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Carbenes in action

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Much like many people get highly attracted by wild cats, chemists have a strong appeal for molecules that behave like wild cats, perhaps because of their unpredictable, seemingly dominant and determined behavior. Are they really as unpredictable as judged at a first glimpse? And can we, somehow, master their activity, thus making them less dominant but, perhaps, useful? In this issue, two articles report on the domestication of such molecular wild cats, disclosing the unexpected stabilization of so-called 'abnormal carbenes' *(1)* and the application of carbenes for developing unprecedented organometallic reactions *(2)*, thus opening new opportunities in synthesis.

Carbenes are compounds comprising a divalent carbon that possesses only six valence electrons (Fig. 1a). This electron deficiency, which violates Lewis' octet rule, renders carbenes highly reactive, much like wild cats *(3)*. For long time, carbenes have been considered to be too reactive for being isolated and studied. One strategy that has proven successful in recent years for stabilizing carbenes consists of cooling them to very low temperatures, only a few Kelvin, thus slowing down all chemical processes *(4)*. Disadvantageous to this strategy is the fact that chemical reactions may occur that may be less relevant under normal conditions — just imagine riding a bicycle at exceedingly slow speed.

Domestication of these chemical wild cats has met great success in the late eighties. A combination of electronic stabilization and steric protection has allowed for generating the first free carbenes that are stable at room temperature *(5)*. Extension of this principle by introducing two nitrogen atoms adjacent to the carbene carbon further enhanced the stability of the carbene and made them resistant towards air and moisture *(6)*. Once sufficiently tamed, these carbenes, in

particular N-heterocyclic carbenes rapidly became very useful for synthesis, especially in homogeneous catalysis and as ligands for transition metals (Fig. 1b) *(7)*.

Catalysis with these carbenes has largely concentrated on constructing chemical bonds to and with carbon, an area where carbenes are more efficient, though often not fundamentally different from ubiquitous phosphines. Now, Lavallo and Grubbs have disclosed *(2)* a unique procedure for using N-heterocyclic carbenes as ligands for the formation of iron–iron bonds, representing a rare case of a catalytic organometallic transformation (Fig. 1c, left). Along the way, the catalytic reaction leading to the formation of the star-like molecule challenges the paradigm that metal-carbene bond making and breaking are one-way processes. The turnover numbers observed by Lavallo and Grubbs — despite being low — imply that the carbene is used multiple times as temporary ligand. It remains to be seen whether reversible metal-carbene bond formation is general or just limited to iron and metals in related configuration.

Apart from the esthetic appeal of the prepared star-like compounds, such bond making between iron centers may become very attractive for the construction of electronically active systems. Iron is known to undergo swift oxidation and reduction processes, thus acting as a source and a receptor for electrons, respectively, and rendering them attractive components for molecular electronics. Tailor-made molecular wires with conducting properties are just one of the many exciting applications that are likely to emerge from this new organometallic reaction. Future work will need to show whether such wires comprising only iron in the main chain rather than cyclic products could become accessible, for example upon variation of the carbene catalyst.

Modifications in the skeleton of N-heterocyclic carbenes are known to have a pronounced effect on the key properties of these ligands, that is, on their electron donor ability, which is more pronounced as compared to phosphines. This concept has been expanded in recent years by using a variation termed 'abnormal carbenes', originally because they do not bind in the normal way *(8)*. These abnormal carbenes contain only one nitrogen adjacent to the carbene carbon, a situation which reduces their stability and, simultaneously, increases their ability to donate electron density to a coordinated metal center, thus allowing the reactivity of the metal center to be substantially altered *(9)*. As a consequence of the low heteroatom stabilization, free abnormal carbenes have been considered to be unstable under ambient conditions, representing a considerably wilder cat than normal N-heterocyclic carbenes. On p. xxx of this issue, Bertrand and coworkers now describe *(1)* an elegant strategy for creating abnormal carbenes that are stable

at room temperature and that can be crystallized, allowing for a detailed structural analysis. Building on their earlier success in stabilizing typically reactive carbenes *(10)*, they introduced aryl substitents on all nuclei but the carbene carbon. These substituents assist in balancing the charge density within the heterocycle. Steric shielding may be less relevant, since carbon dioxide or metal centers such as gold(I) readily bind to the carbene carbon (Fig. 1c right). Likely, the availability of stable abnormal carbenes provides a new platform for carbene- and for metal-mediated processes.

