**Sc$_3$N@I$_h$-C$_{80}$ as a novel Lewis acid to trap abnormal N-heterocyclic carbenes: the unprecedented formation of a singly bonded [6,6,6]-adduct†**

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The reaction between an N-heterocyclic carbene (NHC), namely 1,3-bis(diisopropylphenyl)-imidazol-2-ylene (1), and Sc$_3$N@I$_h$-C$_{80}$ successfully affords a Lewis acid–base pair (2a). Single crystal X-ray crystallographic results unambiguously reveal the unexpected structure of 2a where the abnormal carbene center of the NHC is connected to a triple-hexagon-junction (THJ) carbon atom of Sc$_3$N@I$_h$-C$_{80}$ via a single bond. Theoretical calculations reveal that selective entrapment of the abnormal carbene 1 is caused by the steric hindrance between the normal NHC moiety and the fullerene cage, which precludes the formation of normal carbene adducts. Furthermore, the analysis of the electronic density distribution on the cage of Sc$_3$N@I$_h$-C$_{80}$ indicates that THJ carbons bear relatively low negative charge densities and, accordingly, are easily attacked by the electron-rich NHC 1 to form the singly bonded [6,6,6]-adduct 2a instead of the corresponding [5,6,6]-adduct 2b. It is thus confirmed that the regioselective formation of 2a is a synergistic effect of both cage size and electron density distribution. Sc$_3$N@I$_h$-C$_{80}$, although with a highly charged cage, is proven to show excellent Lewis acidity, opening a wide avenue toward carbon-based Lewis acids taking into account the diversity of endohedral metallofullerenes.

In contrast, carbon-based Lewis acids are limited merely to trityl cations and some electron-poor allenes.$^4$ Recently, Bazan and coworkers reported that fullerenes such as C$_{60}$ and C$_{70}$ can behave as all-carbon Lewis acids to form the corresponding Lewis acid–base pairs with a normal NHC structure (1′).$^{10}$ This work opens a new perspective on the research of carbon-based Lewis acids. Meanwhile, as a novel class of metal–carbon hybrid molecules, endohedral metallofullerenes (EMFs) feature electron transfer from the internal metallic species to the carbon cage, forming zwitterionic compounds.$^{11}$ Accordingly, it is of

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**Scheme 1** The reaction between 1 and Sc$_3$N@I$_h$-C$_{80}$. 

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†Electronic supplementary information (ESI) available. CCDC 1406974. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc04070a

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special interest to study whether the highly charged carbon cages of EMFs are willing to accept additional electrons to act as Lewis acids or not.

Herein, taking Sc$_3$N@I$_h$-C$_{80}$ as a representative, we show that EMFs also exhibit excellent Lewis acidity to form Lewis acid–base pairs with NHCs. Surprisingly, our unambiguous X-ray results reveal that the abnormal NHC 1 is bonded to Sc$_3$N@I$_h$-C$_{80}$, instead of the normal one 1' (Scheme 1). More interestingly, a singly bonded [6,6,6]-adduct (2a) of Sc$_3$N@I$_h$-C$_{80}$ is formed during the reaction, which has never been observed or even predicted, in contrast to the commonly observed [5,6,6]-adduct (2b). Our theoretical results reveal that the regioselective formation of the unprecedented [6,6,6]-adduct with an abnormal carbene moiety (2a) is synergistically affected by the cage size of Sc$_3$N@I$_h$-C$_{80}$ and the electronic density distribution on the cage.

Results and discussion

In a typical reaction, an ortho-dichlorobenzene (ODCB) solution of Sc$_3$N@I$_h$-C$_{80}$ and an excess amount (ca. 50-fold) of 1,3-bis-(diisopropylphenyl)-imidazol-2-ylene (1) was heated to 90 °C under an argon atmosphere (Scheme 1). The reaction progress was monitored via high performance liquid chromatography (HPLC). After the solution was heated for 12 hours, a new peak appeared at 18.3 min, which is ascribed to the adduct 2a as identified using mass spectrometry (Fig. 1). The reaction was terminated after 24 hours, and 2a was isolated with preparative HPLC in ~80% conversion yield based on consumed Sc$_3$N@I$_h$-C$_{80}$. The matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of 2a displays a single peak at m/z 1498.2, firmly confirming the successful attachment of the NHC moiety onto the fullerene cage (Fig. 1b).

