

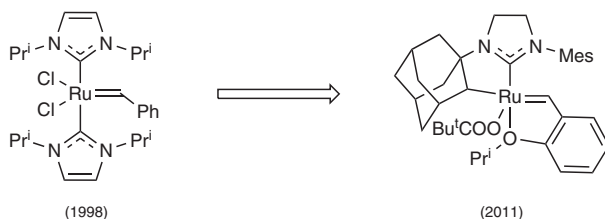
## Abstracts

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### 2.1.1 Historical Overview of N-Heterocyclic Carbenes in Alkene Metathesis

*C. Slugovc*

This chapter is a short outline of the historic development of the use of N-heterocyclic carbenes as co-ligands in alkene metathesis catalysts.



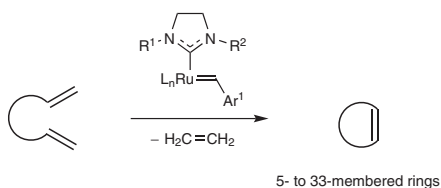
**Keywords:** alkene metathesis • N-heterocyclic carbenes • alkenes • ruthenium • molybdenum

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### 2.1.2 Ring-Closing Metathesis

*J. Broggi and H. Clavier*

This chapter describes the use of ruthenium alkylidene complexes bearing N-heterocyclic carbene ligands as catalysts for the preparation of cyclic compounds (from 5- to 33-membered rings) by metathesis. Also included are examples of asymmetric metathesis using catalysts bearing chiral N-heterocyclic carbenes.



**Keywords:** alkenes • asymmetric catalysis • N-heterocyclic carbenes • carbon–carbon double bonds • cycloalkenes • metal–carbene complexes • metathesis • ring closure • ring formation • cyclization • ruthenium catalysts

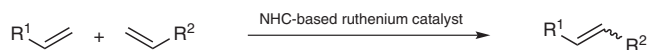
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### 2.1.3 Cross Metathesis

*A. Jana, P. Małeck, and K. Grela*

During the past two decades, among all the types of transition-metal-catalyzed reaction, olefin metathesis has become arguably the most powerful synthetic tool for carbon–carbon bond formation. The reason for this is undoubtedly the development of well-defined functional-group-tolerant N-heterocyclic carbene (NHC) based ruthenium alkylidene catalysts. Among the types of olefin metathesis, cross metathesis is probably the most useful

due to its numerous advantages and has found a wide range of application in almost every field of organic synthesis. Introduction of NHCs has made the ruthenium catalysts more stable and more functional group tolerant. The efficiency and selectivity of the reaction and the activity of the catalyst are three key issues that need to be considered in cross metathesis and introduction of NHC-based ruthenium catalysts addresses all three. This chapter focuses on different types of cross metathesis, performed under different conditions and using different NHC-based catalysts.



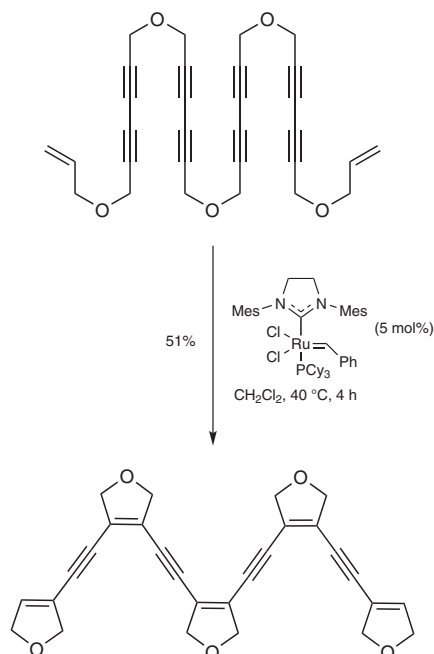
**Keywords:** alkenes • metathesis • N-heterocyclic carbenes • ruthenium • ethenolysis • carbon–carbon double bonds • carbenes • ligands • metal–carbene complex • isomerization • asymmetric • oleochemistry • selectivity

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#### 2.1.4 Enyne Metathesis

*C. E. Diesendruck*

Enyne metathesis is a metal-catalyzed reaction between an alkene and an alkyne, resulting in C–C bond formation to give a 1,3-diene. This chapter explores the different forms of this powerful reaction, both as a single reaction and as part of a reaction cascade to form polycyclic compounds.

