UNIVERSITAT ROVIRA I VIRGILI

PYRENE-TAGGED LIGANDS AS A BRIDGE BETWEEN HOMOGENEOUS AND HETEROGENOUS CATALYSIS

Myriam Yasmine Souleymanou

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

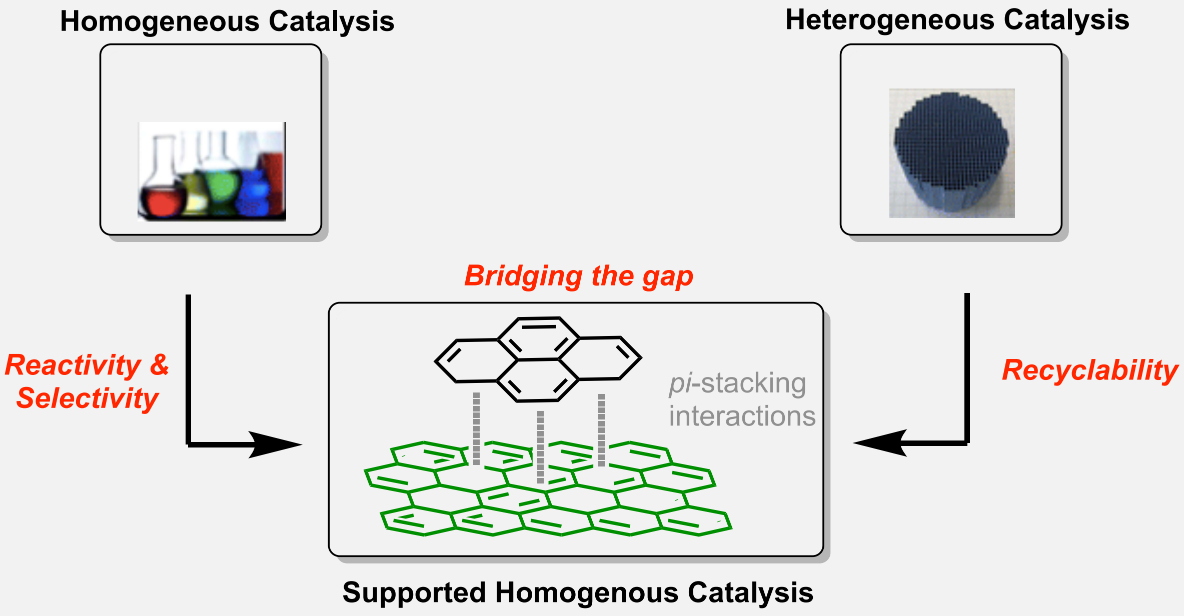
WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.

UNIVERSITAT
ROVIRA i VIRGILI

Pyrene-tagged Ligands as a Bridge between Homogeneous and Heterogenous Catalysis

---

Myriam Yasmine Souleymanou



DOCTORAL THESIS
2019

Myriam Yasmine Souleymanou

Pyrene-tagged Ligands as a Bridge between Homogeneous and Heterogenous Catalysis

DOCTORAL THESIS

Supervised by
Prof. Dr. Cyril Godard and Prof. Dr. Anna Maria Masdeu-Bultò

Departament de Química Física i Inorgànica

UNIVERSITAT
ROVIRA I VIRGILI

Tarragona 2019

UNIVERSITAT ROVIRA I VIRGILI

Departament de Química i Física i Inorgànica
C/ Marcel.lí Domingo s/n, Edifici N4
Campus Sescelades, 43007 Tarragona
Tel. 977 55 80 46

Prof. Dr. Cyril Godard, and Prof. Dr. Anna Maria Masdeu-Bultó from the Department of Physical and Inorganic Chemistry at Universitat Rovira I Virgili,

STATE that the present study, entitled “Pyrene-tagged Ligands as a Bridge between Homogeneous and Heterogenous Catalysis”, presented by Myriam Yasmine Souleymanou for the award of the degree of Doctor, has been carried out under our supervision at the Department of Physical and Inorganic Chemistry at Universitat Rovira I Virgili and that it fulfils all the requirements to be eligible for the International Doctorate Award.

Tarragona, 2019

Doctoral Thesis Supervisors

Prof. Cyril Godard Prof. Anna Maria Masdeu-Bultò

The present Doctoral Thesis has been carried out thanks to the “a Martí Franquès scholarship (2016-PMF-PIPF-47).

The work developed in this doctoral thesis has been possible thanks to the financial support from the following research projects:

- El Ministerio de Economia y Competividad through the project CTQ2016-75016-R
- L’Agencia de Gestió l’Ajuts Universitaris i de Recerca mitjançant el projecte 2014 SGR 670
- L’Agencia de Gestió l’Ajuts Universitaris i de Recerca mitjançant el projecte 2017 SGR 1472
- Europeo de Desarrollo Regional FEDER (AEI/FEDER,UE)
- La Caixa Bank Foundation ayuda de mobilidad 2017ARES-02

This thesis contains confidential data subjected to patent protection in Chapter 5 (pages 98 to 116) through collaboration with Prof. Dr. B. Milani at Trieste University.

> *“Discontent is the first necessity of progress”*
> Thomas A. Edison

Acknowledgements

First of all, I would like to express my sincere thanks to Prof. Carmen Claver for giving me the opportunity to join her group.

I would like to thank Prof. Cyril Godard for the trust, scientific freedom and opportunities I received during these last years. The freedom I was given allowed me to grow and learn more than what I expected when starting my PhD studies.

I would like to thank Prof. Anna Maria Masdeu-Bultó for her guidance, encouragements and help throughout these years.

I would like also to thank Prof. Walter Leitner and Dr. Giancarlo Franciò for the opportunity to work in their laboratories during my Ph.D. I thank those I have met at RWTH Aachen for the valuable advices during my research stay.

I have been lucky to share my time within three research groups and I am grateful to the former students: Alberto, Toni, Fran, Maria, Fatima, Nanette, and current group members: Roger, Lola, Jordi R., Jordi M., Jana, Paul, Joan, Oriol, Jessica, Riccardo, for their support and for making this journey enjoyable. In particular, I am grateful to Raquel, Benedetta and Olivia who have kept me laughing and would spare any time to discuss. To everyone that contributed to this work with daily and practical help, Thank you!

Finally, I am grateful to my wonderful family for their unconditional love, support and endless patience throughout the years.

TABLE OF CONTENTS

The results obtained in this chapter are currently being included in a patent application and will not be described in the public version of this thesis.

CHAPTER 6: Biphasic catalytic system for the telomerization of 1,3-butadiene and carbon dioxide

ABBREVIATIONS AND ACRONYMS

A
acac acetylacetonate
Ad Adamantyl
atm Atmosphere
C
ca. Approximately
CBs Carbon Beads
CNTs Carbon Nanotubes
COD 1,5-cyclooctadiene
conv. Conversion
Cy Cyclohexyl
D
d doublet
dba Dibenzylideneacetone
DCM Dichloromethane
DMAP Dimethylaminopyridine
DMF Dimethyl formamide
DMSO Dimethyl sulfoxide
E
Equiv. Equivalent
Et Ethyl
EtOAc Ethyl acetate
F
FG Functionnal group
G
g Gram
GC-MS Gas Chromatography-Mass Spectrometry
H
H Hours
HB Hydrogen bond
HR-MS High Resolution-Mass spectrometry
Hz Hertz
I
ICP-MS Inductively Coupled-mass spectroscopy
IL Ionic Liquid
IAd 1,3-bis(adamantyl)imidazol-2-ylidene
ICy 1,3-bis(cyclohexyl)imidazole-2-ylidene
IMes 1,3-dimesityl-2-imidazolylidene
iPr isopropyl
IPr 1,3-bis(2,6-diisopropylphenyl)-2-imidazolylidene
IR Infrared spectroscopy
*i*Pr Isopropyl
J
J Coupling constant
L
L Ligand
M
m multiplet
MA Methyl acrylate
Me Methyl
Mes Mesityl
MS Mass Spectrometry
MWCNTs Multi-Walled Carbon Nanotubes
N
NHC N-Heterocyclic Carbene
NMR Nuclear Magnetic Resonance
O
OTs Tosylate
P
$Pd_2(dba)_3$ Tris(dibenzylideneacetone) dipalladium(0)
Ph Phenyl
Py Pyrene
R
rGO reduced graphene oxide
rt Room temperature
X
ppm parts per milion

Pr Propyl
PR_3 Trialkyl phosphine

S

$scCO_2$ supercritical CO_2
s singlet
sept septuplet
SIMes Saturated backbone IMes
SIPr Saturated backbone IPr
SM Suzuki-Miyaura
SWCNT's Single-Walled Carbon Nanotubes

T

t triplet
T temperature
tBu tert-butyl
TFE trifluoroethylene
TEM Transmission Electron Microscopy
THF Tetrahydrofuran
TLC Thin Layer Chromatography
TGA Thermogravimetric analysis
TMS Trimethylsilane
TMSCl Chloro trimethylsilane
TOF Turnover Frequency
TON Turnover Number

U

UV-Vis Ultraviolet-Visible Spectroscopy

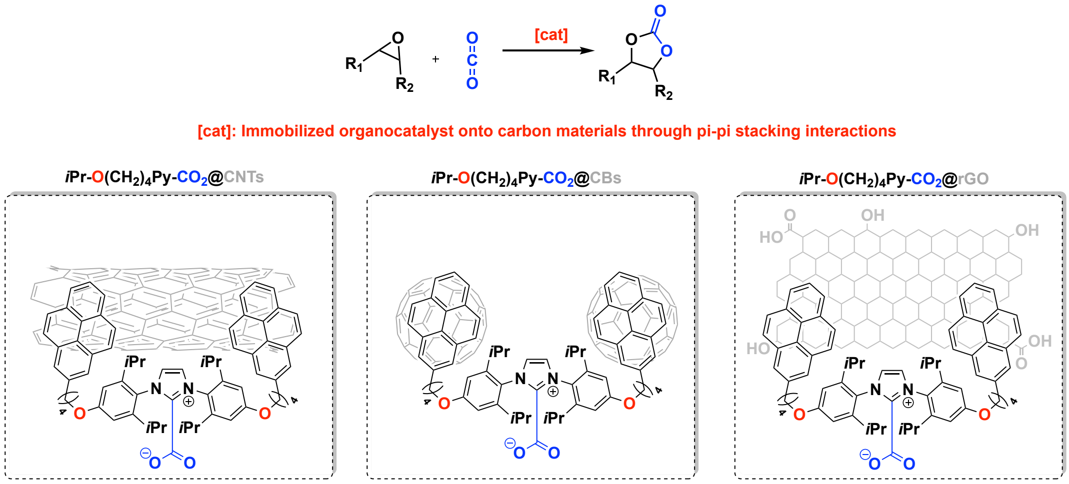
SUMMARY

Homogeneous organometallic complexes of transition metals can be easily modified via modification of the ligand and, after optimization, generally display high catalytic activity and selectivity. However, most homogeneous catalysts have not been widely utilized at industrial scale, especially precious organometallic catalysts, due to limited resources, recycling problems and metal contamination of the products. In contrast, heterogeneous catalysis facilitates the separation and recycling of catalysts, which represents the foremost advantage over homogeneous catalysis.

In recent years, catalyst recycling has increasingly become important with regard to resource conservation and environmental protection. Therefore, seeking an elegant balance between homogeneous and heterogeneous catalysis appears to be particularly significant. Among the reported strategies, the use of immobilized or heterogenized homogeneous catalysts, that are defined modified homogeneous catalysts to render them separable from the starting materials and products, constitutes a potential solution to tackle this challenge.

The present thesis deals with the development of established homogeneous catalysts bearing polyaromatic fragments that would facilitate catalyst grafting and as such, separation and recycling. Pyrene tags were selected as a well-known antenna that promote strong aromatic π-π stacking interactions with carbon surfaces. Consequently, we focused our attention on carbon supports (carbon nanotubes, reduced graphene oxide and carbon beads) as solid supports for this noncovalent anchoring strategy on solid supports.

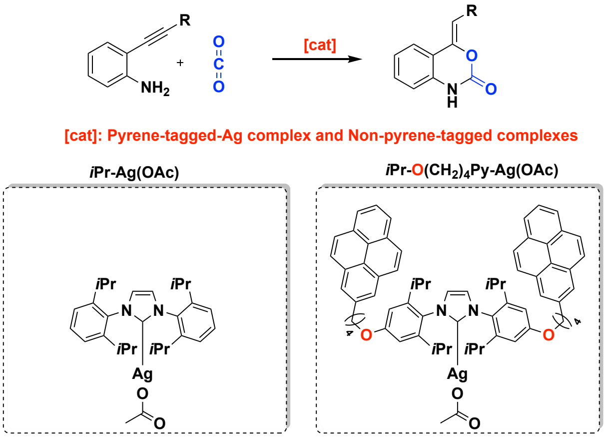
In this context, the general merits and conceptual challenges of summing-up the advantages of homogeneous and heterogenous catalysis are presented in Chapter I. Traditional methods for catalyst recovery and some novel approaches are discussed to highlight both limitations and opportunities of these promising systems. In addition, the current state-of-the-art on transition metal complexes bearing N-Heterocyclic Carbenes (NHC) and NHC as organocatalyst are presented. In Chapter II, the general objectives of the thesis are presented, and Chapter III describes the synthesis of pyrene tags imidazolium carboxylates derived from NHC (Scheme 1). These pyrene-tagged imidazolium carboxylates were applied in the cycloaddition of epoxides and carbon dioxide (CO_2) and compared to their non-pyrene-tagged analogs. Further immobilization of the most active pyrene functionalized imidazolium carboxylate onto carbon surfaces was performed.



Scheme 1. *Cycloaddition of epoxides and carbon dioxide using immobilized organocatalyst onto carbon materials, carbon nanotubes (CNTs), carbon beads (CBs), reduced graphene oxide (rGO)*

Recycling experiments of the supported organocatalyst onto multiwalled carbon nanotubes (CNTs), reduced graphene oxide (rGO), carbon beads (CBs) were carried out in batch mode. Drastic decrease in the 2nd run and 3rd run was observed in the case of pyrene-tagged imidazolium carboxylate supported onto CNTs and CBs respectively due to catalyst leaching. However, the organocatalyst supported onto rGO was recycled up to 5 runs without significant loss of catalytic activity. Therefore, various epoxides were converted into their corresponding cyclic carbonates.

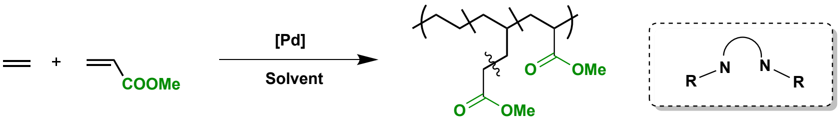
In Chapter IV, the synthesis of a silver(I) complex bearing pyrene functionalized NHC ligand was described. The potential of the non-pyrene-tagged Ag complex and the pyrene-tagged Ag(I) complex were explored in CO_2 conversion to benzoxazine-2-one derivatives (Scheme 2).



Scheme 2. *Synthesis of benzoxazine-2-one derivatives using silver complexes*

The pyrene-tagged Ag(I) complex was immobilized onto the surface of rGO via π-π stacking interactions and after optimization of the reaction conditions, was applied in the incorporation of carbon dioxide into *o*-ethynylaniline to afford the corresponding benzoxazine-2-ones.

The investigation carried out in Chapter V deals with the synthesis and characterization of pyrene tagged-Pd complexes and their application in the copolymerization of ethylene and methyl acrylate (MA). This part of the research was carried out in collaboration with the group of Prof. Dr. B. Milani from Trieste University. An important part of the work consisted in the synthesis of the α-diimine ligands. Next, the neutral Pd(II) complexes were synthesized and subsequent synthesis of the monocationic Pd(II) complexes were easily performed by the PhD Anna Dall'Anese at Trieste University in Italy. These monocationic Pd-complexes were successfully applied in the copolymerization of ethylene and MA under mild reaction conditions (Scheme 3.).

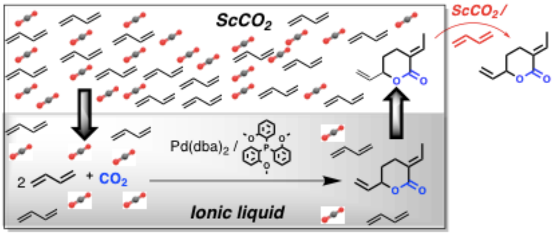


Due to confidentiality, chemical structure's details of the Pd catalysts have been consciously removed

Scheme 3. *Pd-catalyzed copolymerization of ethylene and methyl acrylate, Py= pyrene*

The results obtained are currently being included in a patent application and will not be described in the public version of this thesis.

In the last Chapter (Chapter VI), another strategy for the recycling and reuse of homogeneous catalyst is explored. A biphasic catalytic system consisting of ionic liquids (ILs) and supercritical carbon dioxide ($scCO_2$) was used. The Pd-catalyzed telomerization of 1,3-butadiene and carbon dioxide that yield δ-lactone was explored in this biphasic system. It constitutes an ideal catalytic reaction as CO_2 will be used both as reagent and carrier for product extraction in continuous flow manner (Scheme 5). This part was performed in the group of Prof. Dr. W. Leitner at RWTH Aachen University.



Scheme 5. *Pd-catalyzed telomerization of 1,3-butadiene and carbon dioxide with continuous extraction of δ-lactone product*

Using this biphasic catalytic system, we established the feasibility of the telomerization reaction. Next, optimization of the reaction conditions to obtain δ-lactone with high yield and selectivity is described. The synthesis of nitrile functionalized ionic liquids was carried out to improve the stability of the Pd-active species in the telomerization reaction. Moreover, an application of the telomerization reaction of 1,3-butadiene and carbon dioxide with extraction of δ-lactone in a continuous-flow manner was performed. δ-lactone was extracted with a selectivity of 85% without contamination by the IL and metal catalyst.

Chapter 1

“General Introduction”

1.1 Homogeneous and Heterogeneous Catalysis

The term ‘catalysis’ was first coined by Berzelius in 1836 when he noticed changes in substances when they were brought in contact with small amounts of certain substances later known as ‘catalysts’.[1] The definition that nowadays is used reads: “A catalyst is a substance that increases the rate of a chemical reaction without being consumed in the process”. Indeed, it provides a reaction pathway with lower free energy change to the rate-limiting transition state than the corresponding non-catalyzed reaction. Therefore, the presence of a catalyst, affects the kinetic aspects of a reaction by lowering the activation energy without affecting its thermodynamics, *i.e.* the product distribution at equilibrium (Figure 1.1.).[1]

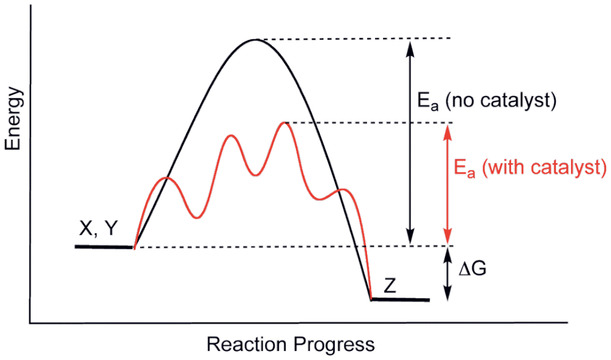


Figure 1.1. *Energy profile for a catalyzed multi-step reaction (in red) and an uncatalyzed reaction (in black)*

In industry, catalysis plays a key role, enabling a wide range of chemical transformations and reducing cost, time, and in many cases preventing the use of stoichiometric reagents, thus minimizing waste and contributing to the development of more environmentally friendly processes.[2] Leaving enzymes apart, catalysts may be generally divided into homogeneous and heterogeneous catalysts, depending on whether the catalysts are in the same or a distinct phase than the reagents.

Typical heterogeneous catalysts are oxides, or supported metal particles. Important factors influencing the activity of these catalysts include the rate of diffusion of reactants towards the catalytic body, adsorption of reactants, desorption of the products, the presence of catalytically active sites which is related to the surface area of the solid, etc… In general heterogeneous catalysts require harsh reaction conditions, such as high temperatures or pressures in order to overcome these series of rate determining processes, however their solid nature has greatly helped their implementation in industrial processes due to the ease of separation from the products which lie in a different phase, and due to the easy handling of these catalysts, which

---

[1] P.W.N.M. Van Leeuwen, Homogeneous Catalysis: Understanding the Art, Eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, **2004**

[2] A. Behr, A.J. Vorholt, T. Seidensticker, *ChemBioEng. Rev*. **2015**, 2, 6-21

are generally very robust and can be used under rather extreme reaction conditions without decomposition.[3] Some examples of the application of this kind of catalysts in industry are the production of sulphuric acid which uses a vanadium catalyst,[4] the Haber-Bosch process[5] for the production of ammonia which uses a heterogeneous iron catalyst or the zeolites used in the cracking of hydrocarbons mixtures. Heterogeneous catalysis is usually associated to the bulk chemical industry.

In contrast, homogeneous catalysis is more related to the field of fine chemistry, although some industrially relevant processes for the production of bulk chemicals also rely on homogeneous catalysis. In contrast with heterogeneous catalysts, homogeneous species have a well-defined structure, and every single catalytic entity can act as a single active site, which makes them intrinsically more active and selective. Several classes of chemical compounds can function as homogeneous catalysts, namely Brønsted and Lewis acids, bases, organic molecules such as proline or quinine… but nowadays, the term homogeneous catalyst usually refers to organometallic or coordination complexes. With this type of catalysts, the choice of the metal and the design of the ligands have an important influence on the reactivity and selectivity of the reaction. Moreover, the reaction mechanisms are considerably easier to study since powerful spectroscopic methods such as NMR can be used to assign structures and follow reaction kinetics. Moreover, diffusion and dissipation of heat rarely is a problem.[6]

Over the last decades, scientific research has led to enormous progress in this field. Nowadays, myriads and myriads of transition metal complexes have been developed showing excellent activity and selectivity in almost any organic transformation known and have helped to discover and develop new chemical processes. Furthermore, they are usually very versatile and able to transform various types of substrates under mild reaction conditions. However, to date, heterogeneous catalysts have been more widely used by industry. The main drawbacks associated with soluble transition metal catalysts are their intrinsic thermal instability and the difficulties in separating them from the products, which result in toxic metal contamination of the products and hamper the recovery and reuse of the often very expensive catalysts (Table 1.1.).[6b, 7]

---

[3] A. Corma, *Cat. Rev.* **2004**, 46, 369-417

[4] H. Müllerl, “Sulfuric acid and sulfur trioxide”, Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH, **2002**, vol. 35, pp141-211

[5] M. Appl, “Ammonia”, Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH, **2012**, vol. 3, pp 107-137

[6] a) L.A. Oro, E. Sola, Fundamentos y aplicaciones de la Catálisis Homogénea, Prensas Universitarias de Zaragoza, Zaragoza, **2000**; b) B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, **1996**

[7] J. A. Gladysz, *Chem. Rev.* **2002**, 102, 10, 3215-3216

Table 1.1. Homogeneous versus Heterogeneous Catalysis[7]

Property	Homogeneous	Heterogeneous
Catalyst recovery	Difficult and Expensive	Easy and Cheap
Thermal stability	Poor	Good
Selectivity	High	Variable
Activity	High	Variable
Reaction conditions	Mild	Mild, Harsh
Catalyst tunability	Advanced	Limited

The recognition of this inherent limitation of homogeneous catalysts has led to a flourishing activity attempting to device heterogenized versions with the aim of combining the advantages of homogeneous catalysts with the facility of heterogeneous systems to recover and reuse the catalyst.[8] Many very ingenious approaches are being studied in this regard which will be described in the next section.