The electronic configuration of 2a was investigated using UV-Vis-NIR spectroscopy in toluene (Fig. 2). Although the spectrum of 2a resembles that of pristine Sc$_3$N@I$_h$-C$_{80}$ in the wavelength range between 540 nm and 1100 nm, their curves at 350–540 nm differ significantly from one another, confirming that the electronic structure of Sc$_3$N@I$_h$-C$_{80}$ has been altered by the modification.

The structure of 2a is unequivocally established via single-crystal X-ray crystallography. The entire system is fully ordered, including the functionalized cage, the internal cluster and even the three CS$_2$ solvent molecules.\textsuperscript{12} It is evident that a single bond is formed between the addend and the cage with a bond length of 1.515 Å (C5–C6), confirming unambiguously the formation of a Lewis acid–base complex (Fig. 3a).\textsuperscript{13,14} More surprisingly, the addition site on the cage of Sc$_3$N@I$_h$-C$_{80}$ involves a triple hexagon junction (THJ) which is generally less reactive than the carbon atoms of other kinds on a fullerene cage. Such an addition pattern has never been observed or even expected for Sc$_3$N@I$_h$-C$_{80}$ because previously reported singly bonded derivatives contained at least two substituents that are exclusively linked to the pentagon–hexagon–hexagon junction (PHHJ) carbon atoms unless the cage is severely functionalized.\textsuperscript{15–17} Because of the substitution, the carbon atom at the site of addition (C6) is slightly pulled out from the cage sphere which causes a ‘Y-shaped’ displacement of the internal Sc$_3$N cluster with the Sc$_3$–N1 bond nearly collinear with the new bond C5–C6, whereas the Sc$_3$N-plane is perpendicular to the N-heterocyclic ring of the addend (Fig. 3b).

Surprisingly, the NHC moiety is linked to the cage of Sc$_3$N@I$_h$-C$_{80}$ with its abnormal carbene center C5 instead of the normal site C2, which is completely different from the corresponding Lewis pairs of C$_{60}$ and C$_{70}$.\textsuperscript{10} The bond length of C4–C5 (1.367 Å) falls into the range of a C=C double bond, confirming the existence of imidazol-2-ylene. The lengths of the

Fig. 1  (a) Monitoring the reaction between 1 and Sc$_3$N@I$_h$-C$_{80}$ via HPLC. Conditions: Buckyprep column (ø 4.6 mm × 250 mm), 0.8 mL min$^{-1}$ toluene flow, and 330 nm detection wavelength. The peak marked with an asterisk represents an unidentified product. (b) MALDI-TOF mass spectrum of 2a.

Fig. 2  UV-Vis-NIR spectra of Sc$_3$N@I$_h$-C$_{80}$ and 2a.
other four C–N bonds forming the N-heterocyclic ring are similar: 1.384 Å (C4–N2), 1.326 Å (C2–N2), 1.333 Å (C2–N3) and 1.386 Å (C5–N3), excluding the existence of C==N double bonds.