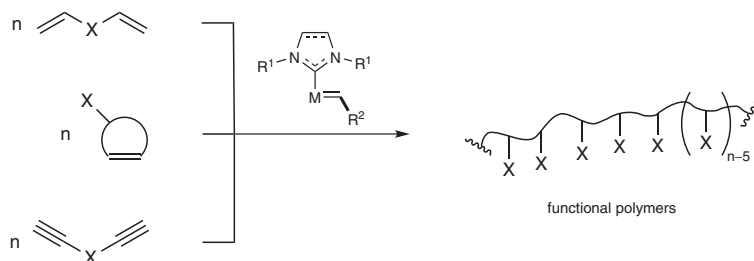


**Keywords:** metathesis • carbon–carbon bond formation • enynes • dienes • cyclization • polycyclic compounds • cascade reactions • metallacycles • N-heterocyclic carbenes

### 2.1.5 Alkene Metathesis Based Polymerization

*J. Liu and J. A. Johnson*

Alkene metathesis based polymerizations that rely on metal complexes with N-heterocyclic carbene (NHC) ligands are discussed in this chapter. Particular emphasis is placed on novel polymer microstructures, architectures, and applications that have been enabled by NHC–metal complexes. Applications of ruthenium–NHC initiated ring opening metathesis polymerization (ROMP) for the synthesis of block copolymers, branched polymers, stereocontrolled polymers, and cyclic polymers are described. Ruthenium–NHC catalyzed acyclic diene metathesis polymerization (ADMET) and cyclopolymerization are also discussed, along with alkene metathesis polymerizations using tungsten- and molybdenum–NHC complexes.

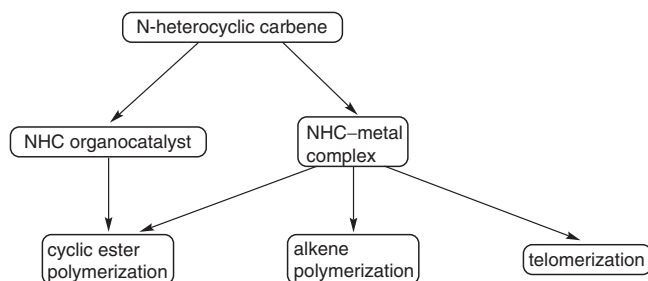


**Keywords:** N-heterocyclic carbenes • alkene metathesis • polymer chemistry • ring opening metathesis polymerization • acyclic diene metathesis polymerization • cyclopolymerization • living polymerization • metal initiators • bottlebrush polymers • tacticity • star polymers • surface grafting • aqueous polymerization • stereocontrolled polymers • sequence-controlled polymers • alternating copolymers

### 2.2 Polymerization, Oligomerization, and Telomerization Involving N-Heterocyclic Carbenes as Ligands or Initiators

*C. Costabile*

This chapter is an overview of recent developments in polymerization and oligomerization of alkenes and cyclic esters involving N-heterocyclic carbenes, both as ligands in organometallic catalysts and as organocatalysts. Telomerization reactions catalyzed by N-heterocyclic carbene–palladium complexes are also briefly discussed.

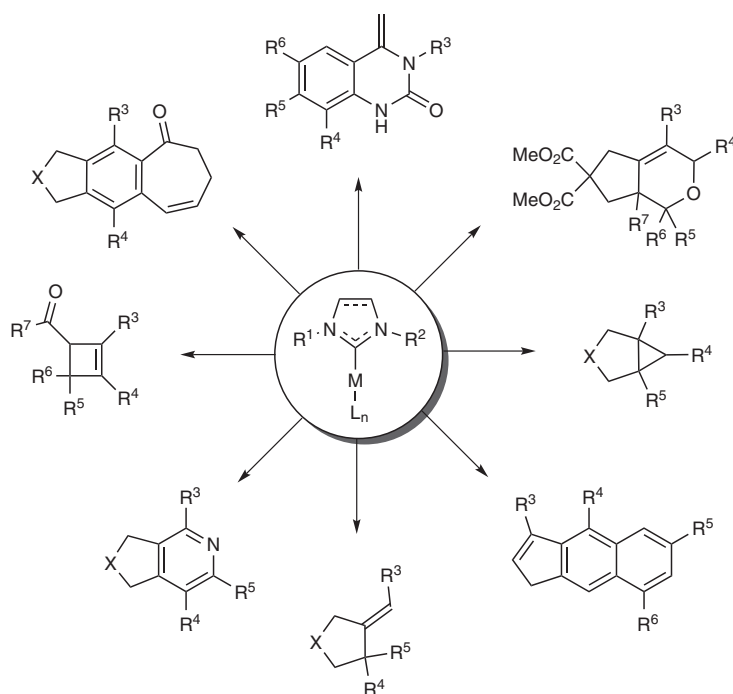


**Keywords:** polymerization • oligomerization • telomerization • organocatalysis • ethene • styrene • norbornene • conjugated dienes • cyclic esters • N-heterocyclic carbenes

