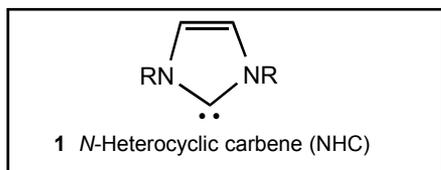


# “Recent Developments in the Organometallic Chemistry of *N*-Heterocyclic Carbenes”

GUEST EDITOR: ROBERT H. CRABTREE (Yale University, U.S.A.), *Coordination Chemistry Reviews*, 2007, Special Issue, Volume 251, Issues 5–6, pp. 595–896

Organometallic catalysis has been based for years on phosphine and cyclopentadienyl ligands. These stood alone as the leading ligand classes because they were sterically and electronically tunable to achieve desired levels of catalyst selectivity and activity. In the case of the phosphine series, such tuning was particularly easy using the Tolman ‘map’ that predicted the steric and electronic effects of almost any phosphine or related phosphorus donor ligand (1, 2).

*N*-Heterocyclic carbenes (NHCs), **1**, are ligands formed by the deprotonation of an *N,N'*-disubstituted imidazolium (or other azolium) salt. Binding of a transition metal to the C2 carbon of the NHC leads to the formation of a very strong metal–carbon bond, the strength deriving from the thermodynamic instability of the free NHC. Unlike metal–carbon bonds in general, those to NHCs do not undergo fast insertion or reductive elimination reactions and so NHCs are relatively reliable spectator ligands. The role of a spectator ligand is to act as a placeholder by promoting a desired reaction at the metal, while avoiding dissociation or entering directly into the reaction. NHCs are significant in being the first new series of spectator ligands in several decades to rise to prominence, having both steric and electronic tunability and the capability to promote catalysis of many useful catalytic reactions.



Early work in the 1960s and 1970s laid out the basis of the field but the full potential of these ligands was not fully realised at that time. Only with

work from the 1990s and specially since 2000 have these ligands achieved major prominence. Perhaps the most dramatic example of their utility was the discovery by Grubbs and coworkers (3) that NHC ligands could greatly improve the performance of the Grubbs ruthenium metathesis catalyst.

A recent special issue of *Coordination Chemistry Reviews*, with guest editor Robert H. Crabtree, has now been devoted to the NHC ligands (4). Among several notable reviews, Ivan Lin and Chandra Vasam address Lin’s metallation procedure for the synthesis of NHC complexes. The procedure is important in that it avoids strong base and instead uses Ag<sub>2</sub>O to metallate the usual *N,N'*-disubstituted imidazolium NHC precursor salt. This is now one of the most popular methods of introducing NHCs into metal complexes, because the silver NHC complexes initially formed readily transmetallate to other metals, such as palladium or rhodium.

Polly Arnold and Stephen Pearson describe the chemistry of abnormal NHCs, in which a metal is bound not at the usual C2 carbon but at C4(5). These are much stronger electron donors, but somewhat more easily cleaved from the metal compared with their normal NHC analogues.

Andreas Danopoulos and David Pugh treat ‘pincer’ versions of NHCs, a ligand type that has been very fruitful in terms of catalytic complexes, both in the NHC and in the phosphine series.

## *N*-Heterocyclic Carbenes in Catalysis and Biomedicine

Lutz Gade and Stéphane Bellemin-Laponnaz’s review deals with oxazoline-modified NHCs in relation to asymmetric catalysis. Steven Diver discusses recent advances in enyne metathesis with NHC ruthenium complexes. Asymmetric catalysis

continues to be of intense interest and many asymmetric NHCs have been developed. For example, Richard Douthwaite discusses palladium-mediated asymmetric alkylation using chiral NHCs derived from chiral amines.

Frédéric Lamaty *et al.* review the NHC-modified Grubbs catalysts. Valerian Dragutan and coworkers review other aspects of ruthenium NHC catalysis. Miguel Esteruelas *et al.* look at a related element, osmium, and its carbene chemistry. Eduardo Peris and coworkers review some ligands with NHCs in bidentate and tripod configurations, together with their catalytic properties. Marcus Weck and William Sommer cover supported catalysis involving NHC ligands with ruthenium and palladium.

In connection with the problem of predicting the stereoelectronic properties of NHCs, Steve Nolan and Silvia Díez-González discuss their development of a set of reliable stereoelectronic parameters for NHC ligands with a view to understanding how stereoelectronic effects control metal-catalysed reactions.

Wiley Youngs and coworkers go far beyond catalysis into the biomedical area. They show that silver NHC complexes can have useful anti-

microbial activity. Encapsulation in a polymer mat allows sustained delivery of silver ions, useful in wound care. Numerous resistant respiratory pathogens in cystic fibrosis are sensitive to a caffeine-derived silver-NHC complex.

## Concluding Remarks

This field holds much promise for future development because of the very large range of possibilities opened up by the availability of a vast range of azole structures of various sorts. We can expect other azoles, such as triazole and thiazole derivatives, for example, as well as a large array of different chelate arrangements and mixed ligand systems. For catalytic applications, NHCs have been chiefly incorporated into platinum group metals, but they prove to have a much wider affinity for *d*-block, *f*-block and main group elements than do phosphines or cyclopentadienyls, so their ultimate potential is vast.

## References

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- 3 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, 34, (1), 18
- 4 *Coord. Chem. Rev.*, 2007, 251, (5–6), 595–896

### The Guest Editor of the Review



Bob Crabtree, educated at New College, Oxford, U.K. with Malcolm Green, did his Ph.D. research with Joseph Chatt at Sussex and then spent four years in Paris with Hugh Felkin at the Centre National de la Recherche Scientifique (CNRS). He has been at Yale University since 1977, where he is now Professor. He has received several awards: A. P. Sloan Fellow, Dreyfus Teacher-Scholar, American Chemical Society (ACS) and Royal Society of Chemistry organometallic chemistry prizes, H. C. Brown Lecturer, Mack Award, Baylor Medal and Sabatier Lecturer. He has chaired the Inorganic Division at the ACS. He is the author of a textbook in the organometallic field, and editor-in-chief of the "Encyclopedia of Inorganic Chemistry" and "Comprehensive Organometallic Chemistry". Early research on catalytic alkane C–H activation and functionalisation chemistry was followed by work on C–F bond activation, H<sub>2</sub> complexes, M–H...H–O hydrogen bonding, and molecular recognition in C–H activation. His homogeneous hydrogenation catalyst is in wide use.