1.2 Homogeneous but recoverable catalytic systems

Several strategies have been developed for the recovery and reuse of homogeneous catalysts and for an appropriate separation of the catalyst from the products.[9] Among the different approaches, attachment of homogeneous catalysts to the surface or to the inner structure of a solid support material is undoubtedly the dominant approach towards the design of so called "heterogenized catalysts".[6a] A variety of strategies have been reported to successfully immobilize molecular metal catalysts onto solid supports.[9] The classification of these strategies is usually based on the type of interaction between the catalyst and the support (Figure 1.2.). Among them, the most common ones are covalent binding, electrostatic interaction, encapsulation and adsorption.

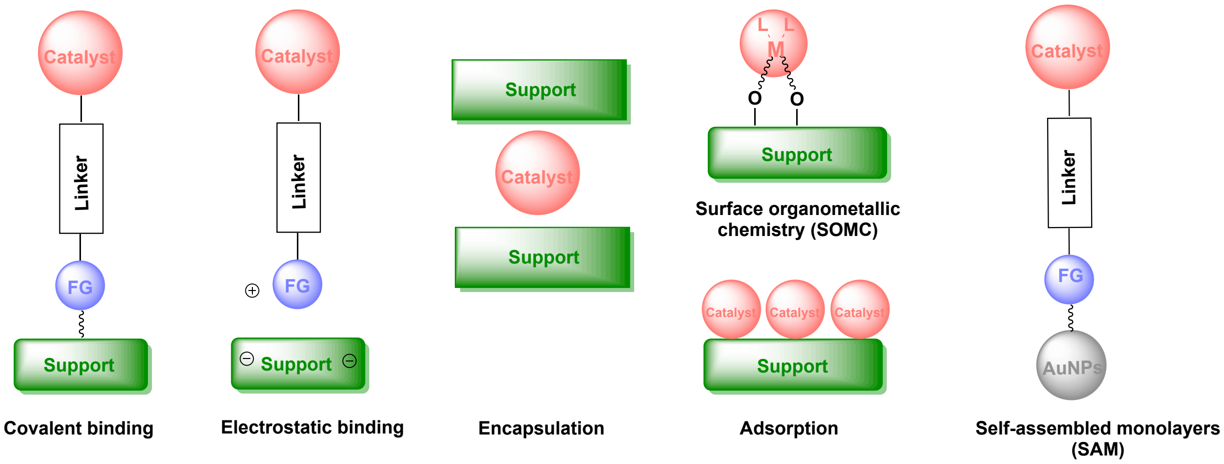


Figure 1.2. *Main strategies for the immobilization of homogeneous catalysts onto solid supports*

---

[8] P. Barbaro, F. Liguori, Heterogenized Homogeneous Catalysts for Fine Chemical Production, Catalysis by Metal Complexes, Eds. Springer, **2010**

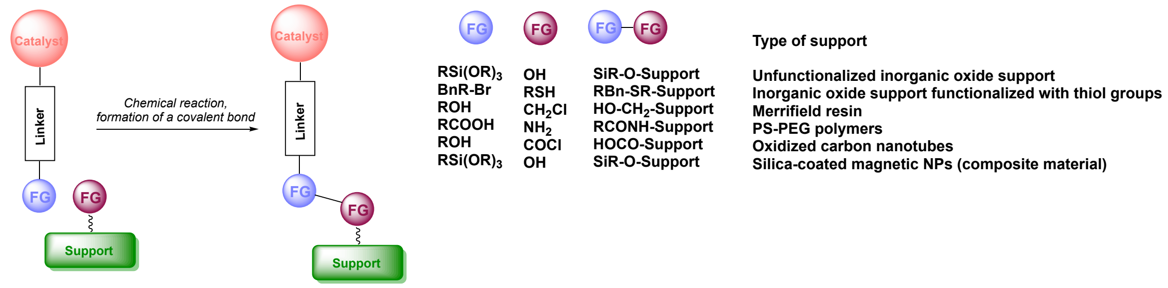
[9] a) D. J. Cole-Hamilton, R. P. Tooze, Catalyst Separation, Recovery and Recycling; Chemistry and Process Design, Eds. Springer, Dordrecht, **2006**; b) M. Bengalia, Recoverable and Recyclable Catalysts, Eds. Wiley-Blackwell, Chichester, **2009**

Less common methods exist, as is the case of Surface Organometallic Chemistry (SOMC),[10] or interaction with gold NPs through a thiol group, forming self-assembled monolayers (SAM).[11] According to the strength of the linkage between the catalyst and the support, the covalent binding and electrostatic interactions represent the strongest types of interactions. When weaker interactions are used, the most relevant types are encapsulation and adsorption. Examples from the latter include catalysts attached to the surface of the support through either Van der Waals forces, hydrogen bonding and hydrophobic interactions. A very interesting type of recyclable systems arising from weak interactions with the support are Supported Liquid Phase Catalysts (SILP),[12] where a thin film of a liquid phase is physisorbed at the surface of the support (usually a thin film of water, or ionic liquid), and the catalyst is dissolved in this thin film. The actual aspect of the supported catalyst is solid, since very low amounts of the liquid film are usually introduced.

1.2.1 Immobilization of homogeneous catalysts through covalent interactions

The covalent binding of a metal complex onto a solid support implies the need of a chemical reaction to establish a covalent bond between one of the ligands in the complex and the support. Therefore, the ligand must be appropriately functionalized.

Additional synthetic efforts are thus required to introduce such functionality, and care needs to be taken to avoid undesired interactions between the pro-immobilizable functional groups and the metal center. However, the enhanced stability provided by this binding usually makes the resulting heterogenized complexes more robust, and less prone to metal leaching compared to softer immobilization strategies.[9] This approach can be applied to almost any type of support material, since functional groups on the support can serve as anchoring points (Scheme 1.1.).



FG	FG	FG–FG	Type of support
$RSi(OR)_3$	OH	SiR-O-Support	Unfunctionalized inorganic oxide support
BnR-Br	RSH	RBn-SR-Support	Inorganic oxide support functionalized with thiol groups
ROH	CH_2Cl	$HO\text{-}CH_2\text{-}Support$	Merrifield resin
RCOOH	NH_2	RCONH-Support	PS-PEG polymers
ROH	COCl	HOCO-Support	Oxidized carbon nanotubes
$RSi(OR)_3$	OH	SiR-O-Support	Silica-coated magnetic NPs (composite material)

Scheme 1.1. *Representation of various linkages created through covalent binding between differently functionalized catalysts and different types of supports*

---

[10] a) C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Esteves, A. Fedoriv, V. Mougel, H. Nagae, F. Nuñez-Zarur, P. A. Zhizhko, *Chem. Rev*. **2016**, 116, 323-421; b) M. K. Samantaray, E. Pump, A. Bendjeriou-Sedjerari, V. D'Elia, J. S. A. Pelletier, M. Guidotti, R. Psaro, J. Marie-Basset, *Chem. Soc. Rev.* **2018**, 47, 8403-8437

[11] D. Sheet, A. Bera, R. Dev-Jana, T. Kanti-Paine, *Inorg. Chem.* **2019**, 58, 8, 4828-4841

[12] a) A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid, *Angew. Chem. Int. Ed*. **2005**, 44, 815-819; b) P. Lozano, Sustainable Catalysis in Ionic Liquids, CRC Press, New York, **2018**; c) J. M. Marinkovic, A. Riisager, R. Frankle, P. Wasserscheid, M. Haumann, *Ind. Eng. Chem. Res.* **2019**, 58, 7, 2409-2420

Inorganic oxide supports (either amorphous such as silica gel or mesoporous crystalline such as MCM-41) can be directly functionalized with a catalyst through their available surface hydroxyl groups.[13] Alternatively, functional groups can be introduced onto the solid surface prior to catalyst immobilization. Amino-[14] and thiosilicas[15] bearing an alkyl linker between the functional group and the support are common examples of this type. Carbonaceous materials, such as carbon nanotubes, usually undergo oxidative treatment to generate hydroxyl or carboxylic groups which are subsequently used to generate ester, amide or ether linkages.[16] Other types of materials that offer the possibility of covalent functionalization are composite materials (such as silica coated maghemite NP's)[17], or membranes.[18]

The covalent binding has been extensively applied, and especially in the case of inorganic oxides and polymeric supports various synthetic alternatives have been described.[9] For the former type of supports, grafting methods, sol-gel synthesis or solid-phase synthesis have been reported, resulting in different properties of the final materials. In the case of polymers, grafted polymers, copolymers or self-supported catalysts are among the alternatives to obtain heterogenized materials.

1.2.2 Immobilization of homogeneous catalysts through electrostatic interactions

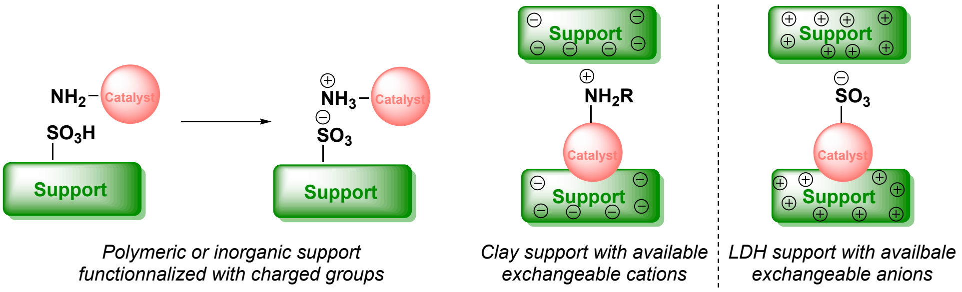
In order to immobilize a catalyst onto a solid support through electrostatic interactions, the support and the catalyst must be electrically charged, but in contrast with covalent binding, no chemical reaction is required between the catalyst and the support. There are two possible ways to immobilize a catalyst onto a support via electrostatic interactions, depending on whether the neat charge is situated in one of the ligands or at the metal center.

To situate the charge on one of the ligands, appropriate (charged) functional groups need to be introduced. Most frequently, ammonium (NR_4^+) or sulphonate (RSO_3^-) groups are used.[19] Polymers and inorganic solids can be functionalized in this way.[20] Moreover, this option has been applied for the immobilization of catalysts onto layered solids, such as clays or Layered Double Hydroxides (LDH).[21] The former supports have exchangeable

---

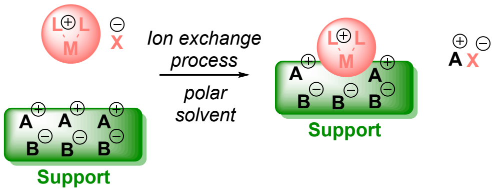
[13] A. Corma, H. García, *Adv. Synth. Catal*. **2006**, 348, 1391-1412
[14] H. Hagiwara, K. Hyeok Ko, T. Hoshi, T, Suzuki, *Synlett* **2008**, 4, 611-613
[15] M. Al-Hashimi, A. Qazi, A.C. Sullivan, J.R.H. Wilson, *J. Mol. Catal. A Chem*. **2007**, 278, 160-164
[16] N. Karousis, N. Tagmatarchis, D. Tasis, *Chem. Rev*. **2010**, 110, 5366-5397
[17] P.D. Stevens, G. Li, J. Fan, M. Yen, Y. Gao, *Chem. Commun*. **2005**, 4435-4437
[18] I.F.J. Vankelecom, *Chem. Rev*. **2002**, 102, 3779-3810
[19] Y. Arakawa, N. Haraguchi, S. Itsuno, *Tetrahedron Lett*. **2006**, 47, 3229-3243
[20] F. Rajabi, D. Schaffner, S. Follmann, C. Wilhelm, S. Ernst, W.R. Thiel, *ChemCatChem* **2015**, 7, 3513-3518
[21] S. Bonnet, C. Forano, A. de Roy, J. P. Besse, P. Maillard, M. Monenteau, *Chem. Mater*. **1996**, 8, 8, 1962-1968

cations and a negatively charged matrix, whereas the latter have a positively charged matrix and exchangeable hydroxide anions (Scheme 1.2.).



Scheme 1.2. *Catalyst immobilization through electrostatic interactions between charges within the ligand and charges in the support*

Alternatively, the electrostatic interaction can be established between the support and the charged metal center in ionic complexes.[22] This strategy does not require the functionalization of one of the ligands with charged groups. Usually, inorganic supports containing exchangeable cations are used. A cation exchange takes place between the charged metal ion in the complex and a cation present in the support, usually Na^+ or H^+ (Scheme 1.3).



Scheme 1.3. *Heterogenization of a metal complex through electrostatic interaction between the metal center and the support*

Typical catalysts that can be immobilized by this approach include Rh(I)diphosphine, Mn(III) salen or Cu complexes with various types of ligands. This approach has provided good results in some cases,[23] however the biggest limitation of this method is that any change in the oxidation state of the metal center during the course of the catalytic reaction may affect the electrostatic interaction resulting in leaching of the catalyst.[24]

In conclusion, the immobilization of catalysts through electrostatic interactions provides robust systems, although appropriate solvents must be selected to reinforce the interactions between the catalyst and the support and special attention must be paid to operate under reaction conditions where ion exchange cannot occur.

---

[22] R. A. Feldman, J. M. Fraile, *Catal. Commun*. **2016**, 83, 74-77

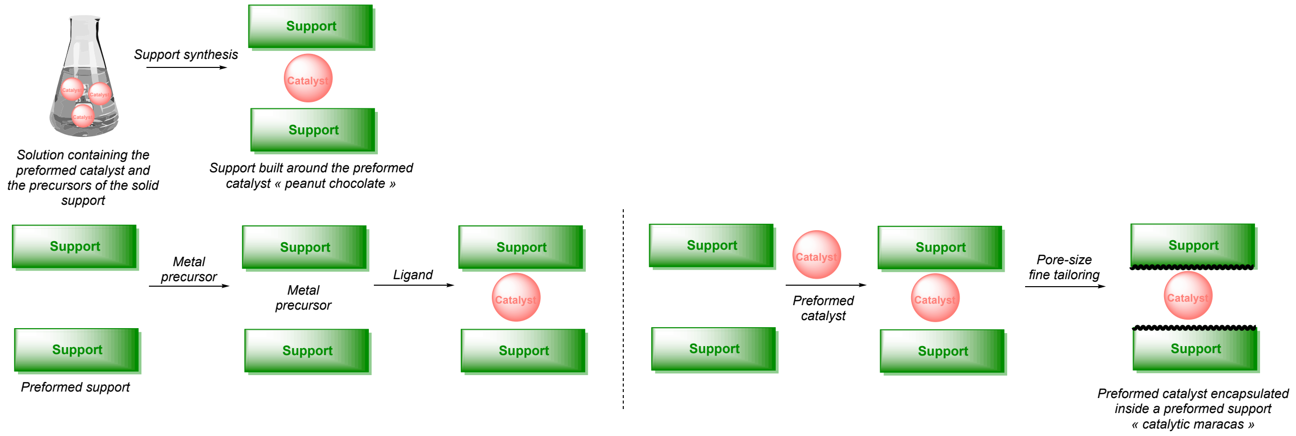
[23] W.P. Hems, P. McMorn, S. Riddel, S. Watson, F.E. Hancock, G.J. Hutchings, *Org. Biomol. Chem*. **2005**, 3, 1547-1550

[24] C. Simons, U. Hanefeld, I.W.C.E. Arends, R.A. Sheldon, T MaschMeyer, *Chem. A. Eur. J.* **2004**, 10, 5829-5835

1.2.3 Immobilization of homogeneous catalysts through encapsulation

When a catalyst is immobilized onto a solid support through encapsulation, the catalyst molecules get occluded within the pores of the resulting solid and cannot diffuse out whereas reactants and reagents do not have any diffusion restriction in principle.[25a] The immobilization thus responds to a physical confinement and further interactions between the catalyst and the support are not required. Therefore, rigid supports with constant pore sizes are preferred over more flexible matrices in order to minimize metal leaching, if the pore and catalyst sizes are adequate. Two main strategies have been described to encapsulate homogeneous catalysts (Scheme 1.4.). They consist on either building the catalyst inside the pores of the support, or alternatively building the support around a preformed catalyst. In principle, both strategies may lead to identical immobilized catalysts.

Building the support around the preformed metal complex is usually selected when the catalyst is too large in relation to the pore size of the support. For instance, metalloporphyrins or larger metallophthalocyanines which have been encapsulated within the supercages of zeolite Y.[25b]



Scheme 1.4. *Possible strategies for encapsulating homogeneous catalysts in the pore structure of a solid support*

Zeolites have also been used to encapsulate catalysts via the method called “ship in a bottle”. Usually, a metal cation is introduced first by ion exchange, and then the ligand is introduced, yielding the complex.[26] Support materials with larger pore sizes can help to overcome diffusion limitations that are sometimes encountered with microporous materials. This is the case of Ordered Mesoporous Silicas (OMS) with supercage-like structures (mimicking the crystalline structure of zeolites). To prevent catalyst diffusion out of the nanocages of the material, the size of the entrance to these spaces is reduced

---

[25] a) J. M. Fraile, J. I. Garcia, J. A. Mayoral, *Chem. Rev*. **2009**, 109, 360-417; b) B. Z. Zhan, X.Y. Li, *Chem.Commun*. **1998**, 349-350

[26] a) W. Kahlen, A. Janssen, W.F. Holderich, *Stud. Surf. Sci.Cata*. **1997**, *108*, 469-476; b) A. Zsigmond, K. Bogar, F. Notheisz, *Catal. Lett*. **2006**, *83*, 55-58

by treating the material with a silylating agent.[27] Following this approach, the catalyst can be either built inside the support, or introduced as a preformed complex if the pore sizes are large enough compared to the size of the molecular catalyst. In the latter case, the presence of un-complexed metal that may act as competing catalytic species is avoided.

1.2.3 Immobilization of homogeneous catalysts through adsorption

Immobilizing homogeneous catalysts onto a solid by mere physisorption may be considered as the most straightforward strategy available, since in principle, neither catalyst nor support have to be modified. The main drawback associated to this strategy however, is the weak van der Waals forces associated to the physisorption phenomenon, so leaching of the catalyst into the solution is usually observed.[28] To overcome this problem, efficient catalyst adsorption must rely on stronger interactions, such as hydrogen bonding,[29] hydrophobic effect[30] or π-π stacking interactions.[31] Hydrogen bonding interactions can be established between a polar (or charged) functional group, sulfonate groups for instance in one of the ligands and surface hydroxyl groups present on the support.[32] In the case of cationic metal complexes, the counter anion can establish hydrogen bonds with the support.[33] Hydrophobic interactions can also be used to attach the catalyst to a support. The most typical example of this strategy involves the use of hydrophobic silicas, obtained after trialkylsilylation of the surface hydroxyl groups.[34]

Other interactions that can be included among these types of relatively weak surface are those occurring between polyaromatic systems and carbonaceous surfaces, namely π-π stacking interactions. For these interactions a direct relationship between aromatic ring size and strength of the interaction was demonstrated.[32] Using this method, very robust catalytic systems bearing pyrene moieties have been reported, with negligible metal leaching.[35] Their most important drawback is that during catalysis, factors such as the polarity of the solvent, or the reaction temperature must be well controlled to avoid metal leaching.[29]

---

[27] Q.H. Yang, D.F. Han, H.Q. Yang, C. Li, *Chem. Asian. J.* **2008**, *3*, 1214-1229

[28] M. Inoue, K. Ohta, N. Ishizuka, S. Enomoto, *Chem. Pharm. Bull.* **1983**, *31*, 3371-3376

[29] P. Gamez, F. Fache, M. Lemaire, *Bull. Soc. Chim. Fr.* **1994**, *131*, 600-602

[30] N. Ishizuka, M. Togashi, M. Inoue, S. Enomoto, *Chem. Pharm. Bull.* **1987**, 35, 1686-1690.

[31] B. R. Lydon, A. Germann, J. Y. Yang, *Inorg. Chem. Front.* **2016**, 3, 836–841

[32] P. Barbaro, C. Bianchini, V. Dal Santo, A. Meli, S. Moneti, R. Psaro, A. Scaffidi, L. Sordelli, F. Vizza, *J. Am. Chem. Soc.* **2006**, *128*, 7065-7076

[33] F.M. de Rege, D.K. Morita, K.C. Ott, W. Tumas, R.D. Broene, *Chem. Commun.* **2000**, 1797-1798

[34] P. Handa, K. Holmberg, M. Sauthier, Y. Castanet, A. Mortreux, *Micropor. Mesopor. Mater.* **2008**, *116*, 424-431

[35] a) S. Sabater, J. A. Mata, E. Peris, *ACS Catal.* **2014**, *4*, 2038-2047; *Organometallics* **2015**, 3*4*, 7, 1186-1190; b) J. A. Mata, F. E. Hahn, E. Peris, *Chem. Sci.* **2014**, *5*, 1723-1732; c) E. Peris, *Chem. Commun.* **2016**, *52*, 5777-5787

1.3 N-Heterocyclic Carbenes

1.3.1 History of NHCs

Carbenes are neutral compounds featuring a divalent carbon atom surrounded by six-electron valency.[36] Considering a prototype carbene (Figure 1.3.a.), the carbon atom can be either linear or bent depending on the hybridization of the carbene carbon atom. The sp-hybrid orbitals, coupled with two energetically degenerated p orbitals, and the sp^2-hybrid orbitals (δ orbitals), coupled with a p orbital (pπ orbital), promote the linear or bent geometry, respectively (Figure 1.3.b.).[37] The reactivity and the properties of carbenes (with bent geometry) are strongly affected by the ground-state multiplicity of them. Therefore, they are classified into singlet and triplet ground states. Singlet carbenes feature a filled and a vacant orbital, thereby showing ambiphilic character while triplet carbenes have two singly occupied orbitals and are generally regarded as diradicals.[37]

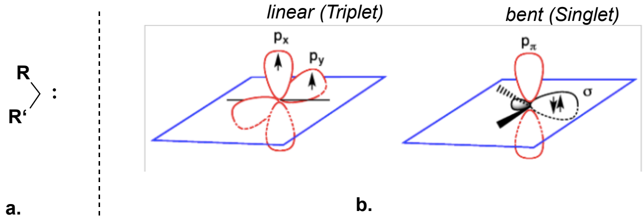


Figure 1.3. *a. Schematic representation of a carbene; b. Geometry at the carbene carbon atom: linear and bent.*

First attempts to isolate carbenes date back to the early 1960s with the studies of Wanzlick.[37] Although carbenes could be trapped in the presence of a metal fragment, only "carbene dimers" were isolated in the absence of an appropriate trapping agent.[38] The first free organic carbene was isolated by Bertrand *et al.* in 1988.[39] However, N-Heterocyclic carbene (NHC) remained a curiosity until reports from Arduengo *et al.* in 1991 (Figure 1.4.).[40] This unequivocal isolation of an NHC and its crystal structure analysis initiated widespread research into NHCs and their metal complexes.