## 2.3 Cyclization Reactions

*Y. Zhong, S. Felten, and J. Louie*

This chapter presents a detailed overview of current research into N-heterocyclic carbene (NHC) coordinated, transition-metal-catalyzed cyclization reactions. Highly efficient and economical access to pharmacologically relevant moieties, such as carbo- and heterocycles, is crucial in synthetic chemistry. Though cyclizations are atom-economical, historically harsh reaction conditions, poor substrate tolerance, and low product selectivity severely limited the practicality of such reactions. However, transition-metal catalysts based on copper, gold, palladium, nickel, rhodium, cobalt, and iron have allowed for the rapid synthesis of cyclization products in good to high yield and with high selectivity. In addition, these cyclizations tolerate starting materials bearing a variety of functional groups. Symmetric and asymmetric NHC ligands have proven to be critical for success in generating efficient transition-metal based catalytic systems. The electronic and steric diversity of NHC ligands allows for the fine-tuning of the transition-metal catalyst, which has resulted in effective  $[n + m]$ -cycloaddition reactions, inter- and intramolecular cycloisomerization reactions, and rearrangement reactions.



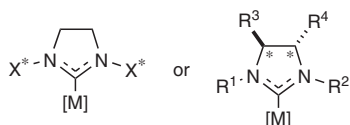
X = O, NTs

**Keywords:** cobalt catalysis • copper catalysis • cyclization • cycloaddition • cycloisomerization • gold catalysis • iron catalysis • N-heterocyclic carbenes • nickel catalysis • palladium catalysis • rearrangements • rhodium catalysis • transition-metal catalysis

## 2.4 N-Heterocyclic Carbenes in Asymmetric Transition-Metal Catalysis

S. K. Collins and M. Holtz-Mulholland

Catalytic asymmetric reactions catalyzed by chiral N-heterocyclic carbene (NHC) complexes have become an important synthetic tool for the synthesis of key chiral building blocks. This chapter describes the different NHC ligand types that have been developed, including both monodentate/bidentate and  $C_1$ - and  $C_2$ -symmetric ligands. In addition, the use of such ligands in a variety of asymmetric transformations is presented, as well as applications in the construction of complex molecules.



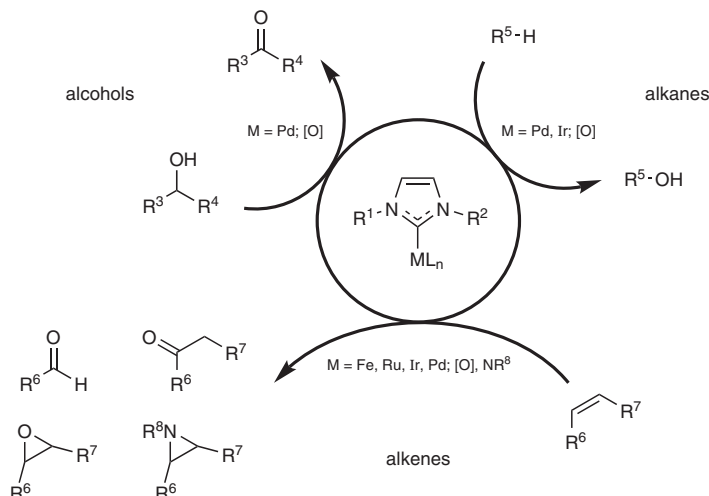
$X^*$  = chirality-inducing group

**Keywords:** asymmetric reactions • hydroboration • hydrosilylation • metathesis • N-heterocyclic carbenes • nickel catalysis • transition-metal catalysis

