We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Late Transition Metal (LTM)-NHC Catalyzed Transformations of Renewable Chemicals to Fine Chemicals, Fuels, and Intermediates

Kurra Mohan, Bollikolla Hari Babu, Khandapu Bala Murali Krishna, Kotra Vijay and Varala Ravi

Abstract

This title of the book chapter deals with the late transition metal-NHC (N-heterocyclic carbene) catalyzed transformations of renewable chemicals, i.e., bio-mass resources (carbohydrates/vegetable oils/natural products) into useful chemicals *via* oxidation, hydrogenation, dehydration, polymerization, hydrolysis, etc. along with brief introductory notes on late transition metals, carbenes, and renewable chemicals for better understanding to the reader.

Keywords: late transition metals, NHC, renewable chemicals, fine chemicals, fuels, intermediates

1. Introduction

Organocatalysis plays a pivotal role in the field of synthetic organic chemistry as well as the pharmaceutical industry through diversifying activation strategies owing to meeting the principles of green chemistry [1–4] in terms of cost-effectiveness, longevity, and less toxic compared to conventional transition metal catalysis [5–8]. In this regard, N-heterocyclic carbene (NHC) plays a major role in diversified organic transformations [9–11].

1.1 Renewable chemicals

Renewable chemicals or "bio-based chemicals" are chemicals obtained from renewable sources, such as agricultural feedstock, agricultural waste, organic waste products, biomass, and microorganisms [12]. In general, in chemical industries, processes include the utilization of fossil resources. As the need for energy consumption and population increasing, limited availability of fossil resources has become a risky task in the low or underdeveloped nations to perform trade. Henceforth, alternative renewable resources such as lignin, hemicellulose, cellulose, starch, and protein have become more focus of utility.

1.2 Carbene

The term "Carbene" refers to the presence of neutral bivalent carbon with six valence electrons in N-heterocyclic compounds (**Figure 1**). The first reported carbene (I) was by Bartrand et al. in 1988 [13], as resonance stabilized ylide form. After a few years, the first stable NHC was reported by Arduengo et al. as an imidazolium ring [14]. In NHC, the singlet state of carbene is more thermodynamically favorable than triplet carbene. Because nitrogen is present near to carbon of carbene, it lowers the energy of the highest occupied molecular orbital (HOMO) while it increases the energy of the lowest unoccupied molecular orbital's. The nucleophilicity of carbene also increases (**A**) not only above energy character but also presence of inductive effect, mesomeric and lone pair to vacant p-orbital favors singlet carbene. Most NHCs are based on imidazolium, triazolium, or thiazolium ring-containing molecules. NHCs dimerize reversible in the form of the Wanzlick equilibrium (**B**) [15–16].

Since the discovery of metal carbenes in 1964 by Fisher et al. [17], fascinating applications in both catalysis and synthesis are being observed [18].

1.3 Late transition metals

Late transition metals are on the right side of the d-block, from group 8 to 11 (and 12 if it is counted as transition metals) as shown in **Figure 2**.

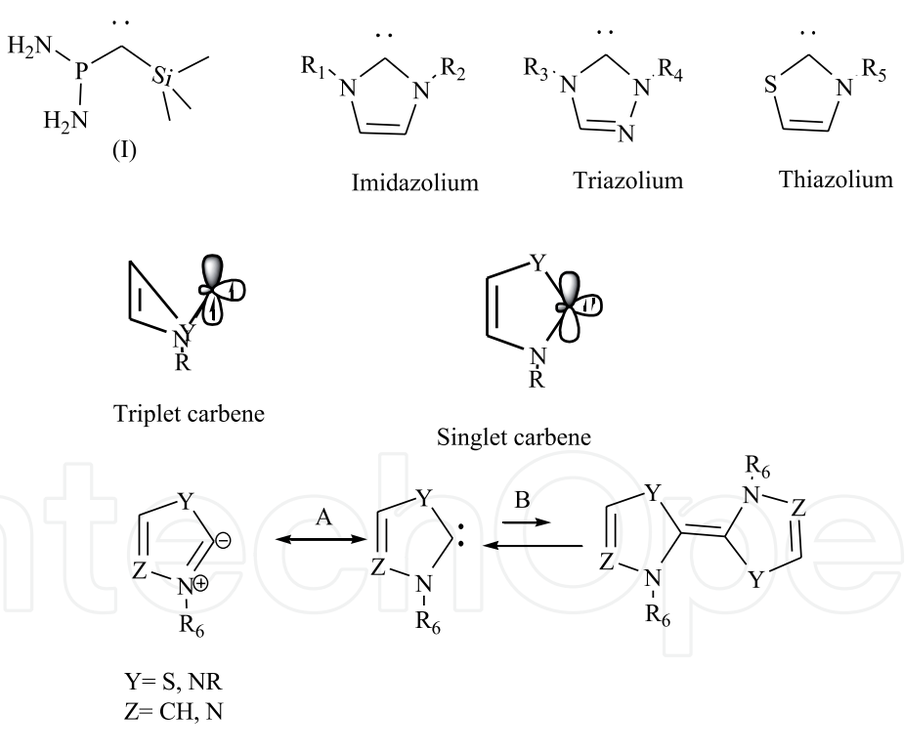

Figure 1.
The structure and stabilization of the first persistent carbene and NHC's.

Rb		**Y**	**$5s^24d^2$ Zr $4d^4$**	**$5s^24d^3$ Nb $4d^5$**	**$5s^24d^4$ Mo $4d^6$**	**$5s^24d^5$ Tc $4d^7$**	**$5s^24d^6$ Ru $4d^8$**	**$5s^24d^7$ Rh $4d^9$**	**$5s^24d^{10}$ Pd $4d^{10}$**	**Ag**	**Cd**	**In**		**Xe**
Cs		**La**	**$6s^25d^2$ Hf $5d^4$**	**$6s^25d^3$ Ta $5d^5$**	**$6s^25d^4$ W $5d^6$**	**$6s^25d^5$ Re $5d^7$**	**$6s^25d^6$ Os $5d^8$**	**$6s^25d^7$ Ir $5d^9$**	**$6s^25d^8$ Pt $5d^{10}$**	**Au**	**Hg**	**Tl**		**Rn**

EARLY **LATE**

Figure 2.
Late transition metals.