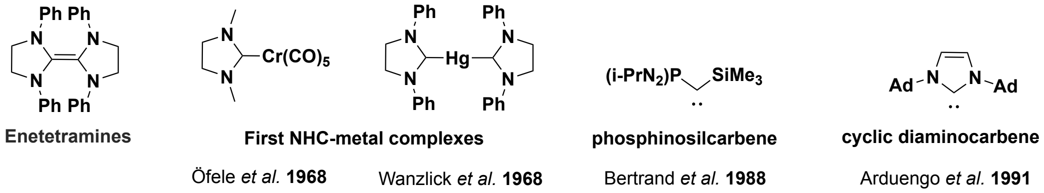


Figure 1.4. *First stable carbenes (Ad= adamantyl)*

---

[36] a) D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*, **2000**, *100*, 39-92; b) M. Feroci, I. Chiarotto, A. Inesi, *Catalysis* **2016**, *6*, 1-23

[37] H. W. Wanzlick, *Angew. Chem., Int. Ed. Ed. Engl.,* **1962**, *1*, 75-80

[38] M. K. Denk, K. Hatano, M. Ma, *Tetrahedron Lett.* **1999**, 2057-2060

[39] A. Igua, H. Grutzmacher, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, **1988**, *110*, 6463-6466

[40] A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, **1991**, *113*, 361-363

1.3.2 Structures and general properties

1.3.2.1 Stabilization of NHCs

Among the five-membered ring NHCs (Figure 1.5.), imidazolylidenes, imidazolinylidenes, thiazolylidenes, triazolylidenes and pyrazolylidenes are the most studied.

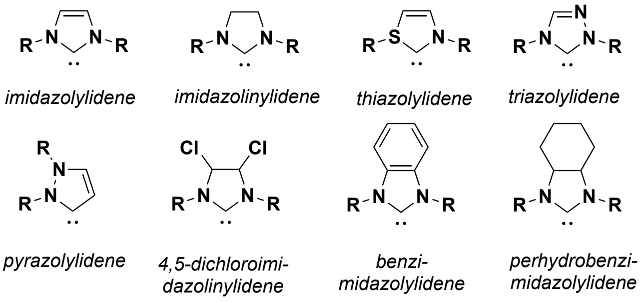


Figure 1.5. *A Selection of NHC structures*

N-Heterocyclic carbenes (NHCs) are defined as heterocyclic species containing a singlet carbene carbon stabilized by two α-bonding nitrogen heteroatoms.[36, 41] Their stability is explained by a combination of both steric and electronic effects of the α-substituents at the carbene carbon atom. For practical use in organocatalysis and/or organometallic chemistry, the long-lived singlet carbene is desired rather than the unstable triplet carbene (half-life time up to 1h at most).[37] Inductively, the adjacent σ-electron-withdrawing nitrogen substituents favor the singlet state by increasing the gap in energy between the pπ orbital and the σ-orbital. Mesomerically, π-electron-donating nitrogen substituents stabilize carbenes *via* interaction with the substituent lone pairs, resulting in bent carbenes. Whereas, triplet ground state is stabilized by σ-electron donating substituents and π-electron-acceptors resulting in linear carbenes (Figure 1.6.).[42]

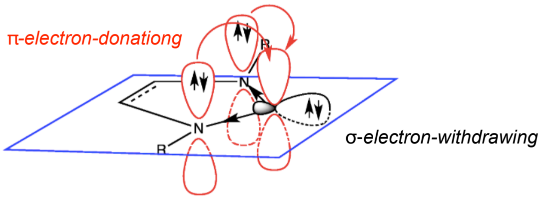


Figure 1.6. *Imidazol-2-ylidene structure showing stabilization by electron donation*[37b]

Figure 1.7 highlights the different mesomeric forms of NHCs due to the presence of two nitrogen atoms next to the carbene center. The formation of the four-electron three-center π system further increases the stability of NHCs.[43]

---

[41] P. de Fremont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.*, **2009**, *253*, 862-892

[42] a) L. Pauling, J. Chem. Soc., *Chem. Commun.*, **1980**, 688-689; b) J. F. Harrison, R. C. Liedtke, J. F. Liebman, *J. Am. Chem. Soc.,* **1979**, *101*, 7162-7168

[43] B. Maji, M. Breugst, H. Mayr, *Angew. Chem., Int. Ed.*, **2011**, *50*, 6915-6919

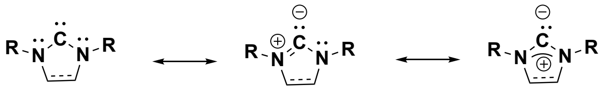


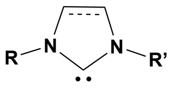
Figure 1.7. *Mesomeric structures of NHCs and mesomeric stabilization of the singlet ground state*

In addition, steric effects can also influence the ground state spin multiplicity. Hence, increasing the steric bulk of the carbene substituents broadens the carbene angle and favors a triplet ground state configuration. However, the electronic effects of the substituents of the carbene center have a larger impact on the reactivity and stability of the carbene. Moreover, the cyclic nature of the NHCs also helps to favor the singlet state by forcing the carbene carbon into a bent, more sp^2-like arrangement.[44]

1.3.2.2 Modularity of NHCs

An appealing feature of NHC ligands is the possibility to tune their steric and electronic properties by varying parts of the ligand structure (Figure 1.8.).

Electronic effets
- N-subtituents
- Introduction of substituents at the NHC backbone
- Number of heteroatoms (2, 3, 4)
- Type of heterocylce (aromatic or not)



Steric effects
- N-subtituents
- Ring size

Figure 1.8. *Versatility in the variation of the steric and electronic parameters of the NHC ligands*

The electronic parameters can be modified by introducing changes within the cyclic core structure,[45] such as varying the number and identity of heteroatoms present, or the location of the carbene center within the ring. Introduction of electron withdrawing substituents at the C4-C5 positions has been shown to greatly influence the properties of the NHC ligands by reducing their electron density.[46] The steric demand of the NHC ligand can be modulated by changing the substituents on the N wingtips, and also by varying the ring size.

1.3.3 Coordination of NHCs to transition metal catalysts

1.3.3.1 N-Heterocyclic Carbene ligand synthesis

There are numerous routes to the various N-heterocyclic carbene systems.[47] The synthesis of 1,3-disubstituted imidazolium salts has long been established,[48] as these can be easily deprotonated to give the carbene species.[49]

---

[44] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature*, **2014**, *50*, 485-496

[45] T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.*, **2010**, *49*, 6940-6952

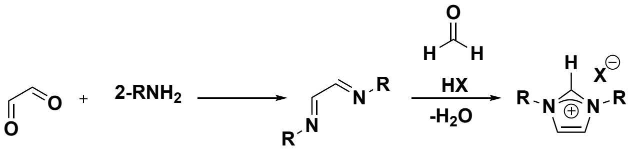
[46] M. Viciano, E. Mas-Marzá, M. Sanaú, E. Peris, *Organometallics*, **2006**, *25*, 3063-3069

[47] L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705-2733

[48] A. Arduengo, U.S. Patent 5077414, **1991**

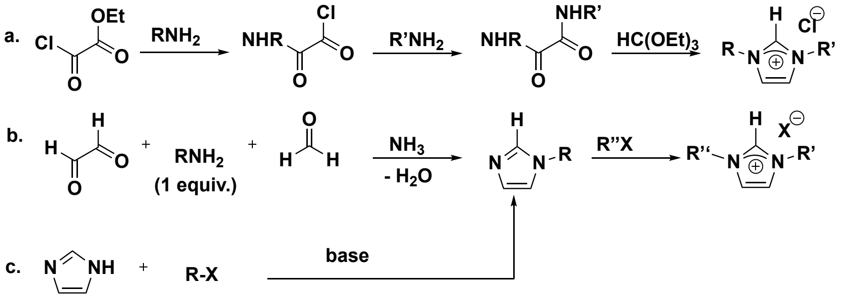
[49] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361-363

The procedure to form symmetrical imidazolium salts is a two-step process, which can be carried out in a single vessel (Scheme 1.5.). This is achieved by the condensation of glyoxal with the primary amine followed by a cyclisation with paraformaldehyde under acidic conditions to give the imidazolium salt. These salts are stable, can be produced on a large scale and can be stored in air.[50]



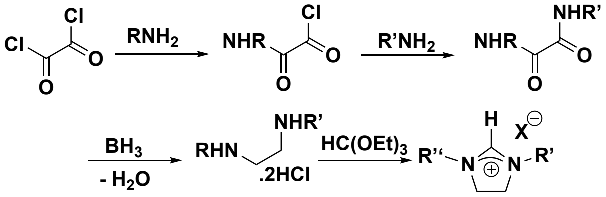
Scheme 1.5. *Symmetrical NHC.HX synthesis*

In order to access unsymmetrical NHCs,[51] the nitrogen substituents are introduced in two different steps. This can be achieved using one equivalent of the amine, with oxalic acid monoethyl ester chloride then adding the other amine group followed by cyclisation using triethylorthoformate (Scheme 1.6.a.). Instead, the mono-substituted imidazolium ring can be prepared first, using one equivalent of the amine, with glyoxal and paraformaldehyde (Scheme 1.6.b.), or from a preformed imidazole (Scheme 1.6. c.) after which the other substituent is introduced.



Scheme 1.6. *Synthetic route to unsymmetrical imidazolium salts*

The synthesis of the saturated ligand involves reduction of the backbone before cyclisation. Symmetrical saturated ligands can be formed using two equivalents of the amine to one glyoxal in the first step. The synthesis is completed by cyclisation with triethylorthoformate and ammonium tetrafluoroborate, whilst removing the ethanol produced (Scheme 1.7.).



Scheme 1.7. *Synthetic route to saturated imidazolium salts*

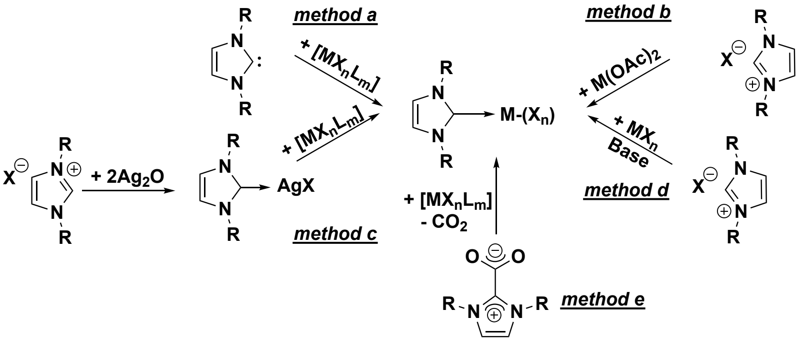
---

[50] L. Jafarpour, E. D. Stevens and S. P. Nolan, *J. Organomet. Chem.*, **2000**, *606*, 49-54 ; b) X. Bantreil, S. P. Nolan, *Nat. Protoc.* **2011**, *6*, 69-77

[51] M. B. Dinger, P. Nieczypor, J. C. Mol, *Organometallics* **2003**, *22*, 5291-5296

1.3.3.2 N-Heterocyclic Carbenes coordinated to transition metal

Scheme 1.8. illustrates the five most common methods used to form NHC-metal complexes. The proton abstraction method ***a.*** consists in the utilization of a preformed, isolated free NHC.[52,53] This method allows a large choice of transition metal complexes as starting materials. However, the isolation of the desired NHC is not always trivial and the use of strong bases could be incompatible with the carbene's functional groups. In the synthesis ***b.*** a metal precursor having a ligand that acts as a base such as acetate, acetylacetonate or alkoxy group is used.[53] Thus, the metal complexes [M(NHC)] are formed in the absence of an external base. Method ***c.*** is another convenient strategy to access NHC transition metal complexes that involves the synthesis of a silver NHC complex and then transmetallating it to the desired transition metal.[54] This method has the advantage of the straightforward formation of [Ag(NHC)] complexes which are usually very labile in solution and efficiently use it for the transmetalation of the NHC fragment to another metal center. Method ***d*** is arguably the most popular way to synthesize [M(NHC)] complexes. It consists in generating free NHC *in situ* with milder bases such as NaOAc, Cs_3CO_3 or Et_3N among others in the presence of a suitable transition metal precursor.[53] This process can also be achieved in the presence of stronger bases such as NaH, *n*BuLi or *t*BuOK followed by addition (or in the presence) of the metal precursor in a one-pot synthesis. This avoids the handling of the free NHC which most of the times are air- and moisture-sensitive. In method ***e***, N,N'-disubstituted imidazolium-2-carboxylates, air- and moisture-stable species, can transfer NHCs to a variety of metal salts with release of CO_2.[55]



Scheme 1.8. *Four general methods to synthesize NHC-M complexes.*[52-55]

---

[52] Fehlhammer et al. *J. Organomet. Chem.* **1995**, 490, 149-153

[53] a) S. Diez-Gonzalez, N-heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, Royal Society of Chemistry, Eds. RSC Publishing, **2011**; b) F. Glorius, S. Bellemin-Laponnaz, N-Heterocyclic Carbenes in Transition Metal Catalysis, Royal Society of Chemistry, Eds. Springer, **2007**

[54] C. H. Leung, A. R. Chianese, B. R. Garrett, C. S. Letko, R. H. Crabtree, *Inorg. Synth*. **2010**, 84-87

[55] A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, *J. Am. Chem. Soc*. **2005**,127, 50, 1724-1725

Symmetrical imidazol-2-ylidenes have been used widely, due to their facile synthesis and complexation to a metal. Commonly imidazol-2-ylidenes used as ligands include 1,3-bis(adamantyl)imidazol-2-ylidene (IAd), 1,3-bis(2,4,6-trimethylphenyl (IMes) imidazol-2-ylidene), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(cyclohexyl)imidazole-2-ylidene (ICy) and the saturated 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes) which are all shown below in Figure 1.9.

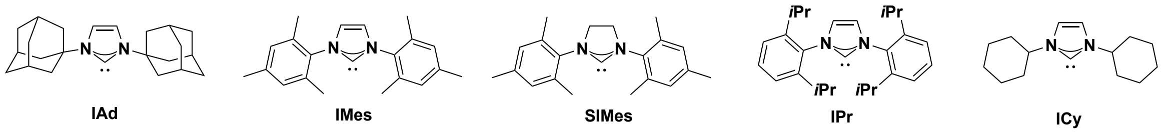


Figure 1.9. *NHCs commonly used as ligands in transition metal catalysis.*[56]

1.3.3.4 Applications of M-NHC complexes

The attractive features of NHC-metal coordination have led to a wide range of applications of these complexes across the chemical sciences (Figure 1.10.).[56]

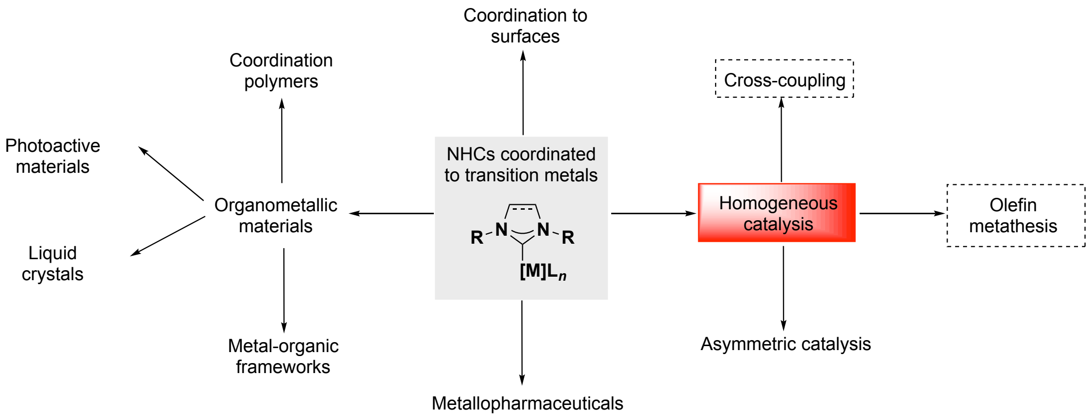


Figure 1.10. *Application of NHCs coordinated to transition metals.*[56]

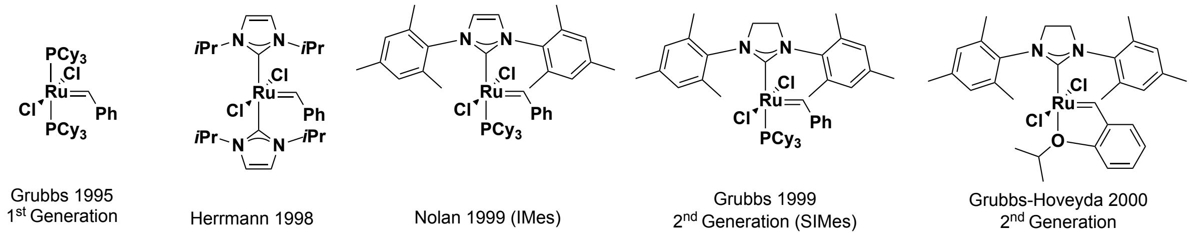
By far the largest application of NHC-transition metal complexes is in homogeneous catalysis and the two most extensively studied classes of catalytic reactions are ruthenium-catalyzed olefin metathesis and cross-coupling. Both catalytic reactions were recognized with the award of the Nobel Prize for Chemistry in 2005 and 2010 respectively.

In 1998, Herrmann modified Grubb's first generation ruthenium metathesis catalyst, $[Ru(=CHPh)Cl_2(PCy_3)_2]$[57a], to incorporate IMes ligands[57b] instead of phosphines (Figure 1.11.). Higher activities and greater stability were observed for this NHC complex compared to the original bis(phosphine) compound. Further investigations on the reaction mechanism led to catalysts bearing the bulky and labile tricyclohexylphosphine

---

[56] M. N. Hopkinson, C. Richter, M. Schelder, F. Glorius, *Nature*, **2014**, 510, 485-496

ligand and different NHCs (IMes and SIMes)[57c-f] (Figure 1.11). This second-generation Grubbs's catalysts exhibit faster reaction times and greater functional group tolerance than the previously leading catalysts due to their greater basicity. The second generation Hoveyda-Grubbs catalyst was later developed, replacing the phosphine ligand with a chelating oxygen[57g] (Figure 1.11. Scheme 1.9.).



Grubbs 1995
1st Generation

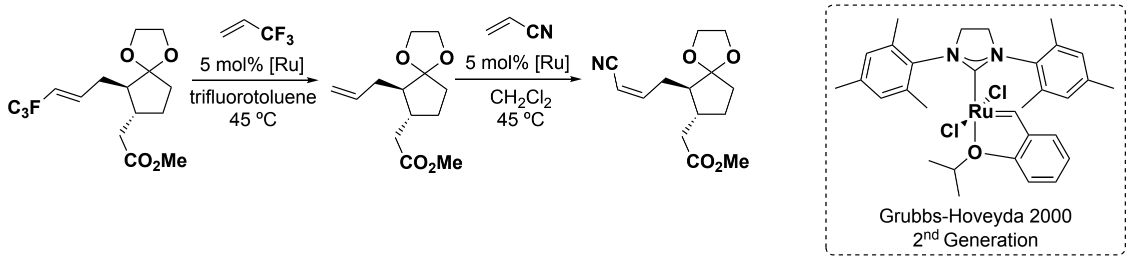
Herrmann 1998

Nolan 1999 (IMes)

Grubbs 1999
2nd Generation (SIMes)

Grubbs-Hoveyda 2000
2nd Generation

Figure 1.11. *Grubbs's Catalyst evolution in the metathesis catalytic reaction.*[57]



Schema 1.9. *Grubbs-Hoveyda [Ru] application in cross metathesis reaction.* [57h,i]

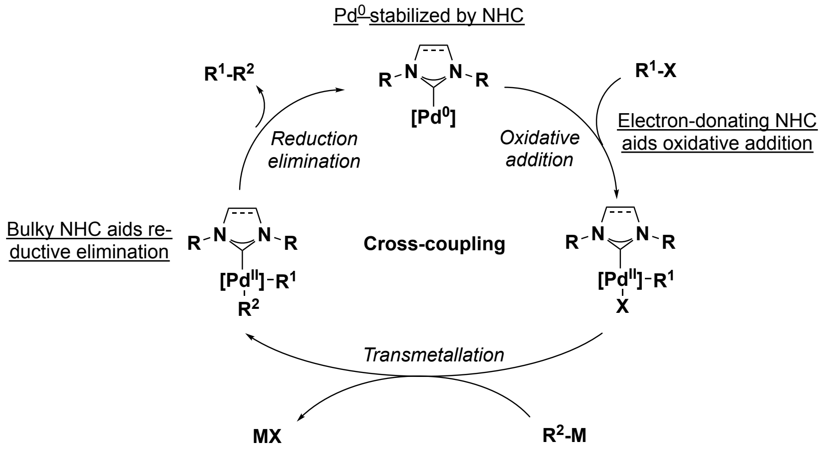
The palladium-catalyzed cross-coupling reactions constitutes one of the most efficient methods for the construction of carbon-carbon bonds.[58] It consists in the carbon-carbon bond formation between a less reactive organic electrophile (R^1-X) and an organometallic nucleophile (R^2-M) in the presence of a catalyst ([M]). Several types of this reaction exist and they are classified depending on the metal present in the nucleophile. These cross-coupling processes follow a reaction mechanism involving three main steps: an oxidative addition of the organic electrophile to an electron rich coordinatively unsaturated Pd(0) complex, transmetalation of an organic fragment carried by a suitable organometallic reagent, and finally a C-C bon is formed from two Pd-bonded organic fragments via reductive elimination, thus regenerating the active catalytic species (Figure 1.12.).[59]

---

[57] a) P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem.* **1995**,107, 2179-2181; b) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Hermann, *Angew. Chem., Int. Ed.*, **1998**, 37, 2490-2493; c) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem., Int. Ed.* **1999**, 38, 2416-2419; d) J. Huang, E. D. Stevens, S. P. Nolan, *J. Am. Chem. Soc.* **1999**, 121, 2674-2678; e) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, 40, 2247-2250; f) M. Scholl, S. Dig, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999** 1, 6, 953-956, g) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, 122, 8168-8179; h) S. Imhof, S. Randl, S. Blechert, *Chem. Commun.* **2001**, 1692-1693; i) S. Randl, S. Gessler, H. Wakamatsu, S. Blechert, *Synlett*, **2001**, 3, 430-432

[58] a) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, 100, 3009-3066; b) R. Chinchilla, C. Nájera, *Chem. Soc. Rev*. **2011**, 40, 5084-5121

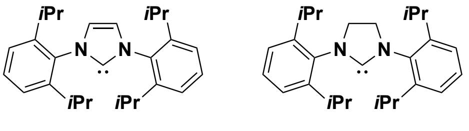
[59] A. de Meijere, F. Diderich, Metal-catalyzed Cross-Coupling Reactions, 2nd Eds. Wiley-VCH: Weinheim **2008**; K. Tamao, N. Miyaura, Introduction to Cross-Coupling Reactions, Eds. Springer, **2002**



R^1, R^2 = aryl, heteroaryl, alkyl
X= halide, pseudohalide
M= $B(OR)_2$, (Suzuki-miyaura), SnR_3 (Stille), ZnR (Negishi) and also heteroatom coupling partners such as HNR_2 (Buchwald-Hartwig)

Figure 1.12. *General mechanism of Pd-catalyzed cross-coupling.*[58,59]

The suitability of NHCs as spectator ligands in this cross-coupling reaction is explained by the improved stability and reactivity of the resulting Pd-NHC catalyst. Indeed, the strong sigma-donating carbene leads to an electron-rich catalytically active metal center that is better activated towards oxidative addition into carbon-halogen or pseudohalogen bonds of the substrates. This feature is particularly important for the coupling of challenging aryl chloride substrates, which possess strong carbon-chlorine bonds usually resistant to oxidative addition. The large steric influence of NHCs can also result in a more favorable reductive elimination step. Furthermore, both steric and electronic factors play a part in stabilizing the coordinatively unsaturated low-oxidation-state of the M^n in the active catalytic species and avoiding the reducing process of decomposition to heterogeneous material such as palladium black, which is often a major problem in these processes. Among the various NHCs provided, imidazol-2-ylidene and imidazoline-2-ylidene carbenes with sterically bulky derivatives such as IPr and SIPr tend to dominate in terms of catalytic activity (Figure 1.13.).



