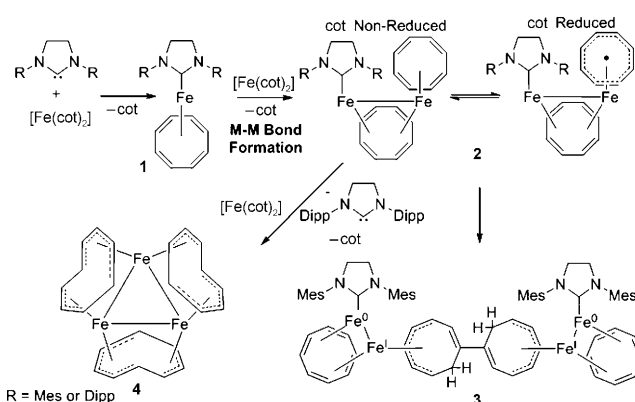


Insights Into the Carbene-Initiated Aggregation of $[\text{Fe}(\text{cot})_2]^*$

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In the last 20 years stable carbenes^[1] have found numerous applications. They are excellent ancillary ligands for transition metal catalysts,^[2] as exemplified by the state of the art ruthenium-based olefin metathesis catalysts.^[3] Moreover, they coordinate main group elements in their zero oxidation state,^[4] stabilize highly reactive species,^[5] activate small molecules,^[6] and act as efficient organocatalysts.^[7] For the latter application, a myriad of other organocatalysts are known.^[8] In marked contrast, before our recent report,^[9] organic species capable of mediating complicated stoichiometric and catalytic organometallic transformations were virtually nonexistent. We found that the interaction of the *N,N*-bis(2,4,6-trimethyl)phenyl-substituted *N*-heterocyclic carbene (NHC) IMes with bis(cyclooctatetraene)iron ($[\text{Fe}(\text{cot})_2]$) produced the novel tetrametallic cluster **3**, featuring two bound NHCs (Scheme 1, bottom right). When the *N,N*-bis(2,6-diisopropyl)phenyl-substituted NHC SIPr interacted with $[\text{Fe}(\text{cot})_2]$, a carbene-catalyzed process formed the unprecedented trimetallic cluster $[\text{Fe}_3(\text{cot})_3]$ (**4**, Scheme 1, bottom left), which is a hydrocarbon analogue of Dewar's classic $[\text{Fe}_3(\text{CO})_{12}]$.^[10]

We postulated that the observed reactivity was due to the NHC's ability to induce a key M–M bond forming reaction, and we proposed that discrete monometallic intermediates **1**



Scheme 1. The interaction of IMes and SIPr with $[\text{Fe}(\text{cot})_2]$ induces the stoichiometric or catalytic formation of tetra- and trimetallic iron clusters, respectively.

($[(\text{L})\text{Fe}(\text{cot})]$) and bimetallic intermediates **2** ($[(\text{L})\text{Fe}_2(\text{cot})_2]$) were involved (Scheme 1, top). We believe the outcomes of these reactions are different based on steric effects of the NHC initiators. The SIMes ligand remains bound to intermediate **2**, and is not bulky enough to kinetically block the dimerization^[11] process or the cot-reduced form (Scheme 1, top right). On the other hand, the increased steric hindrance of the SIPr carbene, both protects the transient species **2** and also destabilizes the M–carbene bond to encourage the expulsion of $[\text{Fe}_2(\text{cot})_2]$, which ultimately is incorporated into the $[\text{Fe}_3(\text{cot})_3]$ triangle.

Herein we report the reaction of $[\text{Fe}(\text{cot})_2]$ with three types of stable carbenes, namely an abnormal NHC (aNHC), a cyclic (alkyl)(amino)carbene (CAAC) and a carbocyclic carbene (BAC). Several hitherto unknown organometallic architectures have been isolated, including mono- and bimetallic iron complexes related to the plausible intermediates **1** and **2** along the carbene-catalyzed pathway to form $[\text{Fe}_3(\text{cot})_3]$.