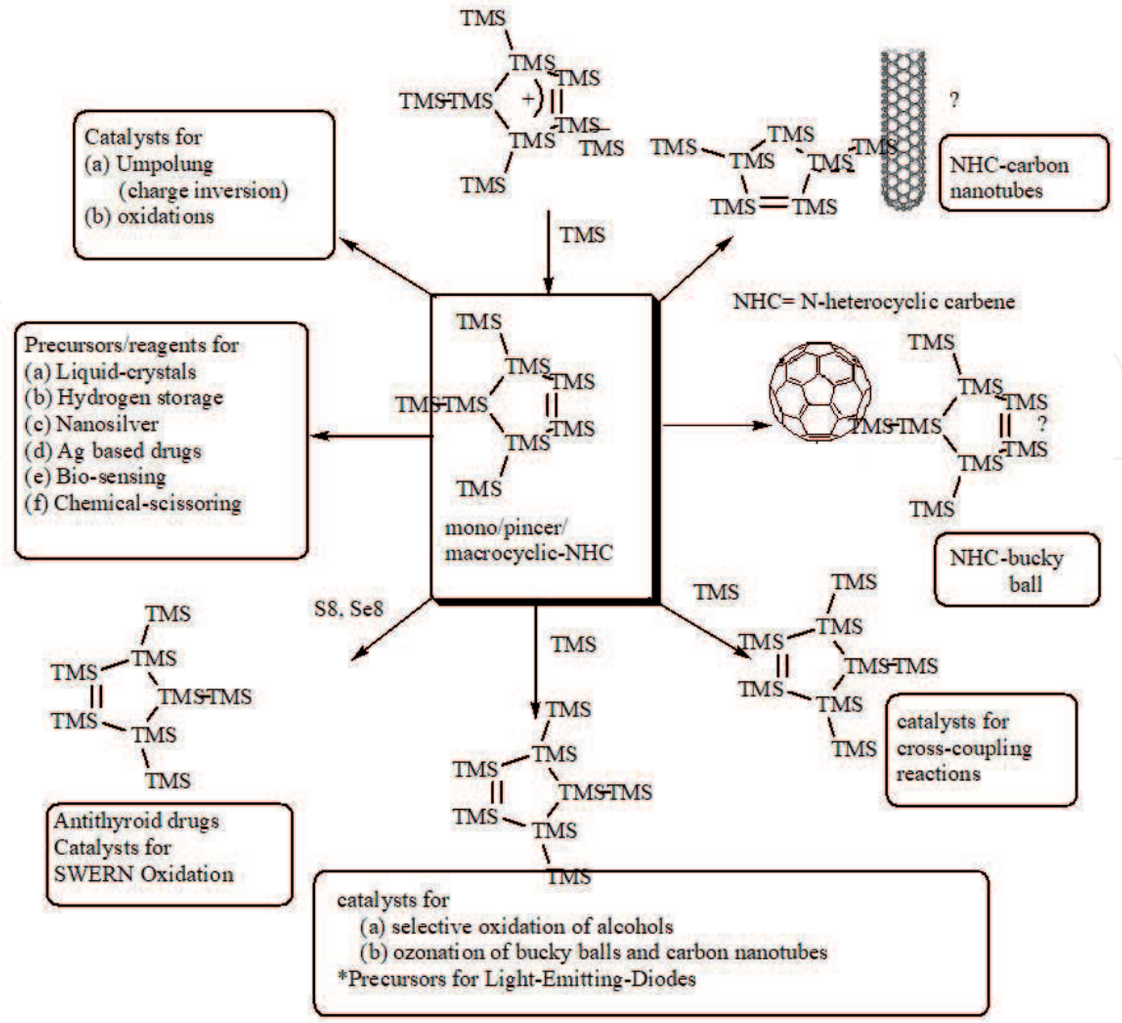

Figure 3.
Transmetalation route for the synthesis of carbenes.

1.4 Free carbine route

The general synthesis of carbene complexes involves the utilization of strong bases and harsh reaction conditions which involves high cost and more time.

1.5 Transmetalation route

It involves the transfer of the carbine fragment from a suitable metal center [generally Ag(I) or Cu(I)] to a precursor of the metal center of interest [19–22] as shown in **Figure 3**.

Even though, transmetalation method has operational simplicity but lacks atom economy. Hence, it is applied, in general, in scalable industrial processes.

2. Applications of late transition metal NHC's

2.1 CO_2 as building blocks

The exploitation of carbon dioxide as a renewable green source of carbon in organic synthesis is of continued interest. In this regard, late transition metal NHCs play a major role for the specified purpose.

2.1.1 Formylation of amines

The use of CO_2 for procuring C_1-containing molecules is an evolved methodology exploiting N-heterocyclic carbenes (NHCs) as efficient catalysts [23, 24]. NHCs promoted the formylation of a wide scope of N-H bonds, with CO_2 and hydrosilanes (**Figure 4**) [25].

2.1.2 Carboxylation of terminal alkynes

Yu and Zhang [26] developed a Cu-NHC catalyzed conversion of CO_2 to carboxylic acids in good to excellent yields under ambient conditions with wide substrate/functional group tolerance (**Figure 5**).

2.1.3 Methylation of amines

Olivier et al. have designed using CO_2 as a $C1^-$ building block for the catalytic methylation of amines using simple zinc salts and ligands (**Figure 6**) [27].

2.1.4 Insertion of CO_2 into terminal alkynes via copper bis-NHC

Silver bis-NHC has exhibited better performance than Copper bis-NHC towards the carboxylation of terminal alkynes using Cs_2CO_3 as an additive (**Figure 7**) [28].

2.1.5 Carboxylative cyclization of propargylamine

Tahani et al. synthesized dinuclear gold (I) complexes and investigated the carboxylative cyclization of propargylamine (PPA) (**Figure 8**) [29].