## 2.5 Transition-Metal-Catalyzed Oxidations

D. Munz

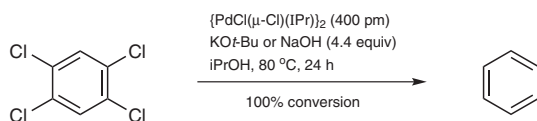
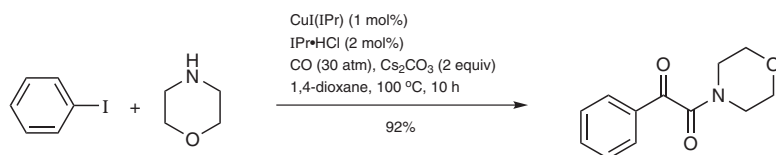
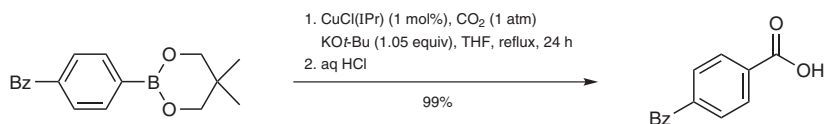
The use of transition-metal complexes with N-heterocyclic carbene (NHC) ligands for oxidative catalysis is summarized in this chapter. Special attention is given to the applicability in organic synthesis and the comparison of results for different reaction conditions and catalyst types. The stoichiometric reactivity of NHC-transition-metal complexes (Ru, Co, Ir, Ni, Pd) with molecular oxygen and the stabilization of high-valent metal complexes with chelating ligands are discussed. The oxidation of alcohols to aldehydes and ketones, Wacker-type oxidation, aziridination and epoxidation of olefins, oxidative scission of alkenes to aldehydes, and oxidation of saturated and aromatic hydrocarbons are addressed.



**Keywords:** oxidation • N-heterocyclic carbenes • ligands • catalysis • oxygen • metal • transition-metal complexes • alcohols • alkenes • hydrocarbons • aromatics • aziridination • epoxidation • alkene scission

**2.6 Carboxylation, Carbonylation, and Dehalogenation***D. J. Nelson*

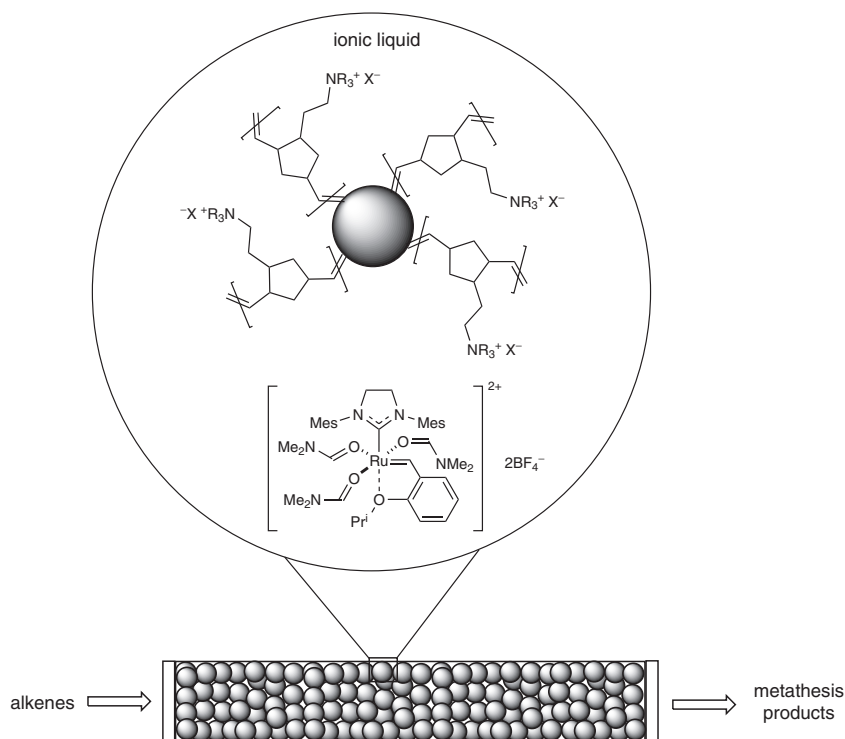
This chapter describes the use of N-heterocyclic carbene–metal complexes in carboxylation, carbonylation, and dehalogenation reactions. Catalysts based on copper, gold, palladium, rhodium, and nickel are considered.



