Volume Editors' Preface

The discovery of a stable N-heterocyclic carbene (NHC) by Arduengo in 1991 was a seminal finding; even Bo (we think he might agree) could not have anticipated the impact it would have on organic synthesis, organometallic chemistry, and catalysis. The isolation of such a (thought to be) *fleeting* species was a veritable feat. What followed took a few years to evolve, but by the end of the last millennium early results on the use of NHCs in organometallic chemistry and homogeneous catalysis began to emerge. The unique properties of this family of ligands made possible significant advances in catalyst design with associated improved performance. One simply has to examine the unexpected stability and reactivity brought about by NHCs in olefin metathesis catalyst architectures to begin to appreciate the impact of such ligands. This simple ligand substitution improved catalyst stability and permitted the study of *challenging* metathesis reactions, viewed as such because of the thermal instability of first-generation complexes. Second-generation catalysts, bearing an NHC, could be heated; this enabled, among many transformations, the ring-closing metathesis of sterically hindered alkenes and high degrees of polymerization in reactions where exotherms previously led to catalyst/initiator decomposition.

The area of palladium cross-coupling catalysis has also been greatly affected by the use of NHCs as supporting ligands. By the late 1990s, Fu had disclosed the beneficial use of sterically demanding/electron-rich phosphines to activate aryl chlorides. With quantification of the steric and electronic properties of the NHCs, it was rapidly realized that they were excellent phosphine surrogates for such catalytic applications. The stability imparted by the NHC also permitted the isolation of well-defined palladium complexes for use in cross-coupling reactions. This is an approach that has since been adopted by numerous researchers focusing on the use of ligands in cross-coupling processes, and has led to significant reductions in the catalyst loading required for high activity.

These two Nobel-Prize-winning research areas have greatly benefited from the use of NHCs as ligands. Another area where NHCs have allowed significant advances is gold-mediated transformations, where ligands such as IPr have permitted increased reactivity and specific selectivity. The IPr ligand has also had a profound effect on nickel chemistry and catalysis, and has permitted advances uniquely associated with the stabilization of organometallic compounds that is brought about by the use of NHCs as supporting ligands. In fact, the IPr ligand has become ubiquitous in catalytic screenings for reactions involving a variety of metals, and oftentimes it is the first tested and also the best NHC for catalysis.

Developments in catalysis surrounding the use of NHCs have not been limited solely to organometallic chemistry; the area of organocatalysis has also evolved greatly because of the design and use of achiral and chiral NHCs. This area has seen remarkable activity and growth since the early work of Breslow using thiamine as a catalyst.

Most NHC-bearing metal catalysts and organocatalysts were originally thought of as curiosities. However, one only has to inspect chemical suppliers' catalogues to see the amazingly growing number of commercially available complexes, ligands, and kits to realize how far the area of NHC chemistry has advanced. NHCs have become standard fare in catalysis, and the availability of such a plethora of ligand precursors, complexes, and ligands has made the development of NHC chemistry rapid, and something that will continue to grow speedily as the tools are now available for researchers to explore novel reactivity. As a testimony to the swift and continuing growth of this area, our initial discussions with the *Science of Synthesis* staff involved the assembly of a single volume presenting various aspects of NHC chemistry. This has evolved into an exciting two-volume project where the contributions comprise a user's guide to NHC chemistry and catalysis.

We are indebted to all authors of this project, as their contributions will undoubtedly facilitate the introduction of NHCs to novices and also help expand the repertoire of synthetic tools available to the more-advanced researcher, enabling the design of new catalysts and reactions.

We would like to express our sincere thanks for the dedication and professionalism of the *Science of Synthesis* staff. Alex Russell and Michaela Frey, in particular, have made this journey a smooth and enjoyable one.

It is our hope the reader will, as we have, learn from the content of this two-volume set and possibly find in it inspiration.

Volume Editors

Steven P. Nolan and Catherine S. J. Cazin Ghent, Belgium, October 2016