2.2 Oxidation

2.2.1 Dehydrogenative oxidation of alcohols

Ir-NHC complexes were synthesized in aqueous media for the oxidation of secondary alcohols to ketones. In addition, primary alcohols were transformed to carboxylic acids in the absence of a base [30].

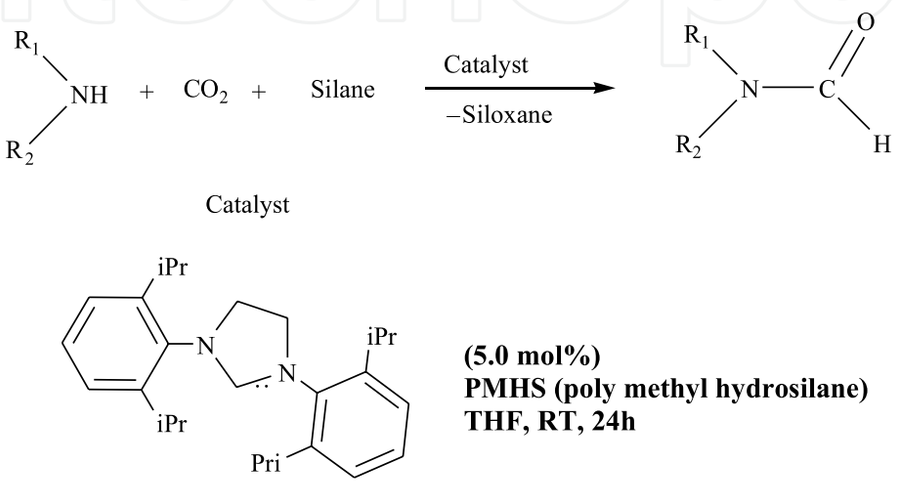

Figure 4.
Formylation of amines with CO_2 and hydrosilanes.

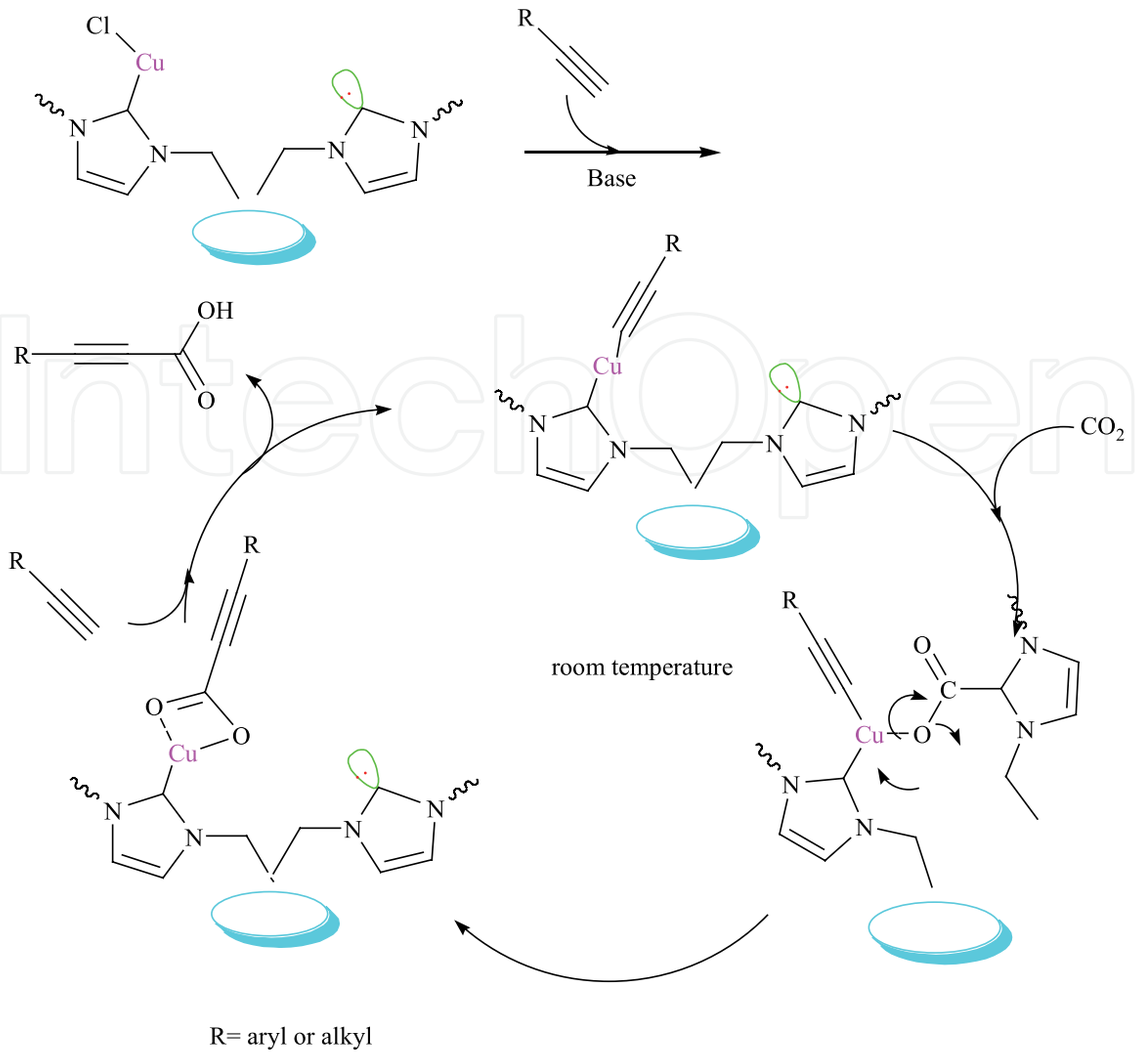

Figure 5.
Mechanistic approach for carboxylation of terminal alkynes.

