withdrawing heterocycles (benzoquinone moiety) can significantly change the electron-releasing power of the carbene ligand. In general, an increase in E_{aroma} shows a decrease in the negative character of V_{min}.

Table 1 also reports the gas phase proton affinity (PA) of the NHC ligands. PA of 259.3 kcal/mol is obtained for **1**, which agrees well with the value 258.3 kcal/mol reported by Yates et

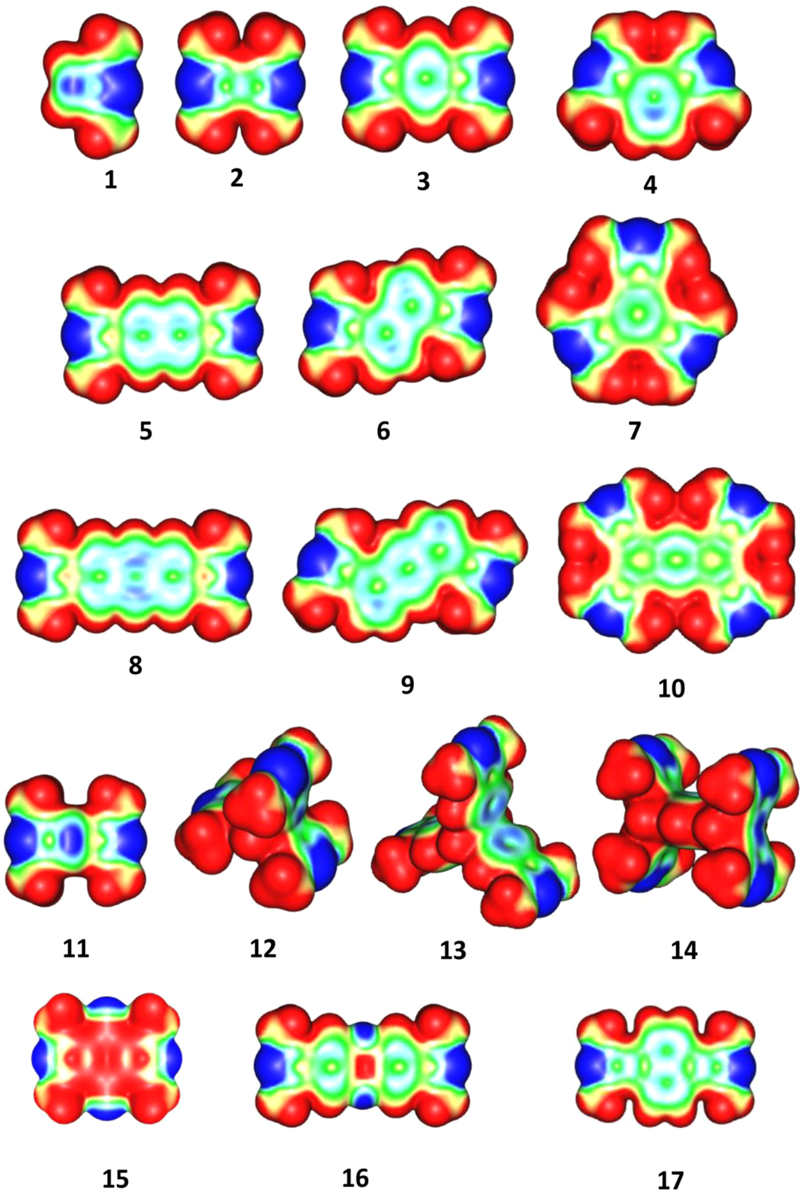


Figure 3. Molecular electrostatic potential mapped on to 0.003 au electron density surface. Color coding, blue −0.02 au to red 0.02 au.

al. using the high accuracy CBS-QB3 method.[69] Compared to **1**, all other NHCs except **15** show slightly higher PA values (260.1−267.4 kcal/mol), with the smallest for **1** and the highest for **14**. The relatively low value of PA observed for **15** (252.3 kcal/mol) can be attributed to the annelated electron-withdrawing benzoquinone moiety. PA has been shown to correlate directly with pK_a, and hence the former is used to assess the pK_a of carbenes.[69,70] Between **1** and **14**, the difference in PA is only 7.1 kcal/mol. A PA difference of 6.6 kcal/mol was reported by Yates et al. for **1** (1,3-dimethylimidazol-2-ylidene) and its higher derivative1,2,3,4-tetramethylimidazol-2-ylidene.[69] For **1**, pK_a was 21.1, while that of the higher derivative was 23.8. Hence, on the basis of these data, we can predict that all of the newly designed NHCs will show pK_a values very close to that of **1**.