Imidazolydidene (IPr) **Imidazolinylidene (SIPr)**

Figure 1.13. *Structures of the most active NHCs in Pd-catalyzed processes.*[56]

1.3.4 NHCs as an organocatalyst

NHCs are generally known as excellent ligands for metal-based catalysis, but there is also an increasing interest in the role of nucleophilic carbenes as organocatalysts

(Figure 1.14.). In fact, the lone pair on NHCs leads to a strong Lewis base behavior[60] and excellent nucleophilic character thus, enabling Michael additions with nitroalkenes,[61] allenoates[62] and alkynes,[63] as well as Morita-Baylis-Hillman reactions,[64] transesterifications[65] and ring-opening polymerizations.[66] Besides, the largest and most diverse array of NHC-organocatalyzed reactions result from their nucleophilic attack on aldehydes.[67]

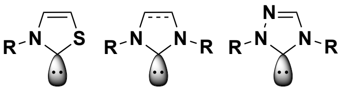


Figure 1.14. *General classes of NHCs employed as nucleophilic catalysts*

1.3.4.1 The Benzoin and Stetter Condensation

Discovered in 1832 by Liebig and Wöhler,[68] the benzoin reaction is the cyanide mediated coupling reaction of aldehydes that leads to the formation of alpha-hydroxy ketones. In 1943, Ukai *et al.* reported that the combination of thiazolium salt and a base could also effectively catalyze the benzoin condensation (Scheme 1.10).[69] This work along with studies of reactions catalyzed by thiamine dependent enzymes indicated that acyl anion equivalents are also likely intermediates in these thiazolium/base catalyzed processes. It was Breslow who proposed the pathbreaking mechanism for this transformation.[70] In 1958, from his model studies he suggested that the catalytically active species is a thiazolin-2-ylidene C2, a carbene compound, which is formed in situ by the deprotonation of thiazolium salt C1 (Scheme 1.10.). The "free carbene" reacts with the aldehyde *via* nucleophilic addition to the carbonyl group, then subsequently rearranges to the "Breslow intermediate". The umpolung of aldehyde reversed the polarity of the carbonyl carbon, so the adduct can be considered as an acyl anion which

---

[60] a) R. W. Alder, P. R. Allen, S. J. Williams, *J. Chem. Soc.*, *Chem. Commun*. **1995**, 1267-1268; b) E. M. Phillips, M. Riedrich, K. A. Scheidt, *J. Am. Chem. Soc.*, **2010**, 132, 13179-13181; c) Y. Coquerel, T. Boddaert, J. Rodriguez, *Chem. Eur. J.*, **2011**, 17, 2266-2271

[61] a) C. Fischer, S. W. Smith, D. A. Powell, G. C. Fu, *J. Am. Chem. Soc.*, **2006**, 128, 1472-1473; b) L. Zhao, X. Y. Chen, S. Ye, Z.-X. Wang, *J.Org. Chem.,* **2011**, 76, 2733-2743

[62] X.-Y. Chen, L.-H. Sun, S. Ye, *Chem. Eur. J.*, **2013**, 19, 4441-4445

[63] L. Sun, T. Wang, S. Ye, *Chin. J. Chem.,* **2012**, 30, 190-194

[64] a) S. Kankala, R. Vadde, C. S. Vasam, *Org. Biomol. Chem.,* **2011**, 9, 7869-7876; b) X.-Y. Chen, S. Ye, *Org. Biomol.Chem.*, **2013**, 11, 7991-7998

[65] a) L. He, T.-Y. Jian, S. Ye, *J. Org. Chem.*, **2007**, 72, 7466-7468; b) L. He, Y.-R. Zhang, X.-L. Huang, S. Ye, *Synthesis* **2008**, 2825-2829

[66] a) M. Movassaghi, M. A. Schmidt, *Org. Lett.* **2005**, 7, 2453-2456; b) T. Kano, K. Sasaki, K. Maruoka, *Org. Lett.,* **2005**, 7, 1347-1349

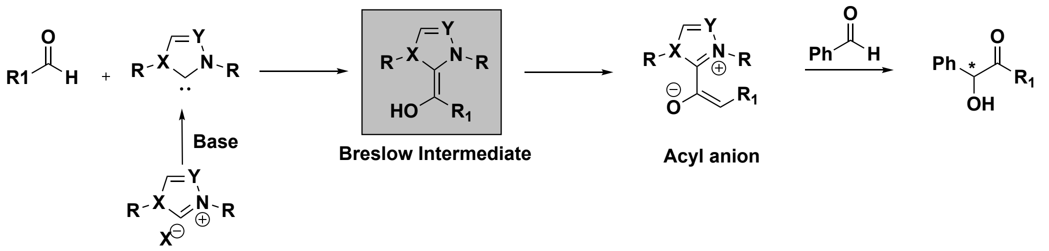
[67] a) D. Enders, T. Balensiefer, *Acc. Chem. Res.*, **2004**, 37, 8, 534–541; b) V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem., Int. Ed. Engl.*, **2004**, 43, 39, 5130-5135; c) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.*, **2007**, 107, 12, 5606-5655.

[68] F. Wohler, J. Liebig, *Ann. Pharm.* **1832**, 3, 249-282

[69] T. Ukai, R. Tanaka, T. Dokawa, *J. Pharm. Soc. Jpn*. **1943**, 63, 296-300

[70] R. Breslow, *J. Am. Chem. Soc.* **1958**, 80, 3719-3726

undergo nucleophilic addition with another equivalent of aldehyde (Scheme 1.10.). Notably, benzoin condensation is an equilibrium reaction and can be reversed.



Scheme 1.10. *NHC-catalyzed reactions of aldehydes via "Breslow intermediate"*

The product of benzoin condensation bears a stereocenter hence, the mechanistic aspects of benzoin condensation have been extensively investigated and the scope of organocatalysts by NHCs has been greatly broadened.[71] In Figure 1.15 are presented a selection of chiral heteroazolium salts which render the benzoin reaction enantioselective.[72]

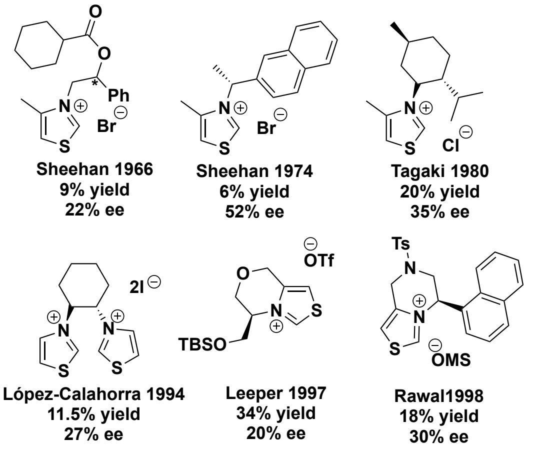
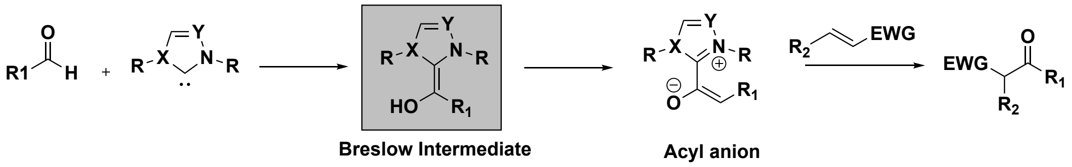


Figure 1.15. *Selected chiral thiazolium salts for the asymmetric benzoin condensation.*[72]

An extension to the benzoin reaction is presented in Scheme 1.11. It involves a Michael acceptor as the electrophilic partner for the acyl anion addition and provides 1,4 dicarbonyl derivatives.[73] Like in the benzoin condensation, a catalytic cycle involving the "Breslow intermediate" has been suggested.



Scheme 1.11. *Stetter reaction involving nucleophilic attack onto electron-deficient alkene*

---

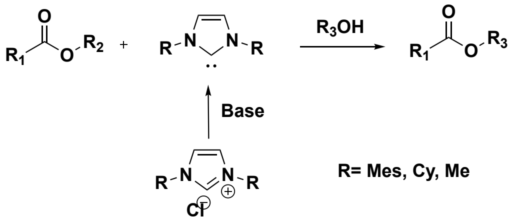
[71] D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, 116, 1348-1350; *Angew. Chem. Int. Ed.* **2004**, 43, 1326-1328

[72] a) J. C. Sheehan, D. Hunneman, *J. Am. Chem. Soc.* **1966**, 88, 15, 3666-3667; b) J. C. Sheehan, T. Hara, *J. Org. Chem.* **1974**, 39, 9, 1196-1199; c) W. Tagaki, Y. Tamura, Y. Yano, *Bull. Chem. Soc. Jpn.* **1980**, 53, 2, 478-480; d) J. Marti, J. Castells, F. Lopéz-Calahorra, *Tetrahedron Lett.* **1993**, 34, 3, 521-524; e) R. L. Knight, F. J. leeper, *Tetrahedron Lett.* **1997**, 38, 20, 3611-3614; f) C. A. Dvorak, V. H. Rawal, *Tetrahedron Lett.* **1998**, 39, 19, 2925-2928

[73] a) H. Stetter, M. Schrecke, *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 1, 81; *Tetrahedron Lett.* **1973**, 17, 1461-1462.

1.3.4.2 Transesterification reactions

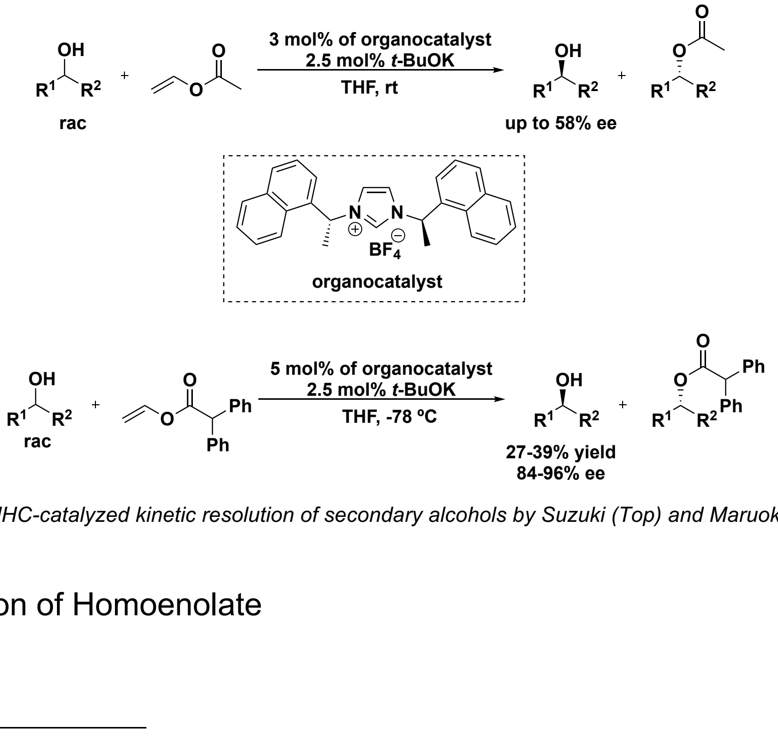
In 2002, the research groups of Nolan and Hedrick concurrently reported the first NHC-catalyzed transesterification reactions using substoichiometric amounts of an NHC catalysts (Scheme 1.12.).[74]



Scheme 1.12. *Transesterification reaction developed by Nolan and Hedrick.*[74]

In 2004, Nolan followed up on his initial report and expanded the scope of the NHC-promoted transesterification to a variety of secondary alcohols including aliphatic, cyclic and aromatic by using NHC in the presence of methyl- or ethyl acetate and molecular sieves to drive the equilibrium reaction.[75]

Following the trend seen for benzoin condensation and Stetter reactions, the asymmetric version of NHC-catalyzed transesterification is under active investigation. The groups of Suzuki and Maruoka reported acylations for the kinetic resolution of chiral secondary alcohols (Scheme 1.13.).[76]



Scheme 1.13. *NHC-catalyzed kinetic resolution of secondary alcohols by Suzuki (Top) and Maruoka (Bottom)*

1.3.4.3 Generation of Homoenolate

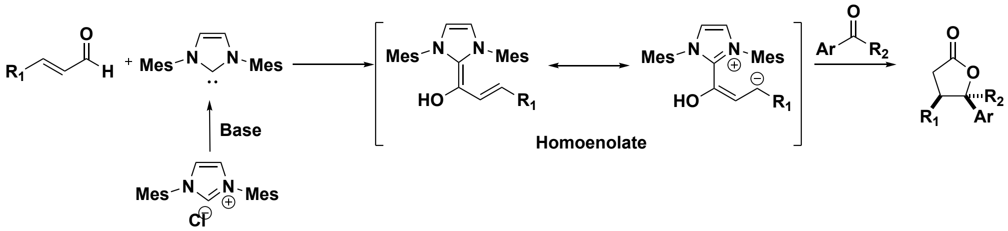
---

[74] a) G. A. Grasa, R. Singh, S. P. Nolan, *Synthesis.* **2004**, 4, 971-985; b) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth, J. L. Hedrick, *Org. Lett.* **2002**, 4, 3587-3590

[75] a) R. Singh, R. M. Kissling, M. A. Letellier, S. P. Nolan, *J. Org. Chem.* **2004**, 69 (1), 209-212; b) G. A. Grasa, R. M. Kissling, S. P. Nolan, *Org. Lett.* **2002**, 4, 3583-3586

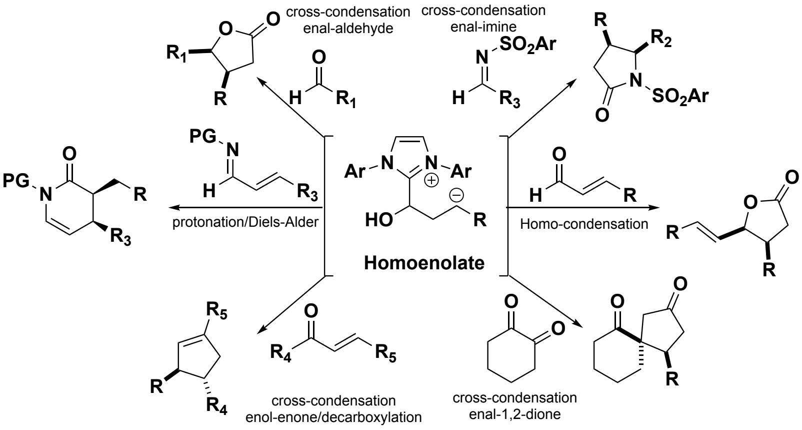
[76] a) Y. Suzuki, K. Yamauchi, K. Muramatsu, M. Sato, *Chem. Commun.* **2004**, 2770-2771; b) Y. Suzuki, K. Muramatsu, K. Yamauchi, Y. Morie, M. Sato, *Tetrahedron* **2006**, 62, 302-310; c) T. Kano, K. Sasaki, K. Maruoka, *Org. Lett.* **2005**, 7, 1347-1349

N-Heterocyclic carbenes have also been shown to be efficient catalysts for promoting the Umpolung of α,β-unsaturated aldehydes and acted as nucleophiles at the β-position. These reactive intermediates are termed homoenolate equivalents and undergo nucleophilic additions to a variety of electrophiles. Seminal reports on this transformation appeared in 2004 by the groups of Bode and in 2006 by the group of Glorius.[77] In both cases the imidazolium NHC precatalyst IMesCl was employed to convert an enal into a conjugate donor that efficiently underwent nucleophilic addition to a carbonyl acceptor (Scheme 1.14.).



Scheme 1.14. *First report of NHC-catalytically generated homoenolates by Bode and Glorius* [72]

The synthetic utility of this reaction was extended to various substrates and proven to be tolerant of a variety functional group (Scheme 1.15.).[78]



Scheme 1.15. *Application of NHC-generated homoenolates. PG= Protecting group*

In this context and taking into account the interest in the immobilization of homogeneous catalysts as well as the possibilities offered by N-Heterocyclic Carbene ligands as organocatalyst and in transition metal catalysis, the research developed in this Thesis focuses on the objectives described in the following Chapter 2.

---

[77] a) S. S. Sohn, E. L. Rosen, J. W. Bode, *J. Am. Chem. Soc.* **2004**, 126, 14370-14371; b) C. Burstein, S. Tschan, X. Xie, F. Glorius, *Synthesis* **2006**, 2418-2439.
[78] K. Zeitler, *Angew. Chem.* **2005**, 117, 7674–7678; *Angew. Chem. Int. Ed.* **2005**, 44, 7506–7510.

Chapter 2

“Objectives”

The general objective of this PhD thesis deals with the utilization of pyrene functional group in the design of organo-(metallic) catalysts supported onto carbon surfaces *via* non-covalent interactions such as π-stacking as a promising solution to green and sustainable chemistry. For this purpose, pyrene tags N-Heterocyclic carbenes and pyrene-tags Brookhart type α-diimine ligands have been developed and used in carbon dioxide utilization and functionalized polyolefins synthesis respectively.

The specific objectives of the thesis are summarized as follows:

1) The application of heterogenized imidazolium carboxylate organocatalyst for the coupling reaction of carbon dioxide (CO_2) with epoxides to give 5-membered ring cyclic carbonates. To achieve this objective the following steps were performed:

- The synthesis and characterization of well-defined imidazolium salts bearing pyrene tags and the preparation of their subsequent imidazolium carboxylate analogues.
- The immobilization of imidazolium carboxylate onto carbon surfaces to yield heterogenized organocatalysts for the coupling reaction of CO_2 and epoxides.
- The study of the catalytic performance and recyclability of the immobilized catalysts in the coupling reaction of CO_2 and epoxides under batch conditions.
- The evaluation of the scope of epoxide substrates that could be transformed for the most efficient supported organocatalysts.

2) The application of heterogenized silver-NHC based catalyst for the coupling reaction of carbon dioxide (CO_2) with *o*-alkynylanilines to give the corresponding benzoxazine-2-ones derivatives. To achieve this objective the following steps were planned:

- The synthesis and characterization of silver-NHC based complexes bearing pyrene tags.
- The immobilization of the pyrene tags silver-NHC based catalysts onto carbon surfaces and characterization of the resulting materials.
- The evaluation of the heterogenized organometallic catalysts in the coupling reaction of CO_2 and *o*-alkynylanilines.

3) The development of a palladium catalytic system efficient for the catalyzed co-polymerization of ethylene and methyl acrylate for the synthesis of functionalized polyolefins. To achieve this objective, the following steps were carried out:

- The synthesis and characterization of pyrene tags alpha-diimine ligands and their related palladium (II) complexes (both neutral and monocationic).
- The application of these monocationic palladium catalysts in the copolymerization of ethylene/methyl acrylate (MA) and characterization of the catalytic products.

- The study of the catalytic behavior of these monocationic palladium (II) complexes in a different solvent and characterization of the catalytic products.

4) The synthesis of δ-lactone under batch wise recycling conditions by telomerization of 1,3-butadiene and CO_2 in a biphasic catalytic system consisting of ionic liquid (IL) and supercritical CO_2 ($scCO_2$) using a palladium catalyst. To achieve this objective the following steps were planned:

- The synthesis and characterization of task specific ionic liquids
- The application of the task specific ionic liquids in the telomerization reaction of 1,3-butadiene with CO_2
- The study of the influence of the counter anion in the telomerization reaction
- The continuous flow extraction of δ-lactone using $scCO_2$

Chapter 3

“Noncovalent immobilization of pyrene-tagged imidazolium carboxylate. Synthesis, characterization and application in the Cycloaddition of epoxides and CO_2”

3.1 Introduction

3.1.1 Carbon dioxide from waste to feedstock

Carbon dioxide (CO_2) is a common product of biological processes such as aerobic respiration or the alcoholic fermentation of sugars.[79] Its emission is also associated with the combustion of fossil fuels arising from anthropogenic activities for the production of energy, transportation, and industrial processes.[80] Since the Industrial Revolution, the concentration of CO_2 in the atmosphere steadily increased, becoming an environmental issue to be addressed (Figure 3.1.).[81]

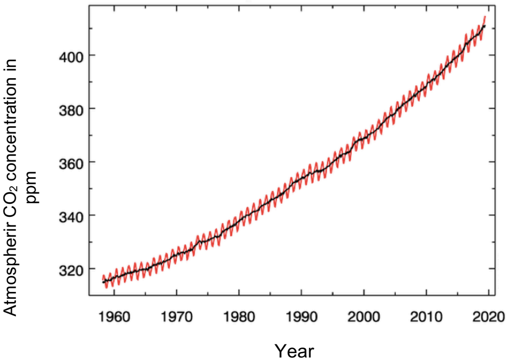


Figure 3.1. *Rising atmospheric CO_2 level.* [81]

In this scenario, carbon dioxide capture, utilization, and storage emerged as tangible processes moving toward sustainable development.[82] Focusing on its utilization, carbon dioxide found application in separation processes, dry-cleaning, refrigerators, fire extinguishers, in the food or agrochemical industry, or as a solvent for several reactions under supercritical conditions.[83] However, they only temporarily store CO_2 to release it again after use. Thus, different strategies for CO_2 conversion into valuable chemicals have attracted attention in current research and industry.[84] Indeed, carbon dioxide is regarded as an abundant, cheap, non-toxic easily available source of carbon.[85]

---

[79] M. Aresta, Carbon Dioxide as a Chemical Feedstock, Eds.: Wiley-VCH Verlag GmbH&Co. KGaA, **2010**

[80] P. Friedleingstein, R. M. Andrew, J. Rogeli, G. P. Peters, J. G. Canadell, R. Knutti, G. Luderer, M. R. Raupach, M. Schaeffer, D. P. Van Vururen, C. Le Quere, *Nature Geosci* **2014**, *7*, 709-715

[81] R. A. Betts, C. D. Jones, J. R. Knight, R. F. Keeling, J. J. Kennedy, *Nature Clim. Change* **2016**, *6*, 806-810

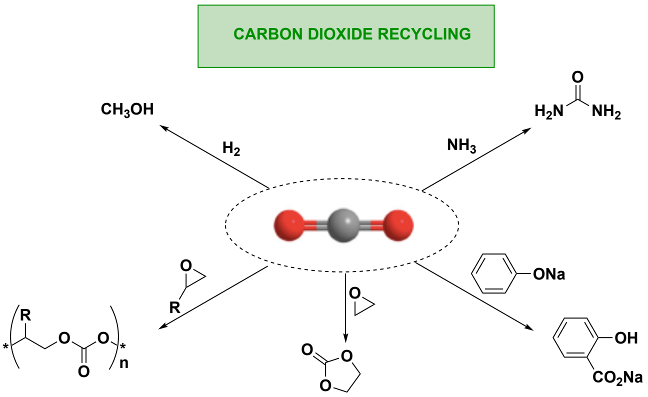
[82] F. A. Rahman, M. M. A. Aziz, R. Saidur, W. A. Bakar, M. R. Hainin, R. Putrajaya, N. A. Hassan *Renew. Sustain. Energy Rev*. **2017**, *71*, 112-126