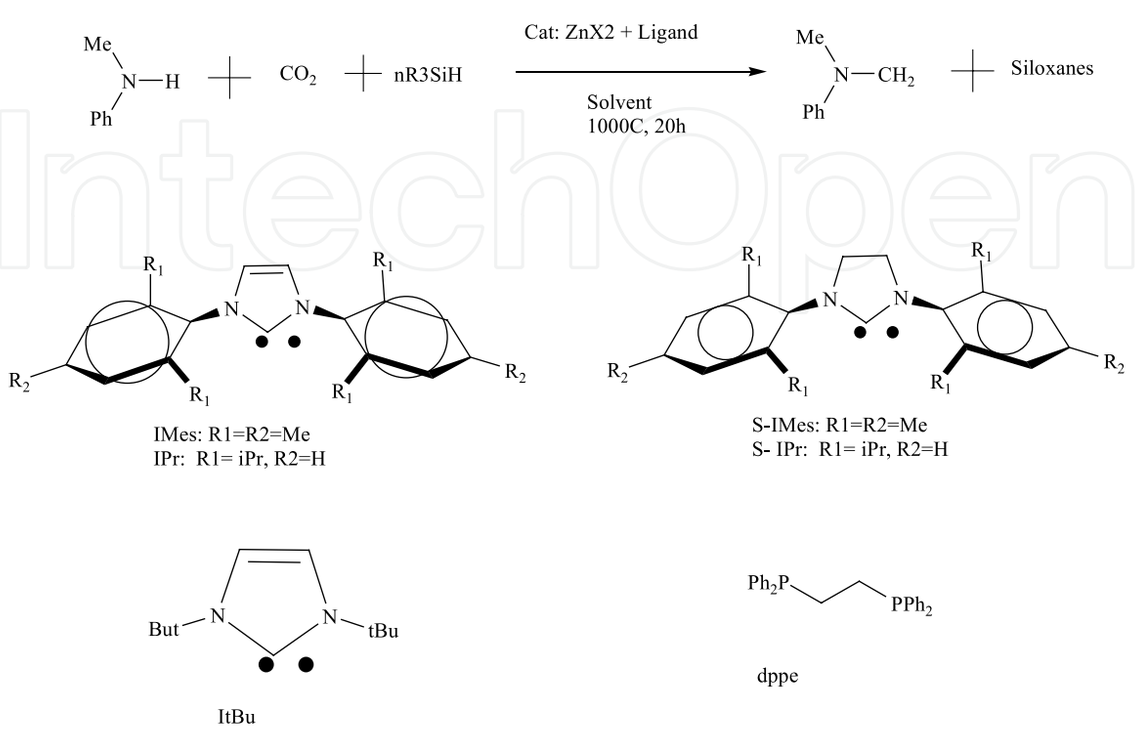

Figure 6.
N-methylation of amines.

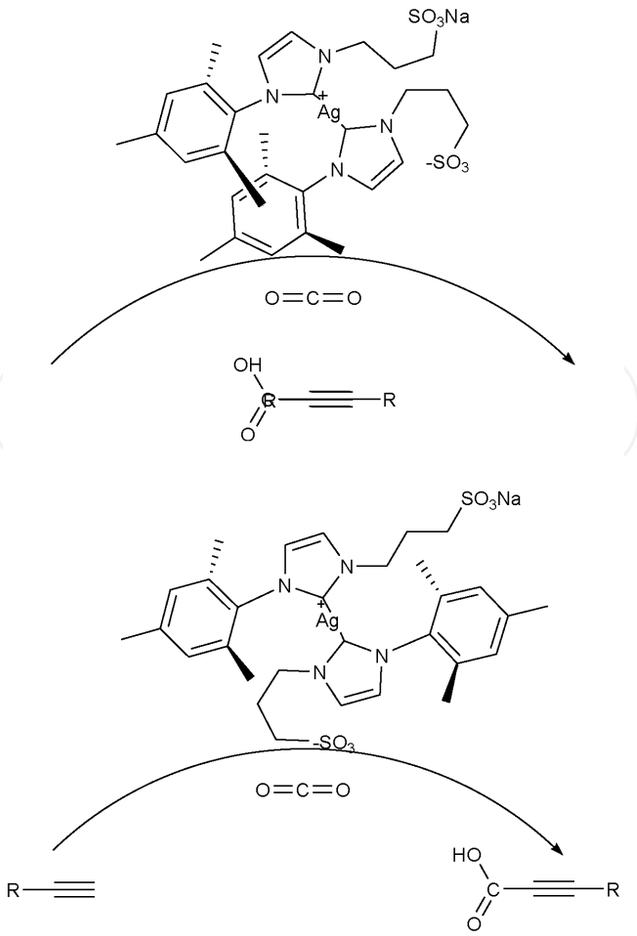

Figure 7.
Carboxylation of terminal alkynes.

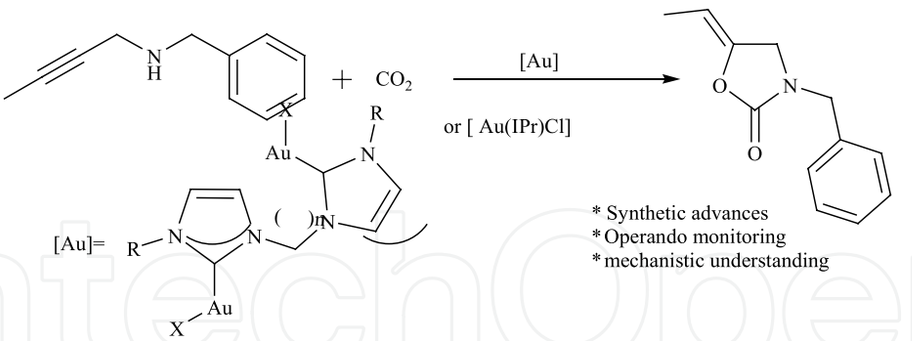

Figure 8.
Carboxylative cyclization of propargylamine.

2.2.2 Oxidation of bio-polyols to lactic acid

Lactic acid has prominent applications in bio-plastics manufacturing. A recyclable NHC-iridium coordination polymer with a porous structure can oxidize a wide range of bio-polyols such as sorbitol to prepare lactic acid with superior selectivity and reactivity [31].