Initially reported by Crabtree et al. in 2001,^[13] and then extensively utilized by Albrecht et al.,^[14] C-5 metal-bound imidazolylidenes or aNHCs are stronger donor ligands than their normal isomers. A possibly even more important characteristic of aNHCs is that they are believed to bind metals much stronger than classical NHCs. The recent isolation of a stable metal-free aNHC^[15] has opened up the doorway to utilize such species as ligands for elements across the periodic table. We hypothesized that since this aNHC features intermediate steric hindrance between IMes and SIPr, and also is *not* known to act as a leaving group, it might be possible to strategically implement this ligand to stabilize the highly reactive $[(\text{L})\text{Fe}_2(\text{cot})_2]$ complex **2** (Scheme 1, top). Treatment of a pentane solution of $[\text{Fe}(\text{cot})_2]$ with half an equivalent of aNHC (Figure 1) leads to a blood-red solution,

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[**] We gratefully acknowledge financial support from the NIH (grants 5R01 GM 31332 and R01 GM 68825, and N.R.S.A. fellowship for V.L. This publication was based on work supported by Award No. K-C1-019-12 made by King Abdullah University of Science and Technology (KAUST). The support of King Fahd University of Petroleum and Minerals (KFUPM) is also highly appreciated. We thank L. M. Henling and M. W. Day (California Institute of Technology) for X-ray crystallographic analysis. The Bruker KAPPA APEX II X-ray diffractometer was purchased via an NSF Chemistry Research Instrumentation and Facilities: Multi-User award to the California Institute of Technology, CHE-0639094.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201005212>.

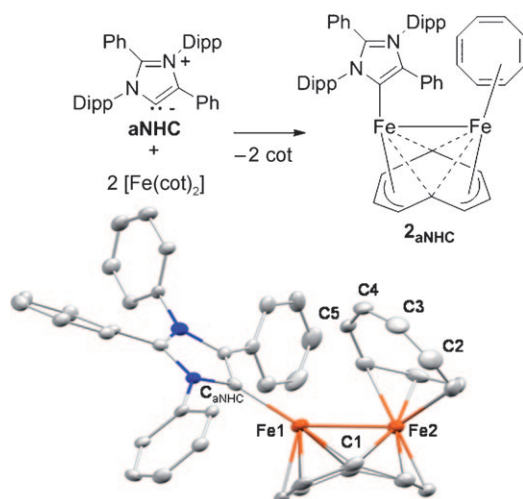


Figure 1. Reaction aNHC with $[\text{Fe}(\text{cot})_2]$, and crystal structure of the resulting $[(\text{aNHC})\text{Fe}_2(\text{cot})_2]$ complex **2_{aNHC}** (displacement ellipsoids drawn at the 50% probability level; protons and isopropyl groups omitted for clarity). Red, Fe; blue, N; gray, C.

which over a 24 h period gives rise to large black crystals. Regardless of the order of addition of reagents, temperature, or equivalents of aNHC used, compound **2_{aNHC}** was the only species obtained. The ^1H NMR spectrum of the crystalline precipitate, redissolved in $[\text{D}_6]$ benzene revealed broad resonances ranging from $\delta = +7.4$ to -1.22 ppm, suggestive of a paramagnetic species. In solution the new compound exhibits an effective magnetic moment of 2.64 B.M., which is close to the spin-only value for two unpaired electrons (2.83 B.M.).