[83] E. Alper, O. Y. Orhan *Petroleum* **2017**, *3*, 109-126

[84] a) G. Fiorani, W. S. Guo, A. W. Kleij, *Green Chem*. **2015**, *17*, 1375-1389; b) P. Styring, E. A. Quadrelli, K. Amstrong, Carbon Dioxide Utilisation: Closing the Carbon Dioxide Cycle, Eds.: Elsevier, **2014**; c) C. Madea, Y. Miyazaki, T. Ema, *Catal. Sci. Technol*. **2014**, *4*, 1482-1497

[85] a) M. Aresta, A. Dibenedetto, A. Angeli, *Chem. Rev*. **2014**, 114, 1709-1742; b) T. Sakura, J.-C Choi, H. Yasuda, *Chem. Rev.* **2007**, 107, 2365-2387; c) Q. W. Song, Z. H. Zhou, L. N. He, *Green. Chem*. **2017**, 19, 3707-3728; d) J. Langanke, A. Wolf, J. Hoffmann, K. Bohm, M. A. Subhani, T. E. Muller, W. Leitner, C. Gurtler, *Green chem*. **2014**, *16*, 1865-1870; e) G. Genti, E. A. Quadrelli, S. Perathoner, *Energy Environ. Sci*. **2013**, *6*, 1711-1731; f) M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem*, **2011**, *4*, 1216-1240

Therefore, it is used as a renewable one-carbon (C1) building block in synthetic chemistry to obtain chemicals such as urea, sodium salycilate, organic carbonates and methanol (Scheme 3.1.).[86]



Scheme 3.1. *Industrialized organic syntheses using* CO_2 *as one-carbon (C1) feedstock*

The utmost challenge in carbon dioxide utilization is its thermodynamic stability and kinetic inertia.[87] Hence, a large energy input is necessary for CO_2 conversion, which leads to high costs and emissions of greenhouse gases.[88] To reduce the energy required to transform CO_2 and overcome the high reaction barrier, highly energetic starting materials are usually employed at elevated temperature or high-performance catalysts able to properly decrease the activation energy of the selected reaction (Figure 3.2.).[89]

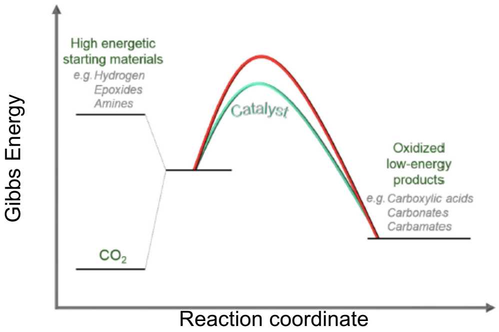


Figure 3.2. *Organic synthesis using* CO_2 *as a building block*

3.1.2 Carbon Dioxide conversion into Cyclic Carbonates

The basic features of CO_2 reactivity must be considered to reach a good conversion of this molecule into useful chemicals. Carbon dioxide is a linear molecule, in

---

[86] a) B. M. Bhanage, M. Arai, Transformation and Utilization of Carbon Dioxide Eds.: Springer, **2014**; b) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun*. **2015**, 6, 5933-5948; c) C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482-1497

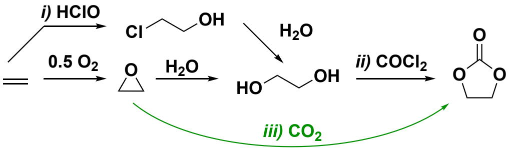
[87] M. Mikkelsen, M. Jorgensen, F. C. Krebs, *Energy Environ. Sci*. **2010**, 3, 43-81

[88] S. Suib, New and Future Developments in Catalysis Activation of Carbon dioxide Eds. Elsevier, Amsterdam, **2013**

[89] G. Centi, E. A. Quadrelli, S. Peathoner, *Energy Environ. Sci*. **2013**, 6, 1711-1731

which the carbon-oxygen bonds are polar, with a net partial charge on carbon and oxygen atoms. Therefore, the carbon atom, bearing a partial positive charge, can behave as an electrophile. On the other hand, the oxygen atoms, with a partial negative charge, can act as nucleophile. Owing to the linear geometry of the molecule, with the two dipole moments opposite each other, the overall molecule is apolar. From the above, the amphoteric CO_2 behavior leads to two possible activation pathways: the oxygen atoms can exhibit a Lewis base characteristic, while the carbon atom can play the role of a Lewis acid center. Thus, its cycloaddition with epoxides producing five-membered cyclic carbonates is an attractive route for carbon dioxide utilization.[90] Those organic carbonates find widespread application as protic high-boiling polar solvents, electrolytes for batteries, precursors for polymeric materials, fuel additives, plastic materials and intermediates for the synthesis of fine chemicals.[91] Additionally, they contain the possibility for further transformation into their linear analogues through transesterification reactions.[92]

In industry, cyclic carbonates are traditionally prepared via synthetic methodologies involving the use of phosgene (Scheme 3.2.). However, such procedures allow the production of equimolar amounts of carbonate and chlorinated salts and large volumes of chlorinated solvents. Moreover, phosgene is highly toxic, corrosive, and exposure to it may cause collateral health effects. Therefore, its replacement by the coupling of CO_2 with epoxides emerged as a low-toxicity alternative.



Scheme 3.2. *Synthetic routes for the production of ethylene carbonate. i) Hydrochlorination of ethene, subsequent hydrolysis and conversion with phosgene. ii) Formation of ethylene oxide, subsequent hydrolysis and conversion with phosgene. iii) Formation of ethylene oxide and cycloaddition with CO_2*

3.1.3 Catalytic systems for the synthesis of cyclic carbonates

High temperatures and pressures are often required for the formation of the corresponding cyclic carbonate in satisfactory yields. To optimize the reaction conditions, a great variety of catalysts have been reported so far.[93] Most of them consist of a

---

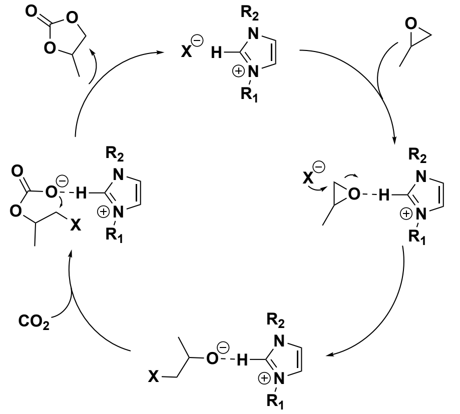
[90] W. Desens, T. Wegner, *Adv. Synth. Catal*. **2016**, *358*, 622-630.

[91] a) T. Sakakura, K. Kohno, *Chem. Commun*. **2009**, 1312-130; b) W. Clegg, R. W. Harrington, M. North, F. Pizzato, P. Villuendas, *Tetrahedron Asymmetry* **2010**, *21*, 1262-1271; Q. Liu, J. Chen, L. Fan, X. Kong, Y. Lu, *Green Energy Environ*. **2016**, 1, 18-42

[92] a) M. Cokoja, C. bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510-8537; *Angew. Chem.* **2011**, *123*, 8662-8690; b) M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514-1539.

[93] a) S.-S. Wu, X.-W. Zhang, W.-L. Dai, S.-F. Yin, W.-S. Li, Y.-Q. Ren, C.-T. Au, *Appl. Catal. A* **2008**, 341,106-111; b) W. Cheng, Z. Fu, J. Wang, J. Sun, S. Zhang, *Synth. Commun*. **2012**, 42, 2564-2573; c)

combination of Lewis acids and nucleophiles. Furthermore, a whole range of metal complexes in combination with nucleophilic cocatalysts have emerged as highly active catalytic systems.[94] The choice between metal-based or organo-catalysts for CO_2 fixation brings strengths and weaknesses. Metal-based systems lead to milder reaction conditions (e.g., lower temperature, reduced catalytic loading) owing to their ability to activate and/or stabilize substrates or intermediates via coordination interactions. On the other hand, metal-free catalysts could represent an attractive alternative, since they are usually significantly cost-effective, readily available, less toxic and stable toward moisture and air.[95] First mentioned in 2002 by Peng and Deng, imidazolium-based compounds represent suitable catalysts for the synthesis of cyclic carbonates from epoxides and CO_2.[96] An imidazolium halide has a proton in the C2 position of the imidazolium ring which activates the epoxide through hydrogen bond, and therefore, facilitates nucleophilic ring-opening during the catalytic cycle (Scheme 3.3.).



Scheme 3.3 *Cooperative mechanism with the application of imidazolium halide catalysts*

With the aim to increase the catalyst lifetime, several supported imidazolium-based organo-catalysts were developed, providing simplified work-up procedures and possibility to use them under continuous flow conditions. It is well known that the design

---

M. E. Wilhelm, M. H. Anthofer, R. M. Reich, V. D'Elia, J.-M. Basset, W. A. Herrmann, M. Cokoja, F. E. Kühn, *Catal. Sci. Technol*. **2014**, 4, 1638-1643; d) A. Sibaouih, P. Ryan, M. Leskelä, B. Repo, *Appl. Catal. A* **2009**, 365, 194-198; d) T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun*. **1997**, 1129-1130; e) B. M. Bhanage, S.-i. Fujita, Y. Ikushima, M. Arai, *Appl. Catal. A* **2001**, 219, 259-266; f) R. Srivastava, D. Srinivas, P. Ratnasamy, *Tetrahedron Lett*. **2006**, 47, 4213-4217;
g) M. Tu, R. J. Davis, *J. Catal.* **2001**, 199, 85-91

[94] a) M. Cokoja, C. bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510-8537; *Angew. Chem.* **2011**, *123*, 8662-8690; b) N. Takeda, S. Inoue, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3564-3567; c) T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1983**, *105*, 1304-1309 ; d) W. J. Kruper, D. D. Dellar, *J. Org. Chem.* **1995**, *60*, 725– 727 ; e) L. Jin, H. Jing, T. Chang, X. Bu, L. Wang, Z. Liu, *J. Mol. Catal. A* **2007**, *261*, 262-266; f) C.-X. Miao, J.-Q. Wang, Y. Wu, Y. Du, L.-N. He, *ChemSusChem* **2008**, *1*, 236-241; g) R. L. Paddock, S. T. Nguyen, *J. Am. Chem. Soc.* **2001**, *123*, 11498-11499.

[95] a) D. W. C. MacMillan, *Nature* **2008**, *455*, 304-308; b) J. G. Hernández, E. Juaristi, *Chem. Commun.* **2012**, *48*, 5396-5409 ; c) M. Reez, Organocatalysis Eds.: Springer, Heidelberg, **2008**.

[96] J. Peng, Y. Deng, *New J. Chem.* **2001**, *25,* 639-641.

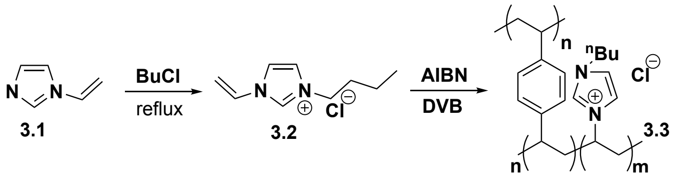
of heterogeneous catalysts is preferred from industrial parties because of their simple recovery from the reaction medium and the possibility of using them in fixed-bed reactors.

3.2 Covalent immobilization of imidazolium halides catalysts

Homogeneous imidazolium-based organocatalysts often face separation issues due to good product solubility, which complicates recycling procedures. Thus, the immobilization of these compounds is a promising approach since separation is facilitated, a higher reaction rate can also be reached using a suitable carrier. The solid supports must have a large particle size and must be mechanically stable to be recovered and reused by means of filtration or centrifugation. Moreover, they must have a large surface area and sufficiently large mean pore size to grant good accessibility of the reagents and products to the active sites and leave the solid with ease. It is also important to have a regular distribution of anchoring points.

3.2.1 Immobilization on synthetic and bio-polymers supports

The first example of polymer-supported imidazolium catalysts was reported in 2007 by Han *et al.*[97] They copolymerized 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) **3.2** with the cross linker divinylbenzene (DVB) (Scheme 3.4.). It resulted in a covalently anchored [VBIM]Cl onto DVB-cross-linked polymer matrix **3.3** which was highly active at 110 ºC and 60 bar of CO_2 for 7h in the cycloaddition of propylene oxide (PO) with CO_2 (Table 3.1. entry 1).



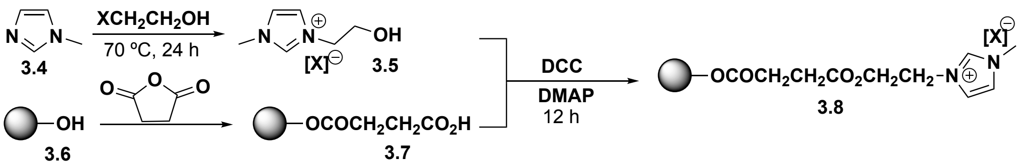
Scheme 3.4. *Synthesis of the cross-linked-polymer-supported (VBIM)Cl. AIBN: azobis(isobutyronitrile).*

Next, alkylimidazolium covalent immobilization onto modified polymers was investigated.[98] Methylimidazolium (MIm) was immobilized onto structurally modified polyethylene glycol (PEGs) **3.7**. The immobilization required 3 steps where the imidazole **3.4** and the support were modified to give PEG-IL catalyst **3.8** (Scheme 3.5.). PEG-IL **3.8** catalyst was active at high temperature and long reaction time in the presence of a co-catalyst in the cycloaddition of allyl glycidyl ether with CO_2 (Table 3.1., entry 2). Increasing the molecular weight of the PEG support resulted in higher viscosity and decrease in the catalyst activity.

---

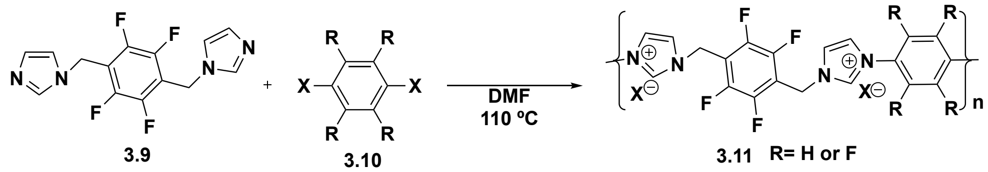
[97] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, *Angew. Chem. Int. Ed.* **2007**, *46*, 7255-7258; *Angew. Chem.* **2007**, *119*, 7393-7396

[98] a) H. J. Choi, M. Selvaraj, D.-W. Park, *Chem. Eng. Sci.* **2013**, *100*, 242-248; b) L. Han, H.-J. Choi, D.-K. Kim, S.-W. Park, B. Liu, D.-W. Park *J. Mol. Catal. A*, **2011**, 338, 58-64; c) J.-I. Yu, H.-J. Choi, M. Selvaraj, D.-W. Park *React. Kinet. Mech. Catal.*, **2011**, 102, 353-365



Scheme 3.5. *Preparation of PEG-supported-MIm.*

Another approach includes the use of fluoro-functionalized polymeric ILs (F-PILs).[99] They are synthesized following a 2-step alkylation under catalyst-free conditions (Scheme 3.6.). The catalytic activity of the resulting F-PILs increases with the fluorine content which is due to possible interactions of fluorine with CO_2. Thus, higher conversion was observed under the reported conditions for the formation of propylene carbonate (Table 3.1. entry 3) and the catalyst could be recycled up to 5 times without significant loss of activity.



Scheme 3.6. *Preparation of F-PILs*

Due to their availability in nature, bio-polymers can be considered as green alternatives to synthetic polymers. Carboxymethylcellulose (CMC)[100] and chitosan (CS)[101] have been used as support of BIm (butylimidazolium) and MIm respectively (Figure 3.3.).

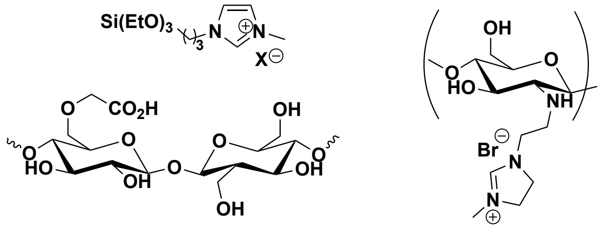

3.12 CMC-BIm *3.13 CS-MIm*

Figure 3.3. *Structures of supported catalysts onto bio-polymers (CMC, CS)*

Because of the carboxy and/or hydroxy moieties on their surfaces, the bio-polymers promote epoxide activation through hydrogen bondings together with the immobilized imidazolium. This leads to a high activity under short reaction time. Nevertheless, recycling studies of the CMC- supported catalyst in the cycloaddition of PO with CO_2 show a loss of activity caused by leaching, in contrast with CS-supported catalyst (Table 3.1., entries 4-5).

---

[99] Z. liu, Z. Z. yang, Y. Zhao, G. Ji, H. Zhang, B. Yu, X. Gao, *Green Chem* **2014**, *16*, 3724-3728

[100] K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G.-A. Park, D.-W. Park, *Green Chem.* **2012**, *14*, 2933-2940

[101] J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang, Y. She, *Green Chem.* **2012**, *14*, 654-660

Table 3.1. Polymer-supported Imidazolium catalysts for the synthesis of cyclic carbonates

Entry	Imidazolium	Co-catalyst	Support	Substrate	T (ºC)	$P(CO_2)$ [bar]	t (h)	Conv (%)	Recycling
1	VinBIm	Cl^-	DVB	PO	110	60	7	97	5 runs
2	MIm	Cl^-	PEG	AGE	120	19	4	88	-[b]
3	$[ImBzF4]_n$	Br^-	PIL	PO	120	10	9	94	5 runs
4	BIm	I^-	CMC	PO	110	18	2	99	4 runs[b]
5	MIm	Br^-	CS	PO	120	20	4	96	5 runs

[a] PO= propylene oxide; AGE= allyl glycidyl ether, VinBIm= 3-butyl-1-vinylimidazolium; MIm= Methylimidazolium, $[ImBzF4]_n$= 1-(2,3,5,6-tetrafluoro-4-methylene)imidazolium; BIm= Butylimidazolium; [b] Loss of activity during the recycling process.

3.2.2 Immobilization on carbon supports

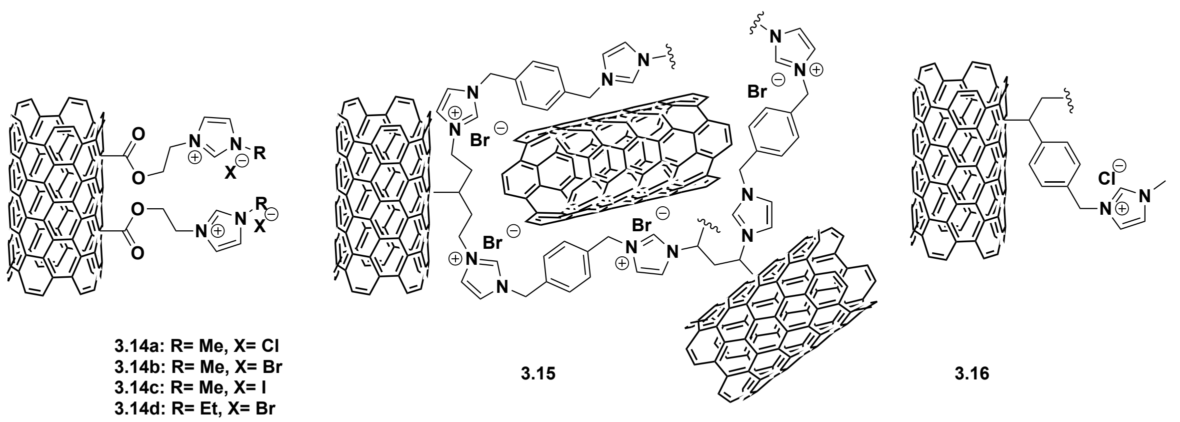
Carbon nanotubes possess high chemical and thermal stability, surface area, and tensile strength, and they are finding applications in catalysis. In 2012, Park *et al.* employed oxidized multi-walled carbon nanotubes (MWCNTs) as support for immobilizing of a series of imidazolium-based organocatalysts with different anions and alkyl chains through esterification of the carboxylic groups present on the nanotubes (Figure 3.4.).[102] The catalyst with iodide co-catalyst resulted as the most active catalyst for the conversion of a series of epoxides into the corresponding cyclic carbonates. Moreover, it was recycled five times with little loss in conversion (Table 3.2., entry 1).

An analogous strategy was reported by Gruttadauria, Aprile and co-workers for the preparation of single walled carbon nanotube (SWCNT)-polyimidazolium salt hybrids.[103] It implies direct radical polymerization of bis-vinylimidazolium chloride and styryl imidazolium chloride in the presence of SWCNTs to give rise to SWCNT-polyimidazolium salt hybrid **3.15** and **3.16** (Figure 3.4.). Both covalently supported catalyst displayed analogous activity. However, only catalyst **3.15** was reused for 4 runs with no deactivation whereas **3.16** suffered significant leaching of polymer as evidenced by the dramatic drop in the epoxide conversion during the second cycle (Table 3.2.).

---

[102] H. L. Han, H. Li, S.-J. Choi, M.-S. Park, S.-M. Lee, Y.-J Kim, D.-W. Park, *Appl. Catal. A* **2012**, 429-430, 67-72

[103] M. Buaki-Sogó, A. Vivian, L.A. Bivona, H. García, M. Gruttadauria, C. Aprile, *Catal. Sci. Technol.* **2016**, *6*, 8418-8427



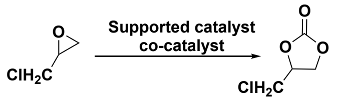
3.14a: R= Me, X= Cl
3.14b: R= Me, X= Br
3.14c: R= Me, X= I
3.14d: R= Et, X= Br
3.14e: R= Bu, X= Br

3.15

3.16

Figure 3.4. *Structures of covalently supported imidazolium salts onto carbon nanotubes (CNTs);* ***3.14 (a-e)*** *Imidazolium salts covalently grafted on MWCNTs.* ***3.15*** *and* ***3.16*** *poly-imidazolium salt covalently grafted onto SWCNTs.* [102 103]

Table 3.2. carbon nanotubes supported imidazolium catalysts for the synthesis of cyclic carbonates



Entry	Imidazolium	Co-catalyst	Support	T (ºC)	P(CO_2) [bar]	t (h)	Conv (%)	Recycling
1	**3.14c**	I^-	MWCNTs	110	10	7	99	5 runs
2	**3.15**	Br^-	SWCNTs	150	50	3	83	4 runs
3	**3.16**	Cl^-	SWCNTs	150	80	3	30	2 runs[b]
4	**3.17**	I^-	GO	140	20	4	95	7 runs

[a] MWCNTs= multiwalled carbon nanotubes; SWCNTs= single walled carbon nanotubes; GO= graphene oxide [b] Loss of activity during the recycling process.

Li *et al*. reported the preparation of imidazolium-based halides grafted onto the surface of graphene oxide (GO) for the cycloaddition reaction.[104] The hybrid material **3.17** endowed with iodide co-catalyst resulted as the best-performing catalysts at 20 bar pressure of CO_2 and 140 ºC for 4 h. Furthermore, it was possible to recycle the catalyst up to seven times without loss of activity (Table 3.2., entry 4).