2.2.3 Dehydrogenative catalysis using alcohols

Huang et al. reported LTM-NHCs for the conversion of alcohols into aldehydes or ketones through acceptors alcohol dehydrogenation (AAD). In addition, they

successfully demonstrated oxidative coupling of alcohols to form C-O, C-C, and C-N/C=N bond formations (**Figure 9**) [32].

2.2.4 Dehydrogenation of sugar alcohols

Manas and Campos et al. [33] reported Ir-NHC catalyzed oxidative protocol for the selective conversion of sorbitol, xylitol, and other polyols into lactic acid (**Figure 10**).

2.3 Dehydration

*2.3.1 Cp*IrCl2(NHC) in hydrogen transfer initiated dehydration (HTID)*

A recyclable $Cp^*IrCl_2(NHC)$ (Cp^* = pentamethylcyclopentadienyl) complex in ionic liquid could covert glycerol into 1,3-propanediol and subsequently to propionaldehyde by hydrogen transfer initiated dehydration (HTID) in excellent yields in the presence of air (**Figure 11**) [34, 35].

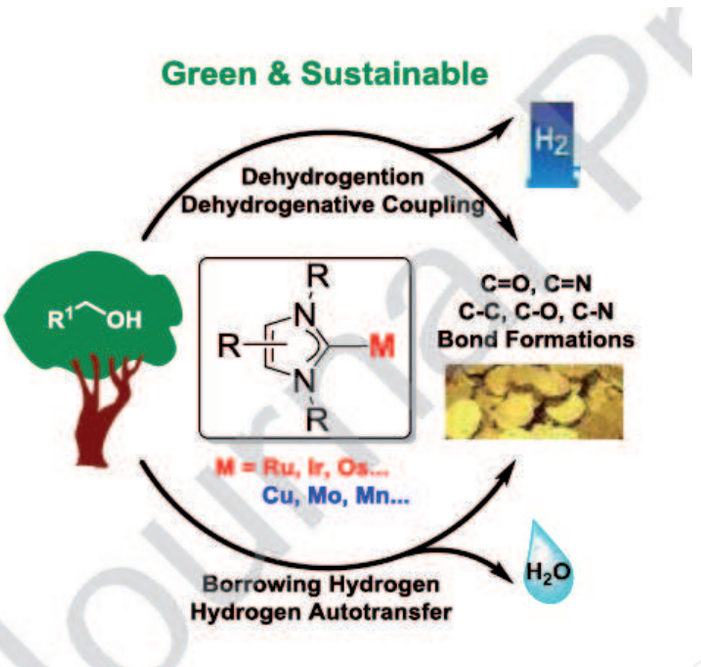

Figure 9.
Dehydrogenative catalysis using alcohols.

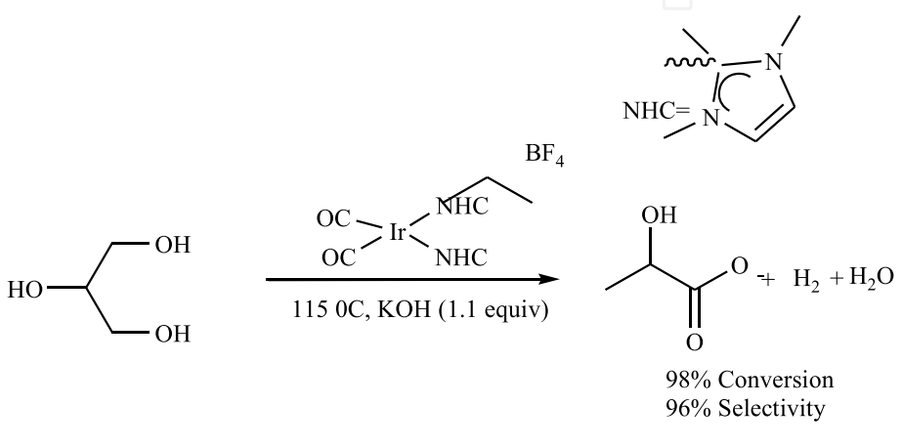

Figure 10.
Oxidation of sugar alcohols to lactic acid.

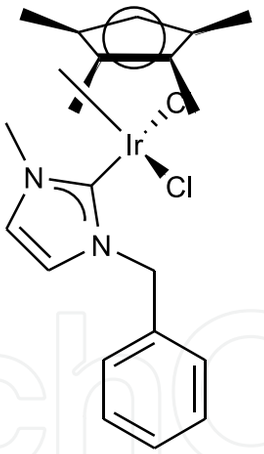

Figure 11.
*Cp*IrCl2(NHC) in hydrogen transfer initiated dehydration (HTID).*

2.3.2 Fructose to 5-hydroxymethylfurfural (HMF)

A new heterogeneous and recyclable Fe-NHCs immobilized on mesoporous expanded starch and Starbon™ 350 could be utilized successfully for the effective dehydration of fructose to HMF [36].

2.4 Reduction/hydrogenation

2.4.1 Hydrogenolysis of aryl ethers using Ni-NHC

Ni-NHC complex in the presence of a suitable base (NaO^{t}Bu) could effectively convert C-O bonds in lignin to various useful scaffolds useful in biomass conversion [37]. Hartwig et al. mechanically investigated the reduction of diaryl ethers to corresponding phenols (**Figure 12**) [38].

2.4.2 Transfer hydrogenation using Ir-NHC

Using water soluble Ir-NHCs proved that glycerol can be exploited as a hydrogen donor to convert a biomass-derived phytochemical, levulinic acid, to selectively produce γ-hydroxyvaleric acid (GHV) and lactic acid (LA) [39].