Since well-defined (NHC)CuCl complexes can be easily prepared from imidazolium salts and copper(I) chloride,[71] the binding energy of CuCl with NHC (E_{CuCl}) is used as a good measure to assess the coordinating power of these ligands. E_{CuCl} also measures the metal−carbon bond energy. Geometric parameters of **1**-CuCl showed excellent agreement to a recently reported X-ray structure of (1,3-diadamantylimidazol-2-ylidene)-CuCl.[71] For instance the (calculated, X-ray) values in Å for C1−Cu, Cu−Cl, C1−N, C2−N and C2−C3 are, respectively, (1.883,1.894), (2.107, 2.111), (1.364, 1.361), (1.380, 1.383), and (1.355, 1.355). E_{CuCl} is nearly same for all of the ligands, the smallest being 62.9 kcal/mol for **15** and the highest being 66.9 kcal/mol for **14**. This indicates that the annelation and branching strategies are highly useful to preserve the coordination power of the carbene in multitopic systems. We also found a linear correlation (correlation coefficient = 0.971) between V_{min} and E_{CuCl} for all of the systems except **1** (Supporting Information), which agrees with the earlier finding that V_{min} of the carbene lone pair gives a good measure of the electron-donating power of the NHC ligands. Since E_{CuCl} values fall in a very narrow range, the linear correlation between V_{min} and E_{CuCl} clearly suggest that V_{min} is highly sensitive to the coordination property of the ligand.

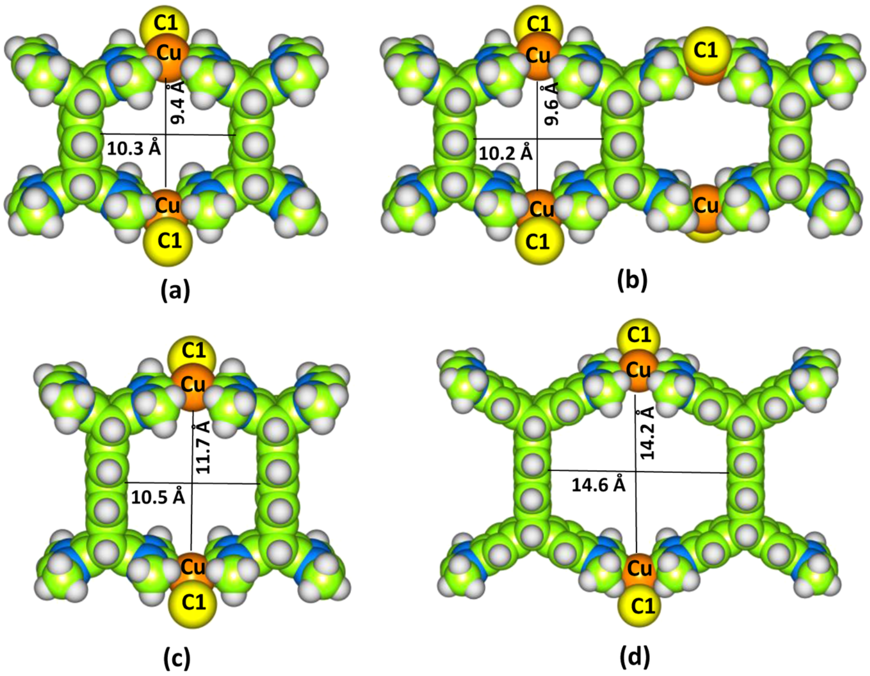


Figure 4. Optimized geometries at the M06L/6-31G(d) level for association complexes of multitopic ligands with CuCl.

Among the 17 systems given in Figure 2, **14** is perhaps the most interesting to design a metal−organic framework because it consists of two pairs of carbene centers, one angling in the upward and the other in the downward directions (Figure 2). This orientation of carbene centers will enable the formation of compact cage/pore structures through metal coordination. To illustrate this, $(\mathbf{14})_2(\mathrm{CuCl})_2$ and $(\mathbf{14})_3(\mathrm{CuCl})_4$ are modeled (Figure 4a and b). The cages formed are hexagonal in shape and show ∼1 nm size for width and length. In the case of the complex given in Figure 4c, the ligand (**18**) has a naphthyl spacer, which will enable the cage to expand more lengthwise. A cage structure with ∼1.5 nm size for width and length is possible if the ligand (**19**) has a naphthyl spacer and annelated carbene centers on benzenoid moieties (Figure 4d). On the basis of M06L/6-31G(d) calculation, C−Cu bond energy is estimated to be 71.1, 70.9, 71.1, and 71.7 kcal/mol for $(\mathbf{14})_2(\mathrm{CuCl})_2$, $(\mathbf{14})_3(\mathrm{CuCl})_4$, $(\mathbf{18})_2(\mathrm{CuCl})_2$ and $(\mathbf{19})_2(\mathrm{CuCl})_2$, respectively. These numbers indicate that stable metal−organic frameworks with precise pore/cage size can be made by multitopic carbene ligands such as **14**, **18**, and **19** and they may find use in accessing porous and related materials needed in gas separation membranes and other applications.

■ CONCLUSIONS

In conclusion, we have designed and characterized theoretically several multitopic NHC systems based on Clar's aromatic sextet theory. Annelation of NHC to a benzenoid moiety as well as branching through C_{sp3} linkage is highly recommended for the synthesis of stable multitopic architectures. The multitopic NHCs can give new topologies for NHC-based complexes as well as improved chemical properties and may find use in various areas such as homogeneous catalysis, organocatalysis, metal-based drug molecules, metal−organic and covalent−organic frameworks, etc. Though synthesis of these systems is a challenge for experiment, the recently established synthetic methodology by Peris et al.[29] on double C−H bond activation of CH_2 groups for the preparation of bisimidazolinylidene complexes as well as the synthetic methods developed by Bielawski et al.[34] for accessing ditopic NHCs could provide breakthroughs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Thermodynamic parameters, details of HOMA calculation, and optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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