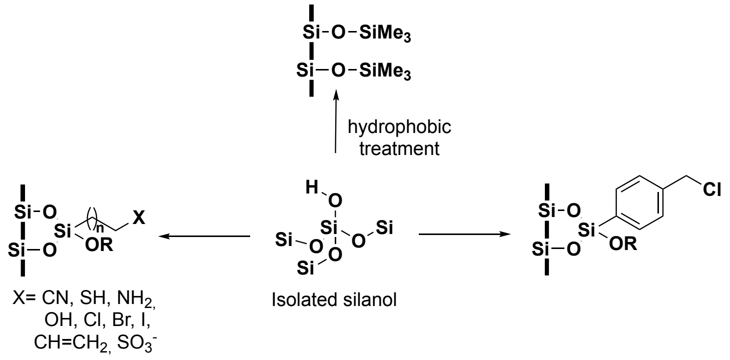
3.2.3 Immobilization on silica supports

Silica gel and ordered mesoporous silicas display useful features such as high surface area, narrow range of pore sizes (microporous to mesoporous), good thermal and mechanical stability, widespread availability, and easy covalent functionalization strategies covering a broad range of organic or organo-metallic moieties.[105] The huge variety of chemical modifications onto the silica surface is linked to the presence of silanol groups (Si-OH). The covalent functionalization of the silica surface is usually performed via condensation reactions between the silanol groups and a selected organo-silane (Scheme 3.7.).[106] Therefore, silylating coupling agents such as chlorosilanes, alkoxy-

---

[104] W.-H. Zhang, P.-P. He, S. Wu, J. Xu, Y. Li, G. Zhang, X.-Y. Wei, *Appl. Catal. A* **2016**, *509*, 111-117
[105] Z. A. Alothman, *Materials* **2012**, 5, 12, 2874-2902
[106] a) A. Vinu, K.Z. Hossain, K. Ariga, *J. Nanosci. Nanotechnol*. **2005**, *5*, 347-371; b) D. Brühwiler, *Nanoscale* **2010**, *2*, 887-892.

silanes, and silyl-amines found widespread application.[107] Their reaction with surface silanol functionalities usually occurs on free and geminal silanol groups, whereas hydrogen-bonded silanol moieties are less reactive owing to the local hydrophilic networks.



Scheme 3.7. *Functionalization of surface silanol groups in silica materials*

In 2006, Xiao *et al.* reported the first example of carbon dioxide conversion into cyclic carbonates using a novel heterogeneous catalyst based on silica-supported imidazolium bromide ionic liquid and different metal salts as co-catalytic species (Figure 3.5.).[108] The silica-supported imidazolium salts and its zinc-based salts co-catalyst proved to be the more active. Thus, it was reused for 3 consecutive runs showing a modest decrease in catalytic activity due to the loss of zinc chloride (Table 3.3., entry 1). Following this work, several imidazolium salts were grafted through organo-silanes onto silica surface. Their catalytic performances were studied considering both the influence of the alkyl chain length, the nature of the nucleophile (Cl^-, Br^-, I^-) as active species and the co-catalytic effect in the epoxide activation promoted by different metal chlorides.[109] Collected data proved that longer alkyl chains and higher nucleophilicity of the anions led to improved epoxides conversion. Moreover, these catalysts were stable up to five consecutive runs with little loss of their initial activities. Imidazolium-based organocatalysts were also immobilized onto MCM-41 and SBA-15 silica (Figure 3.5.).[110] 1-(2-bromoethyl)imidazolium (BrEIm) was immobilized onto MCM-41 showing high activity under neat conditions. However, substantial loss of activity was observed during the recycling process and harsh reaction conditions were applied (Table 3.3., entry 2). In addition, bis-imidazolium bromide supported onto SBA-15 performed best under harsh reaction conditions (Table 3.3., entry 3).

---

[107] a) Y. Xie, C. A. S. Hill, Z. Xiao, H. Militz, C. Mai, *Appl. Sci. Manuf.* **2010**, 41, 806-819; b) P. R. Dvornic, M. J. Owen, Silicone Surface Science, Eds. Springer: Berlin, Germany, **2012**

[108] L.-F. Xiao, F.-W. Li, J.-J. Peng, C.-G. Xia, *J. Mol. Catal. A Chem.* **2006**, *253*, 265-269

[109] a) L. Han, S.-W. Park, D.-W. Park, *Energy Environ. Sci.* **2009**, *2*, 1286-1292; b) L. Han, M.-S. Park, S.-J. Choi, Y.-J. Kim, S.-M. Lee, D.-W. Park, *Catal. Lett.* **2012**, *142*, 259-266

[110] a) J. N. Appaturi, F. Adam, *Appl. Catal. B* **2013**, *136*, 150-159; b) S. Udayakumar, M. K. Lee, H. L. Shim, S. W. Park, S. W. Park, *Catal. Commun.* **2009**, *10*, 659-664; c) F. Adam, J. N. Appaturi, E. P. Ng, *J. Mol. Catal. A* **2014**, *386*, 42-48; d) C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona, M. Gruttadauria, *ChemSusChem* **2011**, *4*, 1830-1837

A few years later, Han *et al.* further explored the catalytic performance of a series of imidazolium-based halides functionalized with carboxyl moieties and grafted onto a silica gel (Figure 3.5.).[111] the synergistic effect of the carboxylic group with the halide anions resulted in higher activity compared to the analogous material based on imidazolium-salts functionalized alkyl moieties. Furthermore, this hybrid material was successfully recycled up to five runs without significant loss of activity (Table 3.3., entry 4).

Recently, several zwitterionic imidazolium-urea derivative framework bridged mesoporous hybrid silica materials were prepared by Arai and co-workers.[112] The hybrid materials displayed hydrogen bond (HB) donor capability and nucleophilicity (Figure 3.5.). The solid bearing iodide as anionic species emerged as the most active in the cycloaddition reaction of CO_2 with epichlorihydrin (ECH). Moreover, the material was used four times without significant loss of activity (Table 3.3 entry 5). More recently, a bifunctional system endowed with imidazolium chloride salts and Tin (Sn) or Zinc (Zn) inserted within the silica was proposed (Figure 3.5.).[113] The chemical fixation of CO_2 into epoxides was carried out using Sn-based catalyst **3.22** with reaction temperature below 150 ºC and a pressure of 40 bar (Table 3.3. entry 6).

Table 3.3. Silica-supported imidazolium catalysts for the synthesis of cyclic carbonates

Entry	Imidazolium	Co-catalyst	Support	Substrate	T (ºC)	P(CO_2) [bar]	t (h)	Conv (%)	Recycling
1	**3.17**	$ZnCl_2$/Br	TEOS	ECH	110	11	1	95	3 runs[b]
2	**3.18**	Br	MCM-41	SO	140	40	4	98	[b]
3	**3.19**	Br	SBA-15	PO	150	100	3	80	5 runs
4	**3.20**	Br	SiO_2	ECH	110	11	5	98	5 runs
5	**3.21**	I	SiO_2	ECH	110	21	4	98	4 runs[b]
6	**3.22**	Sn/Cl	SiO_2	ECH	125	40	3	53	5 runs[b]

[a] PO= propylene oxide; ECH= Epichlorohydrin; SO: Styrene oxide; TEOS= tetraethyl orthosilicate; [b] Loss of activity during the recycling process.

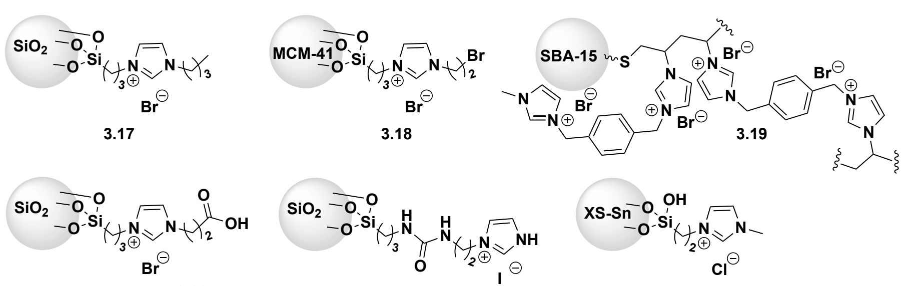


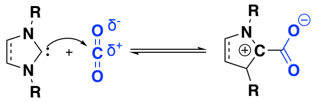
Figure 3.5. *Structures of covalently supported imidazolium salts onto Silica (SiO_2) and mesoporous MCM-41 and SBA-15. XS-Sn: silica-based materials bearing Tin inserted as single sites within the silica architecture.*

---

[111] L. Han, H.-J. Choi, S.-J. Choi, B. Liu, D.-W. Park, *Green Chem.* **2011**, *13*, 1023-1028
[112] M. Liu, X. Lu, Y. Jiang, J. Sun, M. Arai, *ChemCatChem* **2018**, 10, 1860-1868
[113] A. Comès, X. Collard, L. Fusaro, L. Atzori, M.G. Cutrufello, C. Aprile, *RSC Adv.* **2018**, *8*, 25342-25350

3.3 Covalent Immobilization of imidazolium carboxylates

Kuhn *et al.* described for the first time in 1999 the reaction between an NHC and CO_2 to form the corresponding imidazolium-2-carboxylate (Scheme 3.8.).[114]



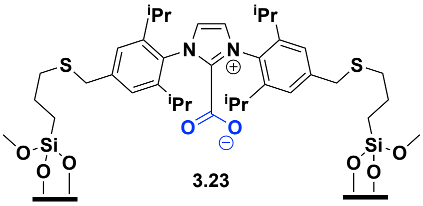
Scheme 3.8. *Synthesis of N, N'-disubstituted imidazol(in)ium-2-carboxylates*

According to the thermal stability of this NHC-CO_2 adduct, it was shown that NHC could effectively activate CO_2 and catalyze the coupling reaction of CO_2 with epoxides.[115] Moreover, in NHC-CO_2 adduct, the angle of the O-C-O bond is close to 130 ºC which indicates a strong activation of CO_2.[116] However, its application has been limited to the preparation of precursors to NHC-metal complexes, halogen free ionic liquids and some stoichiometric transcarboxylation reactions.[117] Only in 2011, due to the development on mesoporous MCM-41 material as solid support for immobilization of homogeneous catalysts, imidazolium carboxylate anchored on MCM-41 and its application in the cycloaddition reaction were reported.[116] Six-steps synthesis provided this hybrid material which was proven to be effective for the coupling reaction of CO_2 with propylene oxide under long reaction time, high temperature and pression (Figure 3.6., Table 3.4.). This result suggested that the MCM-41 supported catalyst suffered from diffusion resistance.

Table 3.4. Silica-supported imidazolium catalysts **3.23** for the synthesis of cyclic carbonates

Entry	T (ºC)	P(CO_2) [bar]	t (h)	Conv (%)	Recycling
1	120	20	24	72	-
2	120	20	48	100	4 runs[a]

[a] Loss of activity during the recycling process.



3.23

Figure 3.6. *Structure of the covalently supported imidazolium carboxylate onto mesoporous MCM-41* ***3.23****.*

---

[114] N. Kuhn, M. Steimann, G. Weyers, *Naturforsch*. **1999**, 54b, 427-433

[115] H. Zhou, W-Z. Zhang, C.-H. Liu, J-P. Qu, X-B. Lu, *J. Org. Chem*. **2008**, *73*, 8039-8044

[116] H. Zhou, Y-M. Wang, W-Z. Zhang, J-P. Qu, X-B. Lu, *Green Chem*. **2011**, 13, 644-650

[117] a) A. M. Voutchkova, A. R. Chianese and R. H. Crabtree, *J. Am. Chem. Soc.*, **2005**, *127*, 17624-17625; b) A. M. Voutchkova, M. Feliz, E. Clot and R. H. Crabtree, *J. Am. Chem. Soc.*, **2007**, *129*, 12834-12846; c) M. Smiglak, J. D. Holbrey and R. D. Rogers, *Green Chem.*, **2007**, ***9***, 90-98; d) I. Tommasi and F. Sorrentino, *Tetrahedron Lett.*, **2005**, *46*, 2141-2145; I. Tommasi and F. Sorrentino, *Tetrahedron Lett.*, **2009**, *50*, 104-107

3.4 Non-covalent immobilization of imidazolium carboxylate onto carbon surfaces

In view of the results described, an efficient approach to support and to recycle homogeneous catalysts avoiding sophisticated designs of the catalyst and the solid surface is needed. Thus, we envisioned noncovalent interactions as a powerful tool to avoid chemical modifications of the support. Among the various supports available for non-covalent anchoring, carbon surfaces possess attractive properties such as high thermal and chemical stability, conductivity and resistance to acid and basic media which have enable their application in fields such as nanoelectronics, nanomaterials science and in catalysis.[118] In addition, these materials with well-defined structure and dimensions often display sharp size distribution, which allows for an homogeneous dispersion of the functionalities and active sites all over their surface, giving rise to reproductible properties. These properties, in combination with their lack of solubility in any solvents make them ideal candidates for the immobilization of organocatalysts and/or organometallic catalysts.

Carbon surfaces (CNTs, rGO, CBs) interact with polycyclic aromatics hydrocarbons via strong π-π stacking interactions. These types of non-covalent interactions, are based on Van der Waals forces and take place between the *pi*-electron densities of planar, stacked aromatic systems and delocalized electron densities in the carbon network of the solid.[119]

To the best of our knowledge, the immobilization of imidazolium carboxylate onto carbon materials by π-π stacking interactions has not been reported to date. Thus, in the following section, the synthesis and characterization of pyrene-tagged imidazolium salts, subsequent carboxylation as well as a study of its non-covalent immobilization onto carbon surfaces through π-π stacking interactions will be presented. The catalytic application of these hybrid materials in the cycloaddition reaction and their recyclability will then be assessed under mild reaction conditions (short reaction time, low temperature and pressure).

3.5 Results and discussion

Following recent reports from our group on bulky NHC ligands featuring N,N'-diaryl substitution such as IMes or IPr bearing hydroxyl group in the aryl *para* positions, we proposed an etherification of these hydroxyl group at the aryl *para* positions with a

---

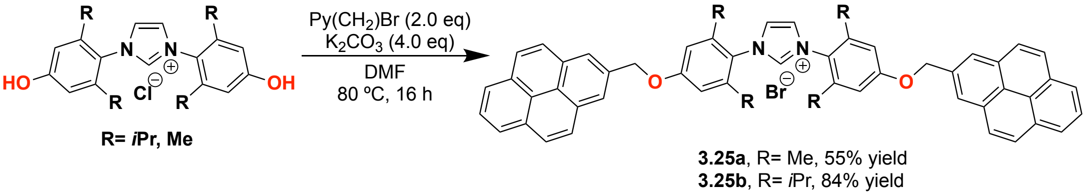
[118] a) Y. L. Zhao, J. F. Stoddart, *Acc. Chem. Res.* **2009**, *42*, 1161; b) H. Huang, Q. Yuang, J. S. Sha, R. D. K. Misra, *Adv. Drug Delivery Rev.* **2011**, *63*,1332; c) C. Schulz-Drost, V. Sgobba, C. Gerhards, S. Leubner, R. M. Krieck Calderon, A. Ruland, D. M. Guldi, *Angew. Chem. Int. Ed.* **2010**, *49*, 6425; d) C. Vijayakumar, B. Balan, M.-J. Kim, M. Takeuchi, *J. Phys. Chem. C*, **2011**, *115*, 4533.

[119] C. Estarellas, Theoretical and experimental study of cooperative effects in noncovalent interactions. Ph. D. Tesis, Illes Balears University, Spain, **2012**

pyrene.[120] Pyrene moiety is well known for its potential to strongly interact with carbon surfaces[121] hence giving a robust heterogenized catalyst with maintained catalytic activity upon 10 recycling runs.

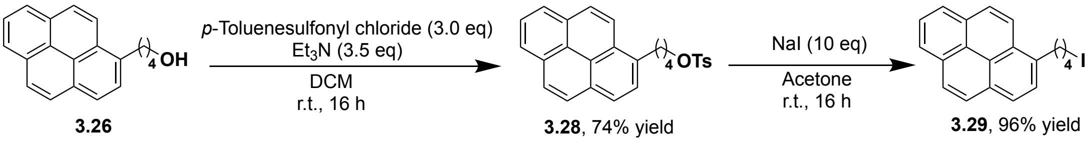
3.5.1 Synthesis of the imidazolium carboxylate organocatalysts

Starting from hydroxy-functionnalized imidazolium salt, the first step of the synthesis was an etherification of IMesOH.HCl **3.24a** and IPrOH.HCl **3.24b** with commercially available 2-(bromomethyl)pyrene halide under controlled reaction conditions. Compound **3.25a** was obtained as an insoluble light brown powder in a significantly lower yield compared to its analogue **3.25b** (Scheme 3.9.).



Scheme 3.9. *Synthesis of pyrene-tagged imidazolium salt* ***3.25a*** *and* ***3.25b***

In order to evaluate the length of the chain between the pyrene moiety and the active site, 2-(4-iodobutyl)pyrene as halide was also used. 2-(4-iodobutyl)pyrene **3.29** was obtained in a two-step synthesis by reaction of the commercially available pyrenebutanol **3.26** with *p*-toluenesulfonyl chloride **3.27** in the presence of triethylamine at room temperature in dichloromethane (Scheme 3.10.). After purification, **3.28** was subjected to a nucleophilic substitution in the presence of NaI in acetone. A clean reaction occurred giving **3.29** in good yield (Scheme 3.10.).



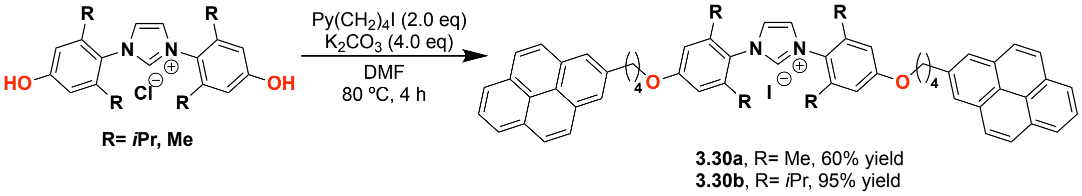
Scheme 3.10. *Two-step synthesis of 2-(4-iodobutyl)pyrene* ***3.29***

Etherification of IMesOH.HCl **3.24a** and IPrOH.HCl **3.24b** with 2-(4-iodobutyl)pyrene gave **3.30b** in good yield. Again, the imidazolium ligand having IMes substitution **3.30a**, is obtained in lower yield and as an insoluble powder compared to its IPr analogue (Scheme 3.11.).

---

[120] a) J. L. Krinsky, A. Martinez, C. Godard, S. Castillón, C. Claver *Adv. Synth. Catal.* **2014**, 10, 460-474; b) A. Martinez, J. L. Krinsky, S. Castillón, K. Loponov, A. Lapkin, C. Godard, C. Claver *Catal. Sci. Technol.,* **2015**, 5, 310-319

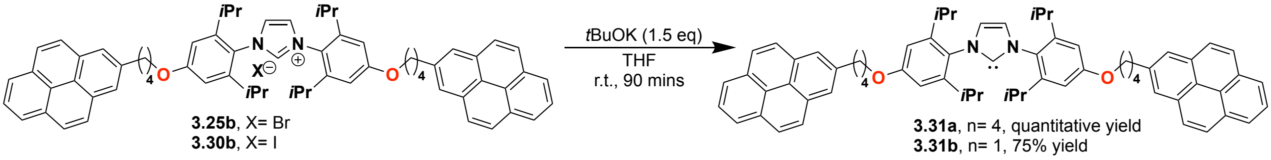
[121] S. Latil, M. Heggie, J. Charlier, F. Tournus, *Phys. Rev.* **2005**, *72*, 075431



3.30a, R= Me, 60% yield
3.30b, R= *i*Pr, 95% yield

Scheme 3.11. *Synthesis of pyrene-tagged imidazolium salt **3.30a** and **3.30b***

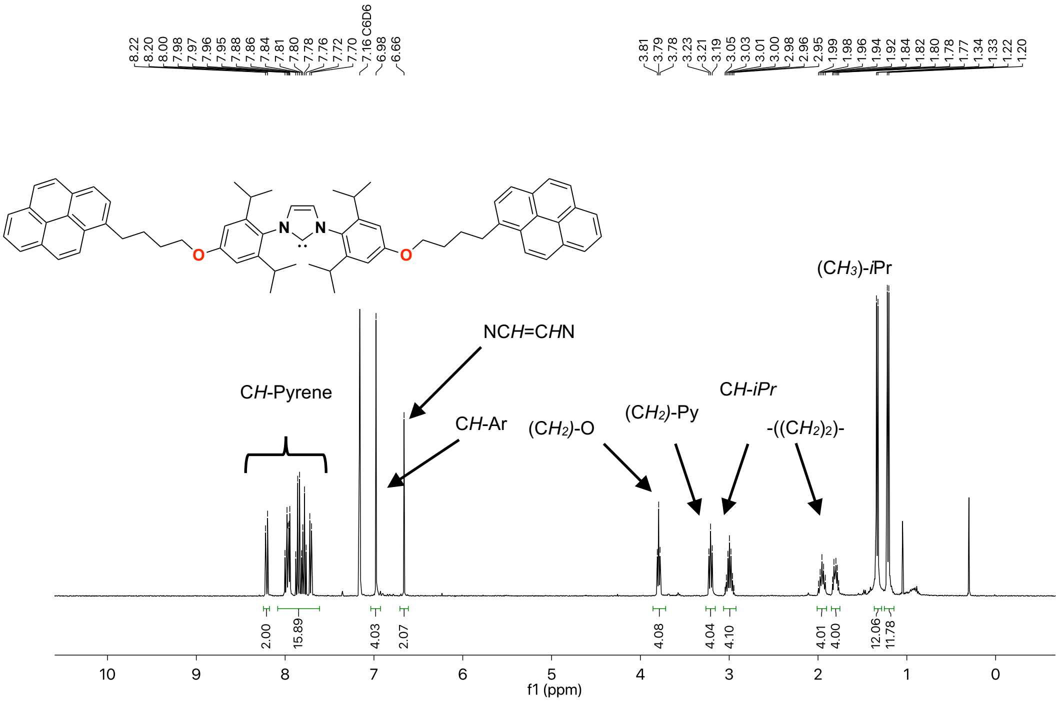
Four new pyrene-tagged imidazolium were synthesized and fully characterized by NMR spectroscopy and mass-spectroscopy (MS). The next step was the deprotonation of the pyrene-tagged imidazolium salts with an excess of *tert*-butoxide (*t*-BuOK) under inert atmosphere which provided free carbenes in high yield (Scheme 3.12.). The formation of the free carbenes was clearly confirmed by ^{1}HNMR analysis due to the disappearance of the acidic N*C*HN signal corresponding to the imidazolium ring (Figure 3.7.). Moreover, these species exhibited a typical ^{13}C NMR resonance shift at 220.6 ppm for **3.31a** and 217.8 ppm for **3.31b** relative to free carbenes.