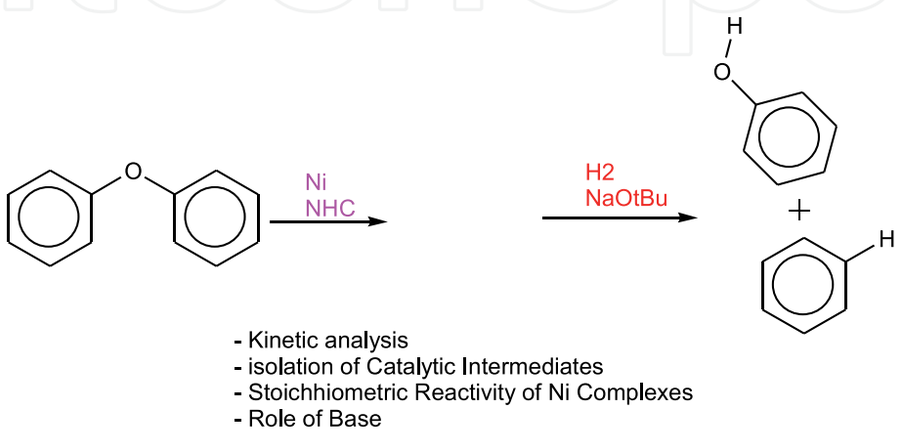

Figure 12.
Hydrogenolysis of diaryl ethers.

2.4.3 Iridium-based hydride transfer catalysts

Lu et al. reported homogeneous Ir-NHC catalysts, which can be utilized for the storage of H_2 and fine chemicals through hydride transfer catalysis [40] (**Figure 13**).

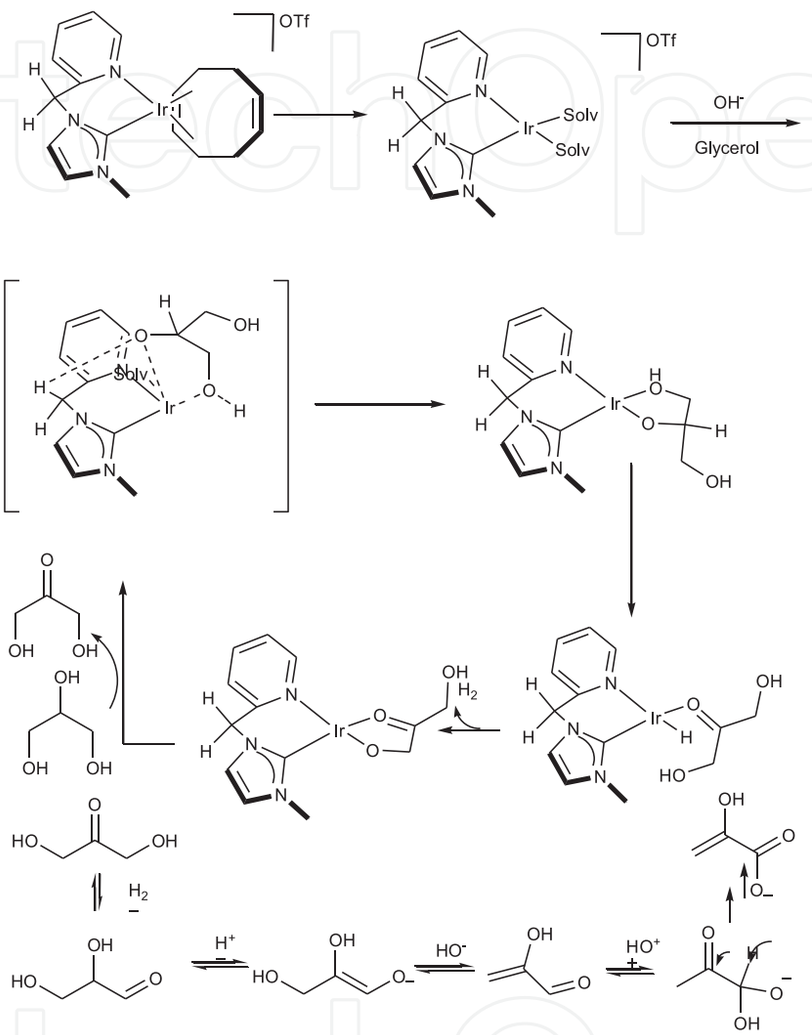

Figure 13.
Iridium-based hydride transfer catalysts.

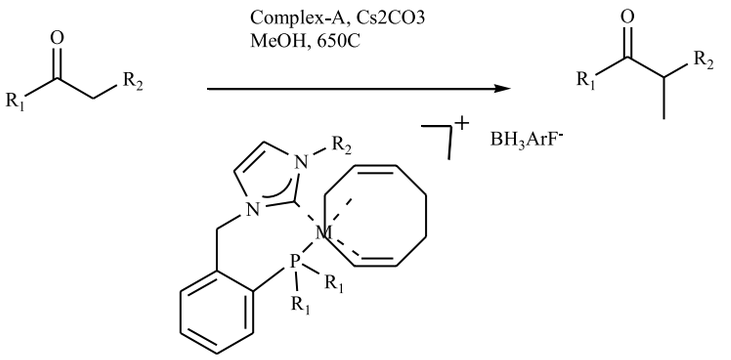

Figure 14.
Conversion of sugars into heterocycles.

2.5 Miscellaneous organic transformations

2.5.1 Sugars to heterocycles

Zhang and Yong developed a synthetic protocol employing Cr-NHC along with ionic liquid for the selective production of 5-hydroxymethylfurfural from glucose and fructose (**Figure 14**) [41].

3. Conclusion

In this book chapter, authors tried to emphasize the applications of "Late Transition Metal" (LTM)-NHC catalyzed organic transformations as given in a nutshell below:

Oxidation of carbohydrates: To develop carbohydrate oxidation products as a useful alternative to those derived from petrochemical sources.

Hydrogenation of carbohydrates/fatty acids: This objective concerns the development of LTM-NHC catalysts for the hydrogenation of carbohydrates and unsaturated vegetable oils.

Dehydration/hydrolysis of carbohydrates/fatty acids: Development of dehydration/hydrolysis of carbohydrates/fatty acids with LTM-NHC catalysts to obtain fine chemicals and fuel intermediates.

Polymerization with renewable resources: This objective deals with the application of LTM-NHC catalysts in the polymerization of natural monomers of renewable chemicals or monomers derived from renewable resources to synthetic polymers (polymerization of lactic acid, glucose, glycerol, terpenes, etc.).