**Keywords:** carboxylation • carbonylation • dehalogenation • carboxylic acids • esters • amides • carbonyl compounds • carbon monoxide • carbon dioxide • cross coupling • N-heterocyclic carbene–metal complexes • copper • gold • palladium • rhodium • nickel

**2.7.1 Biphasic Systems***C. Claver, C. Godard, and A. Martínez Lombardía*

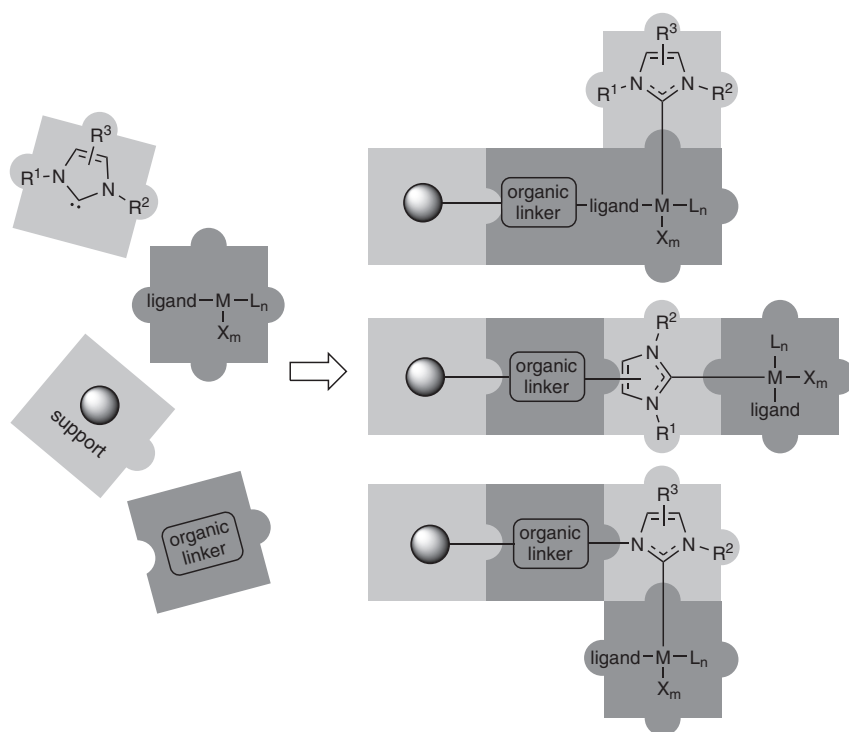
To overcome the inherent issue of catalyst recycling in homogeneous catalysis, much effort has been devoted to the heterogenization of catalysts onto solid supports and to the separation of the reactants (and/or products) and the catalyst using immiscible liquid phases (liquid multiphase catalysis). For these latter systems, solvents such as water, alcohols, ionic liquids, fluoruous media, supercritical fluids, and gas-expanded liquids have been employed successfully as the catalyst phase. In this chapter, the most relevant biphasic catalytic systems involving NHC complexes are discussed. Particular attention is devoted to alkene metathesis, which is considered to be one of the most important processes that uses complexes with carbene ligands. Sulfonated or related water-soluble carbene ligands are also described for biphasic reactions, such as cyclization, C–C bond formation, and hydroformylation.



**Keywords:** biphasic • N-heterocyclic carbene complexes • catalyst recycling • catalysts • hydroformylation • metathesis • solvents • supported catalysis

**2.7.2 Covalently Immobilized N-Heterocyclic Carbene Complexes***C. Thieuleux and D. Crozet*

This chapter focuses on the preparation and the catalytic performance of metal-NHC complexes immobilized on oxide supports, which are designed so that the metal-NHC complex is maintained on the support during catalysis. The major scientific contributions for the covalent immobilization of metal-NHC complexes onto various oxides are covered, with an emphasis on the most distinguished examples. Particular attention is directed toward the anchoring of metal complexes via the substituents or the backbone of the NHC ligand, or via another X/L-type ligand that is not expected to suffer from decooordination during the catalytic process.