On a fundamental level, this work is expected to shed some light on the ongoing debate as to which extent these abnormal carbenes contain a divalent carbon, or whether a zwitterionic notion comprising a carbanion would be more relevant. Sophisticated calculations suggest a sigma lone-pair as highest occupied molecular orbital (HOMO), which is qualitatively very similar to that in normal N-heterocyclic carbenes. This close analogy combined with the absence of any component in the crystal structure that could compensate a putative negative charge at the carbene carbon tends to support the carbene notion. Further data will be essential, however, to clarify this aspect.

From an application point of view, the prospect of bottle-able abnormal carbene ligands breaks up entirely new opportunities for synthesis, last but not least providing access to a plethora of new highly reactive metal complexes for catalysis. Similar to normal carbenes, which rapidly became a classic tool for modern organometallic chemistry and organic synthesis once they were available as stable free ligands some 20 years ago, the accessibility of free abnormal carbenes may become another corner stone in this field and it will be exciting to witness developments in these directions.

References

1 E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **326**, xxx (2009).

2 V. Lavallo, R. H. Grubbs, *Science* **326**, xxx (2009).

3 R. A. Moss, M. S. Platz, M. Jones Jr., Eds., *Reactive Intermediate Chemistry* (Wiley: New York, 2004).

4 P. R. Schreiner, H. P. Reisenauer, F. C. Pickard IV, A. C. Simmonett, W. D. Allen, E. Matyus, A. G. Csaszar, *Nature* **453**, 906 (2008).

5 A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **110**, 6463 (1988).

6 A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **113**, 3122 (1991).

7 F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **47**, 3122 (2008).

8 M. Albrecht, *Chem. Commun.* 3601 (2008).

9 M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Albrecht, *Chem. Eur. J.* **15**, 9375 (2009).

10 V. Lavallo, C. A. Dyker, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **47**, 5411 (2008).

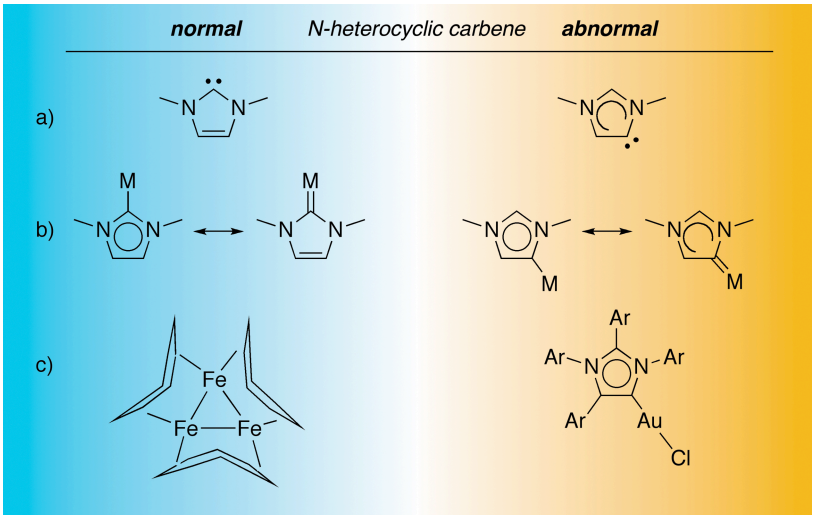

Figure 1. (a) Schematic representation of free normal and abnormal carbenes, illustrating the fact that in contrast to normal N-heterocyclic carbenes, abnormal carbenes cannot be represented by a regular and uncharged Lewis resonance structure; (b) Representation of the contributing resonance structures in metal complexes of N-heterocyclic carbenes (M = metal); (c) new synthetic opportunities resulting from current work (Ar = aryl).

Abstract: New reactions of N-heterocyclic carbenes and the stabilization of abnormal variations of these ligands provide exciting perspectives for organic synthesis and organometallic catalysis.