The present research is directed towards the conversion of methanol to H_2 and CO_2 using LTM-NHC catalysis.

$$CH_3OH(g) + H_2O \xrightarrow{\text{LTM-NHC Catalyst}} 3H_2(g) + CO_2(g) \tag{1}$$

We do hope this compilation on very important LTM-NHC applications would help wide readers among synthetic organic chemists.

Acknowledgements

Dr. RV is thankful to Dr. Ch.V. Rajasekhar, Scrips Pharma, and Dr. P.G. Kiran, Swastha BioSciences for their continued support.

Conflict of interest

The authors declare no conflict of interest.

IntechOpen

Author details

Kurra Mohan[1], Bollikolla Hari Babu[2], Khandapu Bala Murali Krishna[2], Kotra Vijay[3] and Varala Ravi[4*]

1 Department of Pharmaceutical Chemistry, Telangana University, Telangana, India

2 Department of Chemistry, Acharya Nagarjuna University, Guntur, AP, India

3 Faculty of Pharmacy, Quest International University, Ipoh, Perak, Malaysia

4 Scrips Pharma, Hyderabad, Telangana, India

*Address all correspondence to: ravivarala@gmail.com

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

[1] Dalko PI. Enantioselective Organocatalysis. KGaA, Weinheim: WILEY-VCH Verlag Gmbh & Co.; 2007

[2] Berkessel A, Groger H. Asymmetric Organocatalysis—From Biomimetic Concepts to Applications in Asymmetric Synthesis. KGaA, Wienheim: WILEY-VCH Verlag GmbH & Co.; 2006

[3] Aleman J, Cabrera S. Applications of asymmetric organocatalysis in medicinal chemistry. Chemical Society Reviews. 2013;**42**:774-793. DOI: 10.1039/C2CS35380F

[4] Busacca CA, Fandrick DR, Song JJ, Senanayake CH. The growing impact of catalysis in the pharmaceutical industry. Advanced Synthesis and Catalysis. 2011;**353**:1825-1864. DOI: 10.1002/adsc.201100488

[5] Parmar D, Sugiono E, Raja S, Rueping M. Complete field guide to asymmetric BINOL-phosphate derived brønsted acid and metal catalysis: History and classification by mode of activation; Brønsted acidity, hydrogen bonding, ion pairing, and metal phosphates. Chemical Reviews. 2014;**114**:9047-9153. DOI: 10.1021/cr5001496

[6] Ishikawa T. Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts. New York: Wiley; 2009

[7] Zhang Z, Schreiner PR. (Thio)urea organocatalysis—What can be learnt from anion recognition? Chemical Society Reviews. 2009;**38**:1187-1198. DOI: 10.1039/B801793J

[8] Hashimoto T, Maruoka K. Recent development and application of chiral phase-transfer catalysts. Chemical Reviews. 2007;**107**:5656-5682. DOI: 10.1021/cr068368n

[9] Federsel H-J. Asymmetry on large scale: The roadmap to stereoselective processes. Nature Reviews. Drug Discovery. 2005;**4**:685-697. DOI: 10.1038/nrd1798

[10] Breuer M, Ditrich K, Habicher T, Hauer B, Keseler M, Sturmer R, et al. Industrial methods for the production of optically active intermediates. Angewandte Chemie International Edition. 2004;**43**:788-824. DOI: 10.1002/anie.200300599

[11] Fiorani G, Guo W, Kleij AW. Sustainable conversion of carbon dioxide: The advent of organocatalysis. Green Chemistry. 2015;**17**:1375-1389. DOI: 10.1039/C4GC01959H

[12] Chandel AK, Garlapati VK, Kumar SPJ, Hans M, Singh AK, Kumar S. The role of renewable chemicals and biofuels in building a bioeconomy. Biofuels, Bioproducts and Biorefining. 2020;**14**(4):830-844. DOI: 10.1002/bbb.2104

[13] Igau A, Grutzmacher H, Baceiredo A, Bertrand G. Analogous alpha, alpha.'-bis-carbenoid, triply bonded species: Synthesis of a stable lambda.3-phosphino carbene-. lambda.5-phosphaacetylene. Journal of the American Chemical Society. 1988;**110**:6463-6466. DOI: 10.1021/ja00227a028

[14] Arduengo AJ, Harlow RL, Kline M. A stable crystalline carbene. Journal of the American Chemical Society. 1991;**113**:361-363. DOI: 10.1021/ja00001a054

[15] Herrmann WA, Kocher C. N-heterocyclic carbenes. Angewandte Chemie International Edition. 1997;**36**:2162-2187. DOI: 10.1002/anie.199721621

[16] Hopkinson MN, Richter C, Schedler M, Glorius F. An overview of N-heterocyclic carbenes. Nature.

2014;**510**:485-496. DOI: 10.1038/nature13384

[17] Fischer EO, Maasbol A. On the existence of a tungsten carbonyl carbene complex. Angewandte Chemie. 1964;**76**:645. DOI: 10.1002/anie.196405801

[18] Fischer EO, Maasbol A. Übergangsmetall-Carben-Komplexe, II. Phenylmethoxycarben- und Methylmethoxycarben-pentacarbonyl-chrom, -molybdän, -wolfram und -cyclopentadienyl-dicarbonyl-mangan. Chemistry. 1967;**100**(2445). DOI: 10.1002/cber.19671000744

[19] Wang HMJ, Lin IJB. Facile synthesis of silver (I)-carbene complexes. Useful carbene transfer agents. Organometallics. 1998;**17**:972-975. DOI: 10.1021/om9709704

[20] Furst MRL, Cazin CSJ. Copper N-heterocyclic carbene (NHC) complexes as carbene transfer reagents. Chemical Communications. 2010;**46**:6924-6925. DOI: 10.1039/C0CC02308F

[21] Díez-González S. N-Heterocyclic Carbenes. From Laboratory Curiosities to Efficient Synthetic Tools. 2nd ed. London: Royal Society of Chemistry; 2017

[22] Scattolin T, Nolan SP. Synthetic routes to late transition metal—NHC complexes. Trends in Chemistry. 2020;**2**(8). DOI: 10.1016/j.trechm.2020.06.001