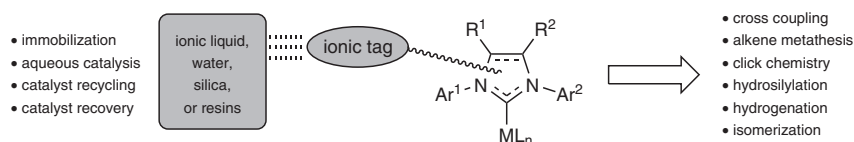


**Keywords:** N-heterocyclic carbene complexes • supported catalysts • grafting • immobilization • oxides • sol-gel process • catalysis



**2.7.3 Catalytic Systems Featuring Ionically Tagged N-Heterocyclic Carbene Ligands***T. E. Schmid, C. Crévisy, O. Baslé, and M. Mauduit*

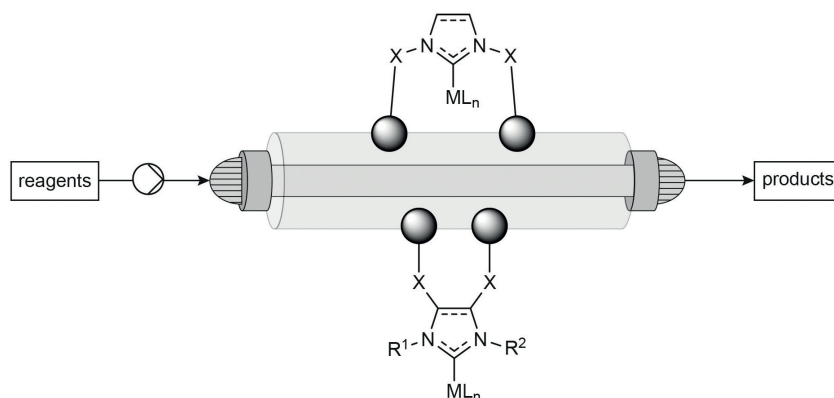
Since the discovery of N-heterocyclic carbenes (NHCs), their unique properties as ligands in organometallic chemistry have enabled the synthesis of a myriad of novel metal complexes. Thanks to the facile modulation of this class of ligands, they can be easily functionalized with ionic tags, which has proven to be useful for various applications. Notably, such groups have enabled the immobilization of metal complexes on a variety of supports, and recyclable catalysis could be realized. This chapter describes organometallic species featuring ionically-tagged NHCs for such applications, focusing on catalytic systems that show the best performance in terms of versatility and reusability.



**Keywords:** N-heterocyclic carbenes • metal–carbene complexes • catalysts • supported catalysis • alkene metathesis • cross-coupling reactions • hydrogenation • hydrosilylation

**2.7.4 Flow Systems for N-Heterocyclic Carbene Catalysis***I. Peñafiel and A. Lapkin*

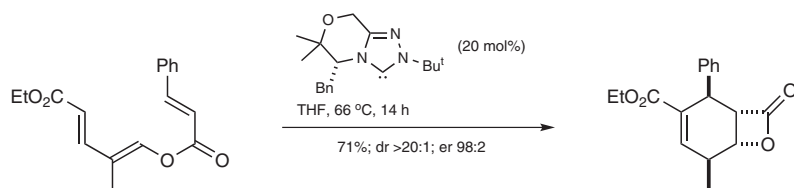
Continuous-flow technology represents a paradigm shift in the manufacture of specialty chemicals and pharmaceuticals. In many such syntheses, catalysis by N-heterocyclic carbenes plays an important role due to the stability, activity, and broad synthetic utility of these species. This chapter explores the “sweet-spot” in the combination of catalysis by N-heterocyclic carbenes and flow-chemistry technology. The chapter opens with a description of the fundamentals of flow technology and then relates the functions of flow reactors to the specifics of N-heterocyclic carbene based catalysis. The chapter provides an overview of up-to-date literature on catalysis by carbenes in flow reactors.



**Keywords:** continuous flow • flow chemistry • process intensification • N-heterocyclic carbenes • heterogenized catalysts

**2.8 Recent Advances in N-Heterocyclic Carbene Organocatalysis***A. T. Davies and A. D. Smith*

In recent years, organocatalysis has seen a rapid rise in popularity and this has led to a subsequent increase in the research output of the area, with organocatalysis by N-heterocyclic carbenes (NHCs) playing a significant role. Beginning with the benzoin condensation, through the work of Breslow and others to modern, asymmetric protocols, NHC organocatalysis has a rich history, which has been covered in many reviews. The focus of this chapter is on recent advances within the area of NHC organocatalysis, offering a brief historical perspective and highlighting what the authors believe to be some of the key advances made within recent times, both in terms of novel processes and significant advancements on previously documented reactions.



**Keywords:** organocatalysis • N-heterocyclic carbenes • azolium enolates • acyl azoliums • acyl anions • Breslow intermediate