3.25b, X= Br
3.30b, X= I

3.31a, n= 4, quantitative yield
3.31b, n= 1, 75% yield

Scheme 3.12. *Synthesis of pyrene-tagged free carbenes **3.31a** and **3.31b***



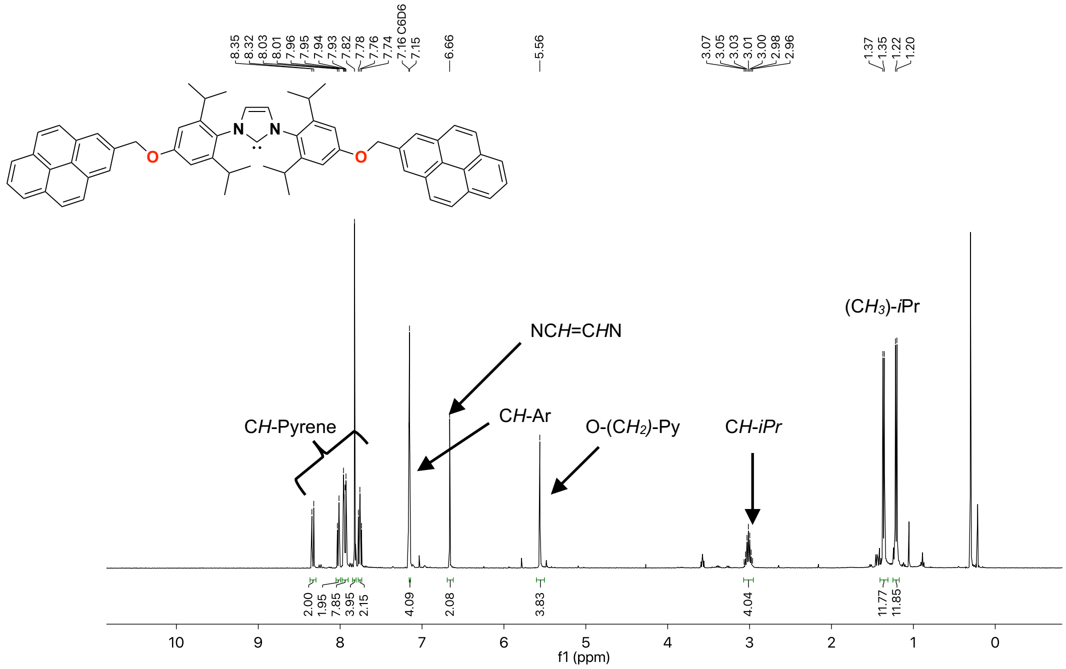
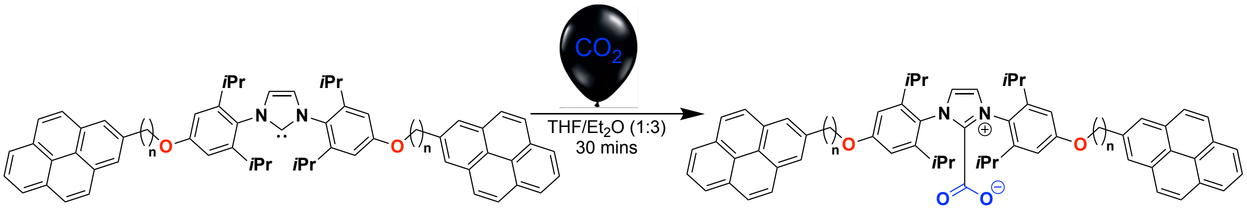


Figure 3.7. *^{1}H NMR of free carbenes **3.31a** and **3.31b** in **C_6D_6***

These free carbenes were then protected by reaction with carbon dioxide atmospheric pressure in a mixture of THF and Et_2O for 30 mins (Scheme 3.13.). The imidazolium carboxylate **3.32a** and **3.32b** were obtained in good yield, 88% and 82% respectively. The successfull capture of CO_2 was confirmed by NMR spectroscopy, thermogravimetric analysis (TGA) and infrared spectroscopy (IR) with a band at 1674 cm^{-1} for **3.32a** and 1671 cm^{-1} for **3.32b**.



3.31a, n= 4
3.31b, n= 1

3.32a, n= 4, 88% yield
3.32b, n= 1, 82% yield

Scheme 3.13. *Synthesis of pyrene-tagged free carbenes **3.32b** and **3.32a***

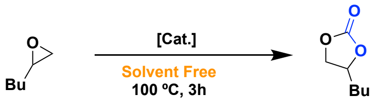
In conclusion, new pyrene-tagged imidazolium carboxylates organocatalysts were synthesized in 3 steps from imidazolium chloride salts **3.24b**.

3.5.2 Proof of concept using pyrene-tagged imidazolium carboxylate organocatalysts

The new pyrene-tagged organocatalysts were tested in the cycloaddition reaction of epoxides with CO_2 to evaluate any possible effect that could be induced by the pyrene tag (Table 3.5.).

First, iPr-CO_2 adduct was synthesized and fully characterized following existing reports.[122] Then, the cycloaddition reaction of an 1-hexene oxide with CO_2 was performed using the classic *i*Pr-CO_2 adduct, imidazolium carboxylate **3.32a** and **3.32b** under neat conditions, at 100 ºC and 1MPa of CO_2. Under such mild conditions, the organocatalyst **3.32a** exhibits similar performance as the classic *i*Pr-CO_2 counterpart (Table 3.5., entry 1 and 2). The organocatalyst **3.32a** was proven to be more active than its analogues **3.32b** indicating a clear effect of the linker length between the pyrene moiety and the active site (Table 3.5., entries 2 and 3).

Table 3.5. New pyrene-tagged imidazolium carboxylate activity in the Cycloaddition reaction



Entry	Organocatalyst	Additives	Yield (%) [b]
1	iPr-CO_2	-	69
2	**3.32a**	-	57
3	**3.32b**	-	46
4	-	KI/18C6	37
5	**3.32b**	KI/18C6	73
6	iPr-CO_2	KI/18C6	99
7	**3.32a**	KI/18C6	87

[a] Reaction conditions: 12.3 mmol of substrate, 2 mol% of homogeneous catalytic system (1:1:1), P(CO_2)= 1 MPa, T= 100 °C, 3h, neat. Work-up: silice filtration using EtOAc. [b] Isolated yield

We can therefore conclude that the pyrene moiety does not affect the catalytic performance of the corresponding organocatalysts when the active site is far from the pyrene moiety. The organocatalyst **3.32a** has further been compared to its carbene analogue and evaluated in the presence or not of additives. The best result was obtained while combining imidazolium carboxylate **3.32a**, KI and 18-crown-6 (Table 3.5., entry 7). It is in accordance with previously published results on a binary activation of the epoxide and the CO_2 by the metal halide and the carbene respectively. Thus, imidazolium carboxylate **3.32a** immobilized onto carbon surfaces in the presence of KI and 18-crown-6 was further used in the cycloaddition reaction.

3.5.3 Immobilization of organocatalyst **3.32a** onto carbon materials

To complete the synthesis of the corresponding heterogenized organocatalysts, the imidazolium carboxylate **3.32a** was reacted with several carbon supports following the procedure described in Figure 3.8.

---

[122] S. Naumann, F. G. Schmidt, R. Schowner, W. Frey, M. R. Buchmeiser, *Polym. Chem.* **2013**, *4*, 2731-2740

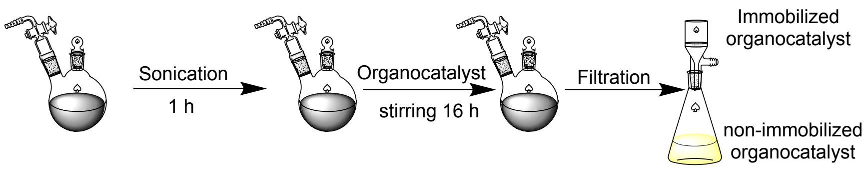
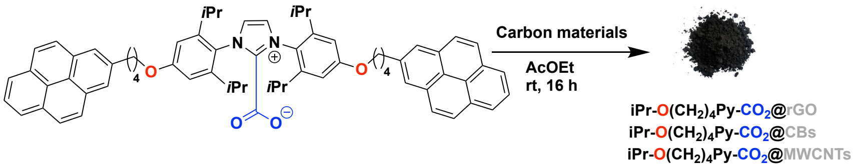


Figure 3.8. *Procedure for the immobilization of pyrene-tagged organocatalyst onto MWCNTs, rGO and CBs.*

Based on previous reports[123] by our group and because polar solvents favor π-π interactions between the pyrene and the supports[124], ethyl acetate (EtOAc) was used for the immobilization using MWCNTs, rGO and CBs as carbon surfaces. The procedure for the immobilization was the following: first, the carbon material was dispersed by sonication in the solvent of choice for 1 h. Then, a solution of the organocatalyst in EtOAc was added to the suspension, and the mixture was left stirring at room temperature for 16 hours. It is worth mentioning that the amount of solvent, and therefore the concentration, is important. When the carbon materials are dispersed into the solvent, a sufficient amount of solvent is necessary to avoid the formation of a muddy solution. Finally, the heterogenized organocatalyst was filtrated and washed with the solvent used for the immobilization. The amount of organocatalyst immobilized was analyzed by TGA of the hybrid materials. The organocatalyst not immobilized can be easily recovered after filtration and subsequently reused.

Table 3.6. TGA analysis under N2 atmosphere of the immobilised pyrene-tagged imidazolium carboxylate **3.32a** onto MWCNTs, CBs and rGO



Entry	Carbon materials	wt%[b]
1	CBs	13
2	MWCNTs	16
3	rGO	25

[a] Reaction conditions: Commercial MWCNTS and rGO were dispersed in AcOEt and sonicated for 1h. The organocatalyst is then added to the suspension and stir 16 h at r.t. [b] TGA analysis under N2 atmosphere

---

[123] a) C. Vriamont, M. Devillers, O. Riant, S. Hermans, *Chem. Eur. J.* **2013**, 19, 12009-12017; b) S. Sabater, J. A. Mata, E. Peris, *Organometallics* **2015**, 34, 1186-1190; c) S. Sabater, J. A. Mata, E. Peris, *ACS Catal.* **2014**, 4, 2038-2047; d) V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, *Chem. Rev.* **2012**, 112, 6156-6214 e) L. Rodriguez-Perez, M. A. Herranz, N. Martin, *Chem. Commun.* **2013**, 49, 3721-3735.

[124] M. Keller, V. Collière, O. Reiser, A. M. Caminade, J. P. Majoral, A. Ouali, *Angew. Chem. Int. Ed.* **2013**, *52*, 3626-3629

A ratio of 1:3 of carbon materials/organocatalyst (wt/wt) was used to immobilize **3.32a** under the conditions presented in Table 3.6. The organocatalyst **3.32a** was successfully immobilized onto MWCNTs, commercially available rGO and CBs. The latter was pre-treated at 2000 ºC for one hour prior to utilization.[125] The TGA analysis of the hybrid material reveals a clean loss of the organocatalyst **3.32a** anchored onto the carbon materials between 250 ˚C and 500 ˚C (Figure 3.9. *in red*).

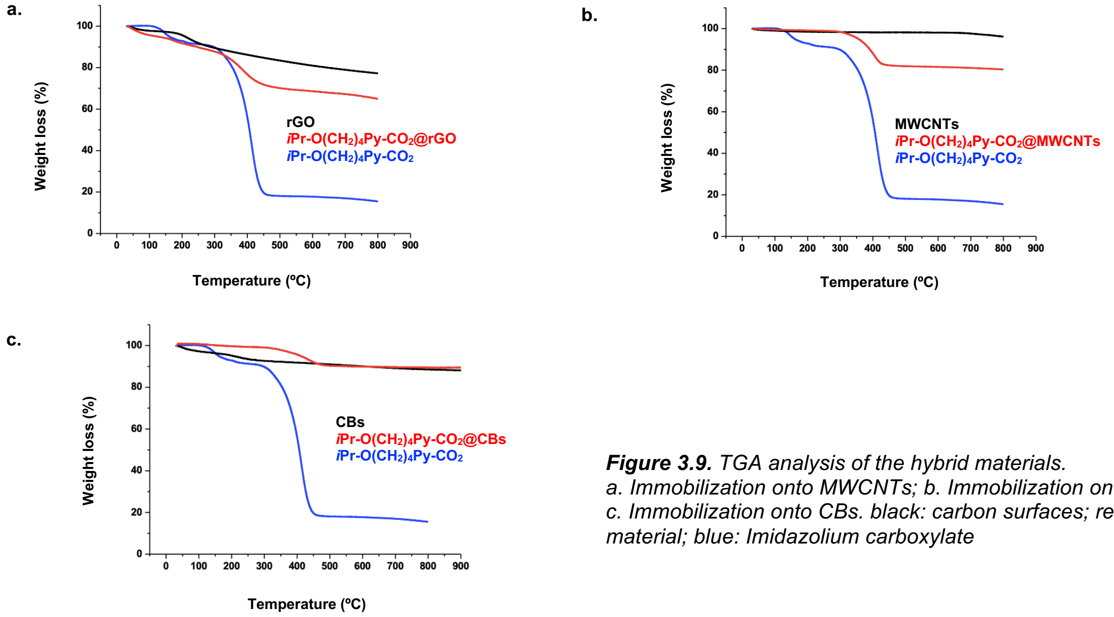


Figure 3.9. *TGA analysis of the hybrid materials. a. Immobilization onto MWCNTs; b. Immobilization onto rGO; c. Immobilization onto CBs. black: carbon surfaces; red: hybrid material; blue: Imidazolium carboxylate*

Interestingly, a higher catalyst loading was observed onto rGO than on MWCNTs and CBs (Table 3.6.). These results suggest that the organocatalyst bearing 2 pyrene moieties is more easily anchored onto the flat structure of the rGO than onto the curved structure of the MWCNTs and CBs.

3.5.4 Recycling studies

At this stage, the heterogenized catalyst **3.32a**@MWCNTs was first tested in the cycloaddition reaction using the same reactions conditions applied to the homogeneous catalyst (Figure 3.10., 1st run). The hybrid material was effective in the cycloaddition reaction and no by-product was observed in the crude by means of ^{1}H NMR analysis. However, low catalytic activity was obtained compared to the homogeneous catalyst. Following this result, recycling study was performed to probe the robustness of the hybrid material under batch conditions (Figure 3.10.). After completion of each run, the reaction mixture was allowed to reach room temperature and the solid catalyst was separated by simple filtration, washed using EtOAc, dried and reused in the next run. The additives were added only in the first run. After the first run, a significant increase in catalytic activity was observed which decreases in the third run to give 48% isolated yield of cyclic

---

[125] E. J. Garcia-Suárez; C. Menédez-Vázquez, A. B. García, *Mol. Liq.* **2012**, 169, 37-42

carbonate product. In the fourth run, the catalytic activity drastically decreases again. TGA analysis of the hybrid materials after the 1st run revealed adsorption of the cyclic carbonate product onto the carbon surfaces, which might have displaced the imidazolium carboxylate organocatalyst. The leaching of the organocatalyst was confirmed by ^{1}H NMR analysis of the carbonate product. Moreover, TGA analysis revealed an incomplete decomposition of the material hence, revealing the presence of iodide in the MWCNTs. Indeed, iodide ability to intercalate into carbon nanotubes has been previously reported[126] therefore, in the absence of the imidazolium carboxylate organocatalyst which role is to activate the carbon dioxide and thus facilitate the cycloaddition, iodide reacts with 1-hexene oxide on a lower rate to produce cyclic carbonate product (Figure 3.10., 4th run).

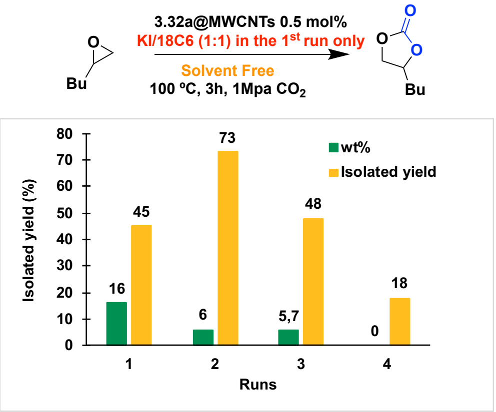


Figure 3.10. *Recycling experiments using heterogeneous catalysts **3.32a@MWCNTs** for the Cycloaddition of CO2 with 1-hexene oxide*

Based on those results, epichlorydrin (ECH) was chosen as model substrate as it contains a polar chloride substituent which could avoid product adsorption onto carbon surfaces compared to the lipophilic butyl group of 1-hexene oxide. The procedure described above was followed for the recycling experiments using **3.32a**@MWCNTs, **3.32a**@rGO, **3.32a**@CBs hybrid materials. Lower temperature (80 ºC *vs* 100 ºC) and longer reaction time (5 h *vs* 3 h) were applied to minimize catalyst leaching. The hybrid materials proved to be effective for the coupling reaction of CO_2 with ECH (1st run, Figure 3.11.). Upon recycling, a drop-in activity was observed after the 1st cycle when **3.32a**@MWCNTs was used and, there is no conversion in the 4th run. In the case of **3.32a**@CBs hybrid material, a high catalytic activity is maintained in the 1st and 2nd run. A notable drop in yield was observed in the 3rd run and no conversion was observed in the 5th run. When the isolated yield of the cyclic carbonate product is ca. 30%, we supposed that leaching of the organocatalyst is complete and the catalytic activity is due to the iodide intercalated into the carbon materials. This is confirmed by TGA analysis of the hybrid materials. Only the supported catalyst onto rGO can be recycled up for 5 runs

---

[126] C. Yam, C. Ma, X. Wang, G. Chen, *Appl. Phys. Lett.* **2004**, *85*, 4484-4486

although with a decrease in activity. These results suggest that the cooperative catalytic system involving iodide's epoxide and NHC's CO_2 activation is viable for a much longer period when rGO is used as support.

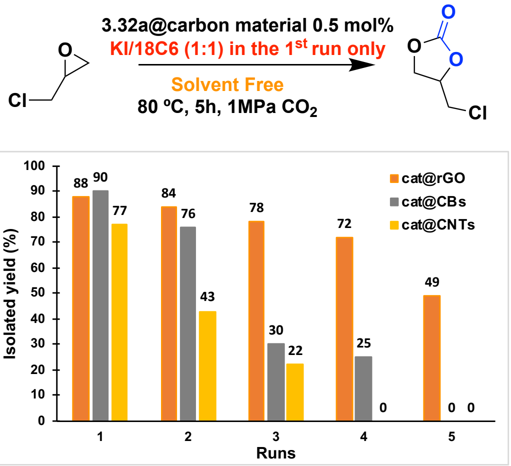


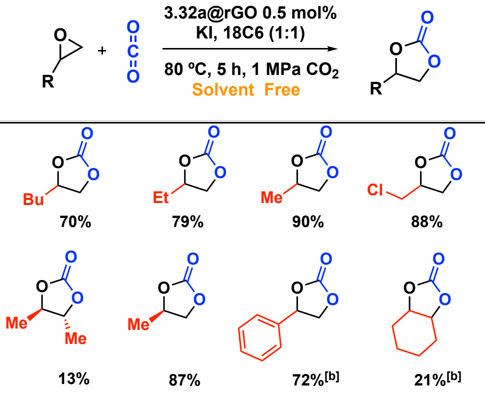
Figure 3.11. *Recycling experiments using heterogeneous catalysts* ***3.32a@MWCNTs****,* ***3.32a@rGO*** *and* ***3.32a@CBs*** *for the Cycloaddition of CO_2 with ECH*

These results clearly reveal a better and/or higher loading intercalation of iodide into rGO compared to CBs and MWCNTs in the cycloaddition reaction of ECH with CO_2. Indeed, a high level of leaching takes place from the CBs and MWCNTs carbon surfaces during the cycloaddition reaction. This could be due to the removal of the weak anchoring organocatalyst on these supports. Indeed, we suppose a weaker π-π stacking interaction of the pyrene-tagged organocatalyst onto these round structures compared to the flat structure of the rGO.

3.5.5 Scope of epoxides

In view of the recycling results, the imidazolium carboxylate supported onto rGO was selected to evaluate the scope of substrates that could be efficiently converted in this process. The standard reaction conditions were set to 80 °C, 1MPa of CO_2 for 5h. Notably, the reactions were performed under solvent-free conditions and all products were obtained by simple filtration over silica gel. The results of the substrate screening are summarized in Table 3.7. The cooperative catalytic system consisting of **3.32a@rGO**/KI-18C6 is effective to convert terminal epoxides providing the corresponding carbonate products in yields from 70 to 90 %. Furthermore, phenylethylene oxide was turned into carbonate in a good isolated yield of 72%. The regiochemistry regarding the epoxide ring-opening in this reaction was further tested by the coupling reaction of (*R*)-propylene oxide with CO_2. The corresponding (*R*)-propylene carbonate was obtained in high yield with retention of stereochemistry. It confirms that the nucleophilic attack of the iodide occurs at the less sterically hindered carbon atom of the terminal epoxide.

Table 3.7. Evaluation of the substrate scope under standard reaction conditions



[a] Reaction conditions: 12.3 mmol of substrate, 2 mol% of KI/18C6 (1:1), P(CO_2)= 1 MPa, neat. Isolated yield after simple filtration using EtOAc with high selectivities (>99%). [b] Purification via column chromatography

The steric hindrance effect is further observed over more challenging disubstituted epoxides such as cyclohexene oxide and *trans*-β-butylene oxide (Table 3.7.). This catalytic system transformed cyclohexene oxide and trans-β-butylene oxide in 21 and 13 % isolated yield, respectively. Hence, additional substituent at the epoxide hinders the nucleophilic attack of the catalyst to the epoxide, preventing the ring opening step of the epoxide and thus subsequent CO_2 addition.

3.6 Conclusions

From the study described in this chapter, the following conclusions can be extracted:

i) The pyrene-tagged imidazolium salts were synthesized in good yield (55%-95%) and fully characterized by NMR spectroscopy and MS.

ii) The imidazolium carboxylates were synthesized in excellent yield and fully characterized by NMR spectroscopy, IR and TGA techniques.

iii) The pyrene-tagged imidazolium organocatalyst were applied in the homogeneous cycloaddition reaction of 1-hexene oxide. **3.32a** gives similar results than the classic imidazolium carboxylate adduct in term of activity in comparison to its analogue **3.32b**. Therefore, a clear effect of the linker length between the active site and the pyrene moiety was revealed to affect the activity of the resulting organocatalyst.

iv) The pyrene-tagged imidazolium carboxylate **3.32a** was successfully immobilized onto MWCNTs, rGO and CBs using EtOAc as solvent under mild conditions to afford the heterogenized catalysts **3.32a@MWCNTs**, **3.32a@rGO**, **3.32a@CBs**.

v) **3.32a@MWCNTs**, **3.32a@rGO**, **3.32a@CBs** were used in the cycloaddition reaction in batch. They proved to be effectives in the cycloaddition reaction.

vi) Recycling experiments with these hybrid materials were perform in a batch mode. The catalyst activity of **3.32a@MWCNTs** drop in the second run due to catalyst leaching. Less leaching was observed in the case of **3.32a@rGO** and **3.32a@CBs**. Among the heterogenized organocatalysts, **3.32a@rGO** hybrid material provided the best performance in term of robustness (recycle up to 5 runs).

vii) The heterogenized organocatalysts **3.32a@rGO** was successfully applied in the cycloaddition reaction of various epoxides under mild conditions (80 ºC, 5 h, 1 MPa of CO_2).

3.7 Experimental Part

General considerations

All operations were carried out under inert atmosphere using Schlenk tube or glovebox. Anhydrous solvents were collected from a Braun MB SPS-800 system except for EtOAc, which was dried with CaH_2 and stored under inert atmosphere. The chemicals were purchased in analytic quality from SigmaAldrich, AlfaAesar and AcrosOrganics and used as received. MWCNTs (SBET = 80 m^2/g, pore size = 5–10nm, outside diameter = 30-50 nm, length = 0.5-200 nm) were purchased from HeJi, rGO (SBET = 500-400 m^2/g) from Graphenea, and CBs (SBET = 200 m^2/g, pore volume = 0.677 cm^3g^{-1})[127] from MAST Carbon International. IPrOH·HCl[120] was prepared according to literature procedures.

Solution Nuclear Magnetic Resonance (NMR). ^1H and ^{13}C NMR spectra were recorded using a Varian Mercury VX 400 MHz spectrometer. Chemical shift values(δ) are reported in ppm relative to TMS (^1H and $^{13}C\{^1H\}$) and coupling constants are reported in Hertz. High-resolution mass spectra (HRMS) were recorded on an Agilent Time-of-Flight 6210 using ESI-TOF (electrospray ionization-time of flight). Samples were introduced to the mass spectrometer ion source by direct injection using a syringe pump and were externally calibrated using sodium formate.