[23] Anis T, Blondiaux E, Xavier F, Thibault C. Reductive functionalization of CO_2 with amines: An entry to formamide, formamidine and methylamine derivatives. Green Chemistry. 2015;**17**:157-168. DOI: 10.1039/C4GC01614A

[24] Riduan SN, Zhang Y, Ying JY. Conversion of carbon dioxide into methanol with silanes over N-heterocyclic carbene catalysts. Angewandte Chemie International Edition. 2009;**48**:3322. DOI: 10.1002/anie.200806058

[25] Jacquet O, Gomes CDN, Ephritikhine M, Cantat T. Recycling of carbon and silicon wastes: Room temperature formylation of N-H bonds using carbon dioxide and polymethylhydrosiloxane. Journal of the American Chemical Society. 2012;**134**:2934. DOI: 10.1021/ja211527q

[26] Yu D, Zhang Y. Copper, and copper-N-heterocyclic carbene-catalyzed C-H activating carboxylation of terminal alkynes with CO_2 at ambient conditions. Proceedings of the National Academy of Sciences of the United States of America. 2010;**107**(47):20184-20189. DOI: 10.1073/pnas.1010962107

[27] Jacquet O, Xavier F, Christophe DNG, Thibault C. CO_2 as a $C1^-$ building block for the catalytic methylation of amines. Chemical Science. 2013;**4**:2127. DOI: 10.1039/c3sc22240c

[28] Velázquez HD, Wu Z-X, Vandichel M, Verpoort F. Inserting CO_2 into terminal alkynes via bis-(NHC)-metal complexes. Catalysis Letters. 2017;**47**(2):463-471. DOI: 10.1007/s10562-016-1920-5

[29] Bayrakdar TACA, Nahra F, Davis JV, Mohan MG, Captain B, Temprado M, et al. Dinuclear Gold(I) complexes bearing alkyl-bridged bis(Nheterocyclic carbene) ligands as catalysts for carboxylative cyclization of propargylamine: Synthesis, structure, and kinetic and mechanistic comparison to the mononuclear complex [Au(IPr)Cl]. Organometallics. 2020;**39**(15):2907-2916. DOI: 10.1021/acs.organomet.0c00404

[30] Fujita K, Tamura R, Yuhi T, Yoshida M, Onoda M, Yamaguchi R.

Dehydrogenative oxidation of alcohols in aqueous media catalyzed by a water-soluble dicationic iridium complex bearing a functional N-heterocyclic carbene ligand without using base. ACS Catalysis. 2018;**7**(10):7226-7230. DOI: 10.1021/acscatal.7b02560

[31] Wu J, Shen L, Duan S, Chen Z-N, Zheng Q, Liu Y, et al. Selective Catalytic dehydrogenative oxidation of bio-polyols to lactic acid. Angewandte Chemie International Edition. 2020;**59**(33):13871-13878. DOI: 10.1002/anie.202004174

[32] Huang M, Liu J, Li Y, Lan X-B, Su P, Zhao C, et al. Recent advances on N-heterocyclic carbene transition metal complexes for dehydrogenative catalysis using alcohols. Catalysis Today. 2020;**370**:114-141. DOI: 10.1016/j.cattod.2020.10.022

[33] Manas MG, Campos J, Sharninghausen LS, Lin E, Crabtree RH. Selective catalytic oxidation of sugar alcohols to lactic acid. Green Chemistry. 2015;**17**:594-600. DOI: 10.1039/C4GC01694G

[34] Wang Y-M, Lorenzini F, Rebros M, Saunders GC, Marr AC. Combining bio- and chemo-catalysis for the conversion of bio-renewable alcohols: Homogeneous iridium catalysed hydrogen transfer initiated dehydration of 1,3-propanediol to aldehydes. Green Chemistry. 2016;**18**(6):1751-1761. DOI: 10.1039/c5gc02157j

[35] Ma Y, Wang Y-M, Morgan PJ, Jackson RE, Liu X, Saunders GC, et al. Designing effective homogeneous catalysis for glycerol valorisation: Selective synthesis of a value-added aldehyde from 1,3-propanediol via hydrogen transfer catalysed by a highly recyclable, fluorinated Cp*Ir(NHC) catalyst. Catalysis Today. 2018;**307**:248-259. DOI: 10.1016/j.cattod.2017.09.036

[36] Matharu AS, Ahmed S, Almonthery B, Macquarrie DJ, Lee Y-S, Kim Y. Novel Starbon™/HACS-supported N-heterocyclic carbene-iron (III) catalyst for efficient conversion of fructose to HMF. ChemSusChem. 2017;**11**(4):716-725. DOI: 10.1002/cssc.201702207

[37] Xu L, Chung LW, Wu Y-D. Mechanism of Ni-NHC catalyzed hydrogenolysis of aryl ethers: Roles of the excess base. ACS Catalysis. 2016;**6**:483-493. DOI: 10.1021/acscatal.5b02089

[38] Saper NI, Hartwig JF. Mechanistic investigations of the hydrogenolysis of diaryl ethers catalyzed by nickel complexes of N-heterocyclic carbene ligands. Journal of the American Chemical Society. 2017;**139**:17667-17676. DOI: 10.1021/jacs.7b10537

[39] Wang K, Heltzel J, Evan S, Culley K, Gabriel L, Adelina V. Transfer hydrogenation of levulinic acid from glycerol and ethanol using water-soluble iridium N-heterocyclic carbene complexes. Journal of Organometallic Chemistry. 2020;**919**:121310. DOI: 10.1016/j.jorganchem.2020.121310

[40] Lu Z, Cherepakhin V, Demianets I, Lauridsen PJ, Williams TJ. Iridium-based hydride transfer catalysts: From hydrogen storage to fine chemicals. Chemical Communications. 2018;**54**:7711. DOI: 10.1039/c8cc03412e

[41] Yong G, Zhang Y, Ying JY. Efficient catalytic system for the selective production of 5-hydroxymethylfurfural from glucose and fructose. Angewandte Chemie International Edition. 2008;**47**:9345-9348. DOI: 10.1002/anie.200803207