The unprecedented structure of 2a with an abnormal NHC moiety singly bonded to a THJ carbon atom is of great interest. First, we try to understand why a [6,6,6]-adduct (2a) is formed instead of the corresponding [5,6,6]-adduct (2b). It is well-known that THJ carbons are less pyramidal and accordingly are less reactive than the carbon atoms of other kinds of fuller- enes. Indeed, our theoretical results suggest that the [5,6,6]-adduct 2b, if formed, is 0.49 kcal mol⁻¹ more stable than the [6,6,6]-adduct 2a (Fig. 4a), indicating that the preferential formation of 2a is not a thermodynamically controlled process. We then consider that the electron density distribution on the cage of Sc₃N@I₈-C₈₀ should be a critical factor. It is widely accepted that pentagons are the sites of the negative charges of highly charged fulleride species such as EMFs. Accordingly, [5,6,6]-junction carbon atoms always accumulate more negative charges than THJ carbons do. As a direct result, NHCs as electron-rich Lewis bases tend to attack the [6,6,6]-junction carbon atoms which have lower electron densities, revealing the Lewis acidic property of Sc₃N@I₈-C₈₀. In summary, the [6,6,6]-addition pattern of 2a is a consequence of the electron density distribution on the cage of Sc₃N@I₈-C₈₀.

We then try to find a reasonable explanation for the unexpected formation of the abnormal carbene structure of 2a. Usually NHCs use the normal carbene center (C2 in 1, Scheme 1) to bind metals. However, abnormal NHC carbene species (1, Scheme 1) can stably exist and can even be isolated. Several examples of abnormal carbene complexes have been reported, which show enhanced catalytic properties for the activation of unreactive bonds. Furthermore, Dagorne and coworkers reported that a normal but sterically congested NHC–AlMe₃ Lewis acid–base pair can isomerize to its abnormal NHC–AlMe₃ species. This result inspires us to speculate that the abnormal carbene structure of 2a is also caused by a steric effect. Our computational results showed that neither the normal [6,6,6]-

![Fig. 3](image-url) Single-crystal X-ray structure of 2a: (a) side view, and (b) front view. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules are omitted for clarity.

![Fig. 4](image-url) Possible structures of NHC–Sc₃N@I₈-C₈₀ complexes and their relative energies calculated at the B3LYP/6-31G*LANL2DZ (Sc) level.

**Scheme 2** Plausible formation mechanism of 2a.
site. Then, the tautomers (1 and 1') turn into the corresponding mesionic compounds. Since the mesionic species of 1' can not form stable adducts (2a and 2b) with Sc₃N@I₈-C₈₀ because of the high steric hindrance between the addend and the cage, only the abnormal carbene structure is possible. As discussed above, the electron-rich NHC 1 (or the corresponding mesionic compound) tends to attack one of the THJ carbon atoms with low electron densities, forming the [6,6,6]-adduct 2a in a highly regioselective manner.

**Conclusions**

In summary, Sc₃N@I₈-C₈₀ is confirmed to be an excellent carbon-based Lewis acid although its cage is negatively charged, representing the first example of EMFs that readily undergo Lewis acid–base complexation reactions with NHCs. The regioselective formation of the unusual singly bonded [6,6,6]-adduct 2a is reasonably interpreted by analyzing the charge density distribution on the cage because the electron-rich NHC is prone to attack one of the THJ carbons with low electron densities. More interestingly, Sc₃N@I₈-C₈₀ here is found to selectively trap the rare abnormal NHC 1 as a consequence of the steric hindrance between the normal NHC moiety and Sc₃N@I₈-C₈₀. Hence, we conclude that the regioselective and unprecedented formation of 2a is a synergistic effect of both the cage size and electron density distribution of Sc₃N@I₈-C₈₀. This synthetic strategy can be easily extended to create various EMF-based Lewis acid–base pairs with different metallic cores and/or cage structures, which may show unique catalytic properties in organic synthesis, taking into account their “frustrated” characteristics.

**Acknowledgements**

Professors M. M. Olmstead and A. L. Balch in UC Davis are gratefully acknowledged for their assistance in single-crystal X-ray measurement. Financial support from the National Thousand Talents Program of China, NSFC (21170161, 51472095), Program for Changjiang Scholars and Innovative Research Team in University (IRT1014) and Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education are gratefully acknowledged. We thank the Analytical and Testing Center in Huazhong University of Science and Technology for all related measurements.

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