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GUEST EDITORIAL

N-Heterocyclic Carbenes

Steven P. Nolan
Guest Editor
University of St Andrews
St Andrews, UK

The N-heterocyclic carbenes (NHCs) have come a long way from being presented as mere tertiary phosphane mimics. At the offset, this description sufficed, but with past and ongoing developments, it is now clear that they do mimic phosphanes in some applications, but their special steric and electronic properties render them unique as illustrated by novel reactivity profiles and product selectivities. In terms of electronics, they are the best phosphanes, and in terms of steric congestion about the metal center, the community is still tackling the question of how to model of this "fan-" or "fence-"like ligand. They are electron-rich/bulky stabilizing moieties as exemplified by their use in olefin metathesis and palladium cross-coupling reactions. They are also nucleophilic organocatalysts, enabling a wide scope of transformations from transesterification to benzoin condensation to Stetter reaction and asymmetric versions of these.

Unique reactivity profiles

More fundamentally, they stabilize organometallic species, having been responsible for the isolation of "proposed" very reactive species. They are also oftentimes noninnocent ligands, as can be seen in various intramolecular C−H activation/catalyst decomposition processes. Some of their potential in this area remains to be realized.

Our group has been involved in the area for more than ten years now. I recall a conversation with Bob Crabtree on a visit to Yale where Bob mentioned that these ligands should keep us busy for ten years. It seems like this prediction was conservative, as we and others have been at it for a while, and the more we do, the more we feel needs to be done as the NHCs keep surprising us. Be it that they can adopt "abnormal" coordination modes or that they bind to actinides, NHCs have kept those investigating them on their toes.

Potential still unlimited

Their use is now quite common and manifests itself in various applications. They are now well-established in palladium cross-coupling chemistry. They have unique reactivity in gold catalysis and, of course, they were at the foundation of the success of second-generation ruthenium olefin metathesis catalysts. More recently, the NHCs have demonstrated intriguing activity/stabilization of copper species and permitted click chemistry with well-defined Cu(I) complexes. They have been found to stabilize low-valent Ni complexes. They have been used to isolate mixed phosphane/NHC Pd(0) species that can in their own right activate small molecules and perform hydrogenation of unsaturated C−C bonds at very low catalyst loadings. Some NHC complexes have even exhibited interesting anticancer activity on numerous cancer cell lines and have been used as therapeutic agents. And the list goes on...

Broad coverage of applications

In this Special Issue, we have attempted to gather a wide breadth of applications involving NHCs to provide the Reader with a flavor of the varied chemistry possible with these compounds. They are ligands, catalyst modifiers, and pre-catalysts. The NHCs are now part of the standard arsenal available to synthetic and catalytic chemists, enabling bond formation and rearrangement reactions. We are convinced that the community will find more uses for "stable" carbenes (in their many incarnations) and their transition-metal complexes.