Gratifyingly, a single-crystal X-ray diffraction study^[16] confirmed that the new species was indeed an $[(\text{aNHC})\text{Fe}_2(\text{cot})_2]$ complex. The metal–aNHC bond length (2.082(2) Å) is in the upper range (1.895–2.111 Å) of reported values for related iron carbenes.^[17] Interestingly, the non-bridging cot ligand of **2_{aNHC}** is η^4 -coordinated to the iron center, with the other half of the non-coordinated eight-membered ring (C2–Fe2 3.085(2) Å, C5–Fe2 3.262(2) Å) displaying a localized butadiene structure (C2–C3 1.342(3) Å, C3–C4 1.410(3) Å, C4–C5 1.350(3) Å). Such a bonding arrangement indicates that in the solid state this $[(\text{L})\text{Fe}_2(\text{cot})_2]$ complex exists in the non-reduced form. This observation suggests that bulky carbene ligands, such as SIPr and aNHC, may not only kinetically protect $[(\text{L})\text{Fe}_2(\text{cot})_2]$ fragments, but also disfavor electron transfer from iron to the non-bridging cot ligand through steric disruption of the required higher hapticity of the reduced cot ligand.^[18] The other cot ligand of **2_{aNHC}** is η^5 -coordinated to both Fe centers forming a very symmetrical bridge between the two iron atoms (Fe1–C1 2.363(3) Å, Fe2–C1 2.325(2) Å), which indicates that the classical bis(π -allyl) two-electron–three-center bonding model^[20] of cot is applicable in this case. The Fe1–Fe2 distance of 2.4530(5) Å argues for an iron–iron single bond,^[21] which gives the two iron centers an overall 15 and 17 electron count, respectively. With a stable $[(\text{L})\text{Fe}_2(\text{cot})_2]$ fragment in hand, we became interested in exploring the possibility of preparing a mononuclear $[(\text{L})\text{Fe}(\text{cot})]$ complex, reminiscent of proposed intermediates **1**. The obvious approach is to implement an even more bulky

carbene ligand to disrupt the metal–metal bond forming process. However, utilizing more sterically demanding NHCs resulted in no reaction with $[\text{Fe}(\text{cot})_2]$, while using a bulky CAAC,^[22] an outer-sphere $[4+1]$ cycloaddition was observed (Figure 2). This unusual and slow reaction (45 °C, 2 d) is attributed to the increased nucleophilicity and electrophilicity of CAACs.^[6a,b]

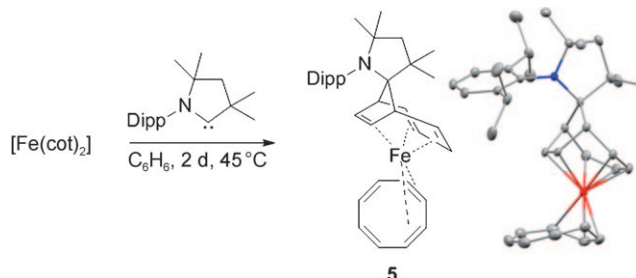


Figure 2. Reaction of a CAAC with $[\text{Fe}(\text{cot})_2]$, and crystal structure of the resulting outer-sphere $[4+1]$ cycloadduct **5** (displacement ellipsoids drawn at the 50% probability level; protons omitted for clarity). Red, Fe; blue, N; gray, C. Range of Fe–C distances (2.0247(10)–2.2058(9) Å) for coordinated carbons.

Notably, in contrast with the parent $[\text{Fe}(\text{cot})_2]$, which readily decomposes around 100 °C, C_6D_6 solutions of the diamagnetic iron(0) complex **5** are thermally stable for at least 2 d at 120 °C.

Considering the previous results we sought to take a different approach to prepare mononuclear iron–carbene complexes related to $[(\text{L})\text{Fe}(\text{cot})]$. We predicted that if a carbene of sufficiently small size reacted with $[\text{Fe}(\text{cot})_2]$, a simple addition product, $[(\text{L})\text{Fe}(\text{cot})_2]$, could be obtained without dislodging a cot ligand. Owing to its unique and non-sterically demanding shape, the carbocyclic carbene, *N,N*-bis(diisopropyl)aminocyclopropenyliene (BAC)^[23] seemed like an ideal candidate. Thus, one equivalent of BAC was carefully added at -78 °C over 30 min to a pentane solution of $[\text{Fe}(\text{cot})_2]$ (Figure 3). The ^1H NMR spectrum of the reaction mixture revealed the complete conversion of $[\text{Fe}(\text{cot})_2]$ into a new complex, which exhibits resonances corresponding to two fluxional and equivalent cot ligands, as well as a single BAC moiety. A single-crystal X-ray diffraction study confirmed the compound's identity as the $[(\text{BAC})\text{Fe}(\text{cot})_2]$ complex **6**. Although the quality of crystals precludes a detailed discussion of the bond lengths and angles, it is evident that this diamagnetic complex adopts a square-pyramidal structure with both cot ligands bound in an η^4 -fashion.

Even after several days $[(\text{BAC})\text{Fe}(\text{cot})_2]$ does not react with $[\text{Fe}(\text{cot})_2]$ to form bimetallic Fe complexes **2**. This suggests that the dissociation of the first cot ligand to form $[(\text{L})\text{Fe}(\text{cot})]$ complexes is sterically controlled, and is a key step in the stoichiometric and catalytic aggregation of $[\text{Fe}(\text{cot})_2]$. Reinforcing this hypothesis is the fact that another molecule of the relatively small BAC displaces a cot ligand from $[(\text{BAC})\text{Fe}(\text{cot})_2]$ at room temperature to afford the $[(\text{BAC})_2\text{Fe}(\text{cot})]$ species **7**. A single-crystal X-ray diffraction study of paramagnetic ($\mu_{\text{eff}} = 2.87$ B.M.) complex **7** indicates that it adopts a tetrahedral geometry, as expected for a high-

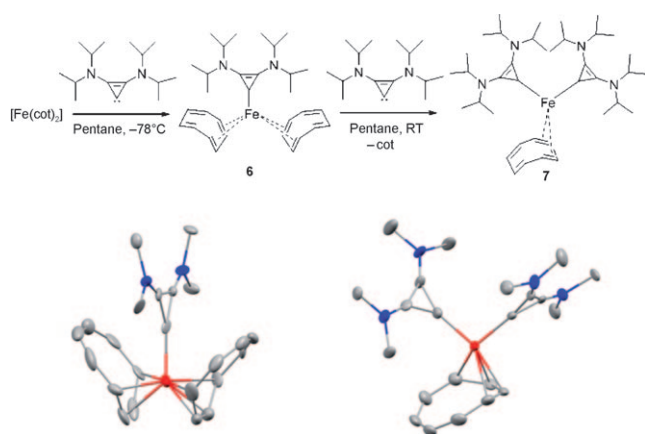


Figure 3. Top: Reaction of carbocyclic carbene BAC with $[\text{Fe}(\text{cot})_2]$. Bottom: Crystal structure of the resulting $[(\text{BAC})\text{Fe}(\text{cot})_2]$ complex **6** (left) and $[(\text{BAC})_2\text{Fe}(\text{cot})]$ **7** (right). Displacement ellipsoids drawn at the 50% probability level; protons and methyl groups omitted for clarity. Red, Fe; blue, N; gray, C. For **7**, Fe–carbene bond lengths are 1.926(3) and 1.944(3) Å.

spin four-coordinate iron(0) species. Notably, simple $[(\text{L})\text{Fe}(\text{cot})_2]$ and $[(\text{L})_2\text{Fe}(\text{cot})]$ complexes have not been reported to be accessible with phosphines^[24] or other^[25] neutral two-electron donor ligands. Moreover, preliminary studies show that these complexes are highly reactive and display a rich stoichiometric and catalytic chemistry toward carbon–carbon and carbon–heteroatom bonds.

The diverse interactions of stable carbenes (NHC, aNHC, CAAC, and BAC) with $[\text{Fe}(\text{cot})_2]$ has provided access to a multitude of hitherto unknown molecular architectures. It is now clear that by understanding the attributes of specific stable carbenes,^[26] it is possible to strategically utilize their properties to induce both simple and complicated organometallic reactions in a controlled manner. Equally important is that by capitalizing on these properties it seems likely that it will be possible to expand the scope of carbene-catalyzed transformations of organometallic molecules, and even extend this idea to main-group elements other than carbon.

Experimental Section

Experimental details are available as Supporting Information.

Received: August 20, 2010

Published online: November 25, 2010

Keywords: carbenes · homogeneous catalysis · iron complexes · organometallic compounds

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