Thermogravimetric analysis (TGA). Measurements were carried out using a Mettler Toledo TGA/DSC 1 microbalance. Analyses were performed in N2 (50 NmL min^{-1}) ramping the temperature from room temperature to 900 °C at 10 °C min^{-1}.

Fourier Transform Infrared (FTIR). The spectra were recorded on a Bruker Equinox 55 spectrophotometer with a spectral window of 4000−500 cm^{-1}

Synthesis of 3.25a

---

[127] S. R. Tennison, O. P. Kozynchenko, V. V. Strelko, A. J. Blackbum, Porous Carbons. US patent 0032092, **2008**

A Schlenk flask was charged with IMesOH·HCl **3.24a** (500 mg, 1.19 mmol), 1-(bromomethyl)pyrene (873 mg, 2.97 mmol, 2.5 equiv.), K_2CO_3 (655 mg, 4.75 mmol, 4.0 equiv.) and anhydrous DMF (10 mL). The flask was then heated with stirring at 80 °C for 16 h. The reaction mixture was then transferred into to a clean round-bottom flask, toluene (3 X 10 mL) was added and the solution was evaporated under high vacuum at 60 °C. The residue obtained was extracted with DCM, filtered through diatomaceous earth and evaporated to afford a yellow oil, which was precipitated with chloroform to yield a white solid; yield: 928 mg (84% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.61 (s, 1H), 8.40 (d, *J* = 9.2 Hz, 2H), 8.27-8.11 (m, 14H), 8.08-8.04 (m, 2H), 7.74 (d, *J* = 9.2 Hz, 2H), 7.09 (s, 4H), 5.85 (s, 4H), 2.43 (hept, *J* = 6.7 Hz, 4H), 1.28 (dd, J = 6.8, 2.2 Hz, 24H). ^{13}C NMR (100 MHz, CH_3OD/CH_3CN): δ 137.61, 129.09, 128.84, 128.34, 127.41, 126.66, 126.58, 125.72, 124.18, 118.31, 69.90.

ESI-HRMS: $C_{53}H_{41}N_2O_2$: Calculated (M^+: 737,3163); Experimental (M^+: 737,3168)

Synthesis of 3.25b

A Schlenk flask was charged with IPrOH·HCl **3.24b** (500 mg, 1.10 mmol, 1.0 equiv.), 1-(bromomethyl)pyrene (806 mg, 2.74 mmol, 2.5 equiv.), K_2CO_3 (606 mg, 4.38 mmol, 4.0 equiv.) and anhydrous DMF (10 mL). The flask was then heated with stirring at 80 °C for 16 h. The reaction mixture was then transferred into to a clean round-bottom flask, toluene (3 X 10 mL) was added and the solution was evaporated under high vacuum at 60 °C. The residue obtained was extracted with DCM, filtered through diatomaceous earth and evaporated to afford a yellow oil, which was precipitated with chloroform to yield a white solid; yield: 928 mg (84% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.61 (s, 1H), 8.40 (d, *J* = 9.2 Hz, 2H), 8.27-8.11 (m, 14H), 8.08-8.04 (m, 2H), 7.74 (d, *J* = 9.2 Hz, 2H), 7.09 (s, 4H), 5.85 (s, 4H), 2.43 (hept, *J* = 6.7 Hz, 4H), 1.28 (dd, J = 6.8, 2.2 Hz, 24H). ^{13}C NMR (100 MHz, CH_3OD/CH_3CN): δ 162.33, 148.22, 132.87, 132.44, 131.91, 130.91, 130.54, 129.11, 128.86, 128.59, 128.39, 127.51, 127.43, 126.67, 126.58, 125.79, 125.71, 125.48, 124.28, 124.23, 118.38, 112.31, 69.90, 49.00, 30.36, 24.48, 23.67.

ESI-HRMS: $C_{61}H_{57}N_2O_2$: Calculated (M+: 849,4415); Experimental (M+: 849,4418).

Synthesis of 3.30a

A Schlenk flask was charged with IMesOH·HCl **3.24a** (500 mg, 1.45 mmol, 1.0 equiv.), 1-(4-iodobutyl)pyrene **3.29** (1.39 g, 3.63 mmol, 2.5 equiv.), K_2CO_3 (802 mg, 5.80 mmol, 4.0 equiv.) and anhydrous DMF (10 mL). The flask was then heated with stirring at 80 °C for 4 h. The reaction mixture was then transferred into to a clean round-bottom flask, toluene (3 X 10 mL) was added and the solution was evaporated under high vacuum at 60 °C. The residue obtained was filtered through diatomaceous earth and evaporated to afford a dark-brown oil, which was precipitated with hot chloroform to yield a light-brown solid; yield: 828 mg (60% yield). ^{1}H NMR (400 MHz, CD_3OD): δ 9.93 (d, *J* = 9.3 Hz, 2H), 9.82 -9.67 (m, 8H), 9.67-9.48 (m, 8H), 9.35 (s, 2H), 8.37 (s, 4H), 5.65 (t, *J* = 7.5 Hz, 4H), 5.01 (t, *J* = 7.5 Hz, 4H), 3.62 (s, 20H). ^{13}C NMR (100 MHz, CH_3OD/CH_3CN): δ 161.58, 138.06, 137.32, 132.60, 132.11, 131.02, 129.68, 128.61, 128.56, 128.22, 127.58, 127.09, 127.03, 126.28, 126.02, 125.89, 125.85, 125.80, 124.57, 118.38, 115.55, 69.04, 33.82, 29.87, 29.13, 17.67.

ESI-HRMS: $C_{59}H_{53}N_2O_2$: Calculated (M^+: 821,4102); Experimental (M^+: 821,4107)

Synthesis of 3.30b

A Schlenk flask was charged with IPrOH·HCl **3.24b** (500 mg, 1.10 mmol, 1.0 equiv.), 1-(4-iodobutyl)pyrene **3.29** (1.06 g, 2.75 mmol, 2.5 equiv.), K_2CO_3 (608 mg, 4.40 mmol, 4.0 equiv.) and anhydrous DMF (10 mL). The flask was then heated with stirring at 80 °C for 4 h. The reaction mixture was then transferred into to a clean round-bottom flask, toluene (3 X 10 mL) was added and the solution was evaporated under high vacuum at 60 °C. The residue obtained was extracted with DCM, filtered through diatomaceous earth and evaporated to afford a yellow oil, which was precipitated with chloroform to yield a white solid; yield: 1.20 g (95% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.34 (s, 1H), 8.34 (d, *J* = 9.3 Hz, 2H), 8.16 (dt, *J* = 15.2, 8.0 Hz, 8H), 8.08-7.91 (m, 8H), 7.73-7.67 (m, 2H), 6.81 (s, 4H), 4.10 (t, *J* = 7.4 Hz, 4H), 3.47 (t, *J* = 7.4 Hz, 4H), 2.31 (hept, *J* = 7.3 Hz, 4H), 2.05 (ddt, *J* = 37.5, 13.9, 6.7 Hz, 8H), 1.20 (dd, *J* = 17.9, 6.8 Hz, 24H); ^{13}C NMR (100 MHz, CH_3OD/CH_3CN): δ 162.85, 148.08, 137.99, 132.76, 132.22, 131.19, 129.80, 128.58, 128.57, 128.28, 127.64, 127.57, 127.06, 126.14, 126.03, 125.97, 125.95, 125.79, 124.52, 123.89, 118.25, 111.50, 69.17, 49.00, 33.91, 30.40, 30.01, 29.28, 24.53, 23.67.

ESI-HRMS: $C_{67}H_{69}N_2O_2$: Calculated (M^+: 933,5354); Experimental (M^+: 933,5389)

Synthesis of 3.31a

A flame-dried schlenk flask was charged with **3.25b** (500 mg, 0.47 mmol, 1.0 equiv.) and anhydrous THF (10 mL). To this suspension was added KOtBu (79 mg, 0.71 mmol, 1.5 equiv.) and the reaction mixture was stirred at room temperature for 90 min. The resulting suspension was filtered off and the filtrate partially evaporated under reduced pressure. Pentane was added resulting in the formation of precipitated product which was subsequently washed with pentane, dried under reduced pressure to afford a light brown solid; yield: 429 mg (98% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 8.21 (d, *J* = 9.2 Hz, 2H), 8.08- 7.61 (m, 16H), 6.98 (s, 4H), 6.66 (s, 2H), 3.79 (t, *J* = 7.6 Hz, 4H), 3.21 (t, *J* = 7.6 Hz, 4H), 3.00 (hept, *J* = 6.6, 6.1 Hz, 4H), 1.96 (p, *J* = 7.4 Hz, 4H), 1.80 (dt, *J* = 12.5, 6.0 Hz, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, C_6D_6):

δ 220.63, 159.96, 147.75, 136.87, 132.22, 132.03, 131.53, 130.47, 129.26, 128.06, 127.04, 126.12, 125.85, 125.76, 125.29, 125.24, 125.13, 123.82, 121.93, 109.68, 67.83, 33.44, 29.71, 29.12, 28.61, 24.80, 23.64.

Synthesis of 3.31b

A flame-dried schlenk flask was charged with **3.30b** (500 mg, 0.54 mmol, 1.0 equiv.) and anhydrous THF (10 mL). To this suspension was added KOtBu (90 mg, 0.80 mmol, 1.5 equiv.) and the reaction mixture was stirred at room temperature for 90 min. The resulting suspension was filtered off and the filtrate partially evaporated under reduced pressure. Pentane was added resulting in the formation of precipitated product which was subsequently washed with pentane, dried under reduced pressure to afford a light brown solid; yield: 341 mg (75% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 8.34 (d, *J* = 9.2 Hz, 2H), 8.03 (d, J = 7.8 Hz, 2H), 7.95 (dd, J = 8.3, 3.6 Hz, 8H), 7.83 (s, 4H), 7.77 (t, *J* = 7.6 Hz, 2H), 6.67 (s, 2H), 5.57 (s, 4H), 3.02 (hept, J = 6.6 Hz, 4H), 1.37 (d, *J* = 6.9 Hz, 12H), 1.22 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, C_6D_6): δ 218.0, 159.85, 147.95, 132.62, 132.05, 131.79, 131.35, 130.72, 130.03, 126.27, 125.74, 125.73, 124.97, 123.82, 121.96, 69.10, 29.19, 24.80, 23.64.

Synthesis of 3.32a

A flame-dried schlenk flask was charged with **3.31a** (400 mg, 0.43 mmol) and an anhydrous mixture of THF:Et_2O (1:3). The resulting solution was cooled in an iced bath and CO_2 was bubbled through the yellow solution. The precipitated solid was filtered, washed with diethyl ether and dried in vacuo to yield a white solid; yield 368.6 mg (88% yield).^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.35 (d, *J* = 9.2 Hz, 2H), 8.27 – 7.83 (m, 16H), 7.02 (s, 2H), 6.77 (s, 4H), 4.09 (t, *J* = 7.2 Hz, 4H), 3.46 (t, *J* = 7.2 Hz, 4H), 2.46 (m, 4H), 2.15 – 1.93 (m, 8H), 1.18 (dd, *J* = 35.2, 6.6 Hz, 24H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.13, 153.00, 148.88, 147.14, 137.33, 131.93, 131.43, 130.32, 129.15, 128.01, 127.88, 127.68, 127.03, 126.38, 125.50, 125.42, 125.39, 125.34, 125.20, 124.00, 123.00, 110.37, 68.39, 54.00, 33.61, 29.79, 28.77, 24.63, 23.52.

Synthesis of 3.32b

A flame-dried schlenk flask was charged with **3.31b** (320 mg, 0.38mmol) and an anhydrous mixture of THF:Et_2O (1:3). The resulting solution was cooled in an iced bath and CO_2 was bubbled through the yellow solution. The precipitated solid was filtered, washed with diethyl ether and dried in vacuo to yield a white solid; yield 276 mg (82% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.45 (d, *J*= 9.2 Hz, 2H), 8.31 -8.01 (m, 16H), 7.05 (s, 2H), 6.57 (s, 4H), 5.25 (s, 4H), 2.40 (m, 4H), 1.15 (d, *J*= 6.7 Hz, 24 H), 1.12 (d, *J*= 6.7 Hz, 12 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.33, 153,09, 148.22, 147.20, 132.87, 132.44, 131.91, 130.91, 130.54, 129.11, 128.86, 128.59, 128.39, 127.51, 127.43, 126.67, 126.58, 125.79, 125.71, 125.48, 124.28, 124.23, 118.38, 112.31, 69.90, 49.00, 30.36, 24.48, 23.67.

Immobilisation of 3.32a onto Carbon Materials

In a Schlenk flask, 300 mg of carbon support was added under argon to a solution of anhydrous EtOAc (10 mL). The mixture was then sonicated in an ultrasound bath for 30 min in order to disperse the support, where after the imidazolium carboxylate (100 mg) in EtOAc (5 mL) was added to the suspension and the reaction left stirring at room temperature for 16 h until the solution become clear. The black solid was filtrated, washed with EtOAc (3 X 5mL) and dried under vacuum, affording the resulting product as a black solid.

General procedure for the cycloaddition of CO_2 and epoxide.

In a typical experiment, a 25 mL stainless steel autoclave equipped with a magnetic stirrer was charged with the corresponding quantities of potassium iodide, 18-crown-6, imidazolium carboxylate or supported homogeneous catalyst and the epoxide. Then, the autoclave was sealed, purged with CO_2 0.3 MPa for three times and heated to the desired temperature. Subsequently, the reactor was pressurized with 1MPa of CO_2 for 3h or 5h with a stirring speed of 500 rpm. The autoclave was cooled in a liquid nitrogen bath below 0ºC and the CO_2 was slowly liberated from the vessel.

Using homogeneous catalysts: The crude reaction mixture was extracted with EtOAc and filtrated through a silica gel plug. After removal of all volatiles under reduced pressure the cyclic carbonates were obtained.

Using heterogenized catalysts: The crude reaction mixture was extracted with ethyl acetate and filtrated through a Büchner funnel with a filter plate. The black powder was washed thoroughly with EtOAc and the resulting filtrate collected and concentrated by rotavapor.

The recycling experiments were carried out under identical reaction conditions as described in the “using heterogenized catalysts”. After completion of each run, the black powder was washed thoroughly with EtOAc, dried and reused as such in the following run.

4-Buthyl-1,3-dioxolan-2-one was obtained in 70% yield (1.24 g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (qd, *J* = 7.5, 5.5 Hz, 1H), 4.52 (dd, *J* = 8.4, 7.9 Hz, 1H), 4.06 (dd, *J* = 8.4, 7.2 Hz, 1H), 1.87 – 1.61 (m, 2H), 1.50 – 1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).Peaks are in agreement with reports in the literature.[128]

---

[128] a) A. Decortes, A. W. Kleij, *ChemCatChem* **2011**, *3*, 831-834; b) A. Coletti, C. J. Whiteoak, V. Corte, A. W. Kleij, *ChemcatChem* **2012**, *4*, 1190-1196

4-Ethyl-1,3-dioxolan-2-one was obtained in 79% yield (1.13 g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 – 4.62 (m, 1H), 4.52 (dd, *J* = 8.4, 7.9 Hz, 1H), 4.09 (dd, J = 8.4, 7.0 Hz, 1H), 1.90 – 1.70 (m, 2H), 1.03 (t, J = 7.5 Hz, 3H).Peaks are in agreement with reports in the literature.[128]

4-Methyl-1,3-dioxolan-2-one was obtained in 90% yield (1.14 g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.93 – 4.76 (m, 1H), 4.54 (dd, *J* = 8.1 Hz, 7.8 Hz, 1H), 4.01 (dd, *J* = 8.0 Hz, 7.2 Hz, 1H), 1.54 – 1.38 (m, 3H). Peaks are in agreement with reports in the literature.[128]

4-Chloromethyl-1,3-dioxolan-2-one was obtained in 88% yield (1.47 g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.96 (m, 1H), 4.64 – 4.55 (m, 1H), 4.41 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.81 – 3.70 (m, 2H). Peaks are in agreement with reports in the literature.[128]

(*4R,5R*)-4,5-dimethyl-1,3-dioxolan-2-one was obtained in 13% yield (186 mg) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 – 4.25 (m, 2H), 1.45 (d, J = 6.1 Hz, 6H). Peaks are in agreement with reports in the literature.[128]

(*R*)-4-Methyl-1,3-dioxolan-2-one was obtained in 87% yield (1.09 g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.84 (ddq, J = 7.6, 7.2, 6.3 Hz, 1H), 4.54 (dd, J = 8.4, 7.7 Hz, 1H), 4.01 (dd, J = 8.4, 7.2 Hz, 1H), 1.47 (dd, J = 6.3, 2.4 Hz, 3H). Peaks are in agreement with reports in the literature.[128]

4-Phenyl-1,3-dioxolan-2-one was obtained in 72% yield (1.07 g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 3H), 7.39 – 7.34 (m, 2H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.84 – 4.76 (m, 1H), 4.34 (dd, *J* = 8.6, 7.9 Hz, 1H). Peaks are in agreement with reports in the literature.[128]

Cyclohexene carbonate was obtained in 21% yield (370 mg) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (m, 2H), 1.90 (m, 4H), 1.64 – 1.58 (m, 2H), 1.46 – 1.40 (m, 2H). Peaks are in agreement with reports in the literature.[128]

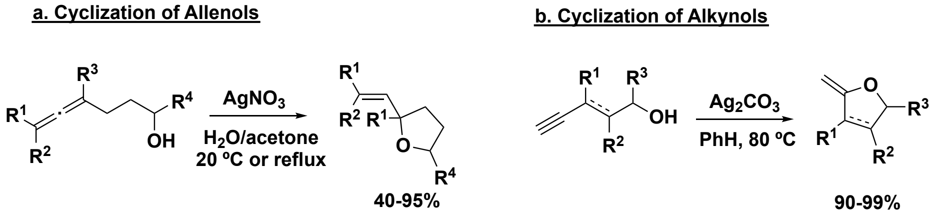
Chapter 4

“Pyrene-tagged N-Heterocyclic Carbene silver(I) complex. Synthesis, characterization and application in the carboxy-cyclization of o-alkynylanilines and CO_2”

4.1 Introduction

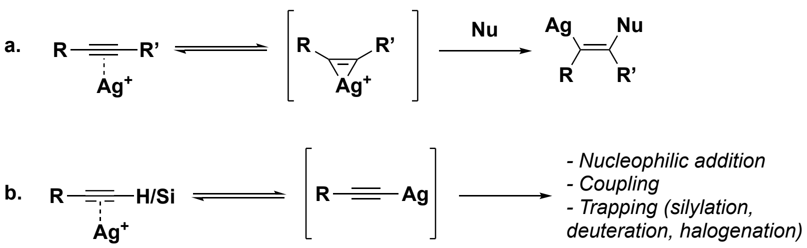
4.1.1 A Brief introduction to silver catalysis

Silver-catalyzed reactions are some of the important methodologies in organic chemistry and have been reviewed[129] and summarized in a book[130]. For example, the silver-catalyzed cyclization reactions of alkyne and allene derivatives are the promising synthetic methods of heterocyclic compounds (Scheme 4.1.).[129a]



Scheme 4.1. *Silver-catalyzed cyclization reactions*

The applications of silver salts, mainly Ag(I) in organic synthesis are mostly motivated by its lewis acidity.[129c, 131] Indeed, Ag(I) is known to easily coordinate with π-donors such as alkenes, alkynes, allenes. Upon coordination, a silver-π-complex is formed and facilitates the formation of a C-X bonds (X= C, N, O, halo, P etc…) by nucleophilic attack on this activated multiple bond (Scheme 4.2.a.). For a terminal or silylated alkyne, the reaction pathway involves a conversion into silver acetylide *via* deprotonation/desiliconization and the formed silver acetylide can react as a nucleophile to be trapped by electrophiles or by engaging in cross-coupling reactions through transmetallation process (Scheme 4.2.b.).[132]



Scheme 4.2. *Carbon-Carbon bond activated by a silver catalyst*

It has since been revealed that silver catalysts show unique reactivity in the sequential carboxylation and cyclization reaction using carbon dioxide for the synthesis of heterocyclic compounds.[133] For example, the sequential carboxylation and cyclization

---

[129] a) J.-M. Weibel, A. Blanc, P. Bale, *Chem. Rev.* **2008**, 108, 3149-3173; b) M. Alvarez-Corral, M. Munoz-Dordado, I. Rodriguez-Garcià, *Chem. Rev.* **2008**, 108, 3174-3198; c) M. Naodovic, H. Yamamoto, *Chem. Rev.* **2008**, 108, 3132-3148; d) Y. Yamamoto, *Chem. Rev.* **2008**, 3199-3222; e) G. Fang, X. Bi, *Chem. Soc. Rev.* **2015**, 44, 8124-8173

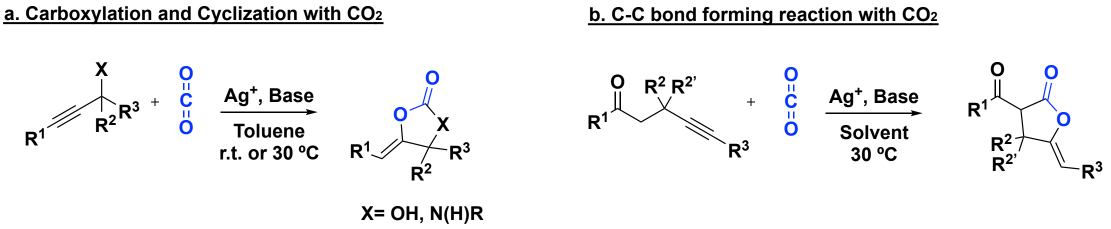
[130] a) M. Harmata, (Ed.) Silver in Organic Chemistry, Wiley-VHC, **2010**

[131] M.P. Munoz, *Chem. Soc. Rev.* **2014**, 43, 3164-3183

[132] G. Fang, X. Bi, *Chem. Soc. Rev.* **2015**, 44, 8124-8173

[133] K. Sekine, T. Yamada, *Chem. Soc. Rev.* **2016**, *45*, 4524-4532

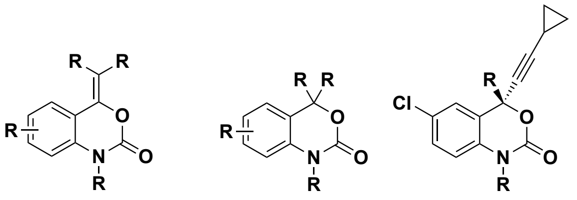
of alkyne derivatives, such as propargylic alcohols and amines, using carbon dioxide, silver catalysts show significant reactivity under mild conditions unlike other transition metals (Scheme 4.3.). Moreover, silver-catalyzed C-C bond forming reactions with carbon dioxide have also provided the synthetic methods of the corresponding carboxylic acid derivatives.[134]



Scheme 4.3. Silver-catalysed reaction with CO_2

4.1.2 Benzoxazine-2-one from *o*-alkynylaniline and carbon dioxide

Benzoxazine-2-one derivatives have attracted much attention as some of the most important heterocycle structures in pharmaceutical science.[133] Indeed, active osteoclast inhibitors and antirheumatic agents bearing *exo*-olefin, 4-ylidene-1,4-dihydro-2H-3,1-benzoxazine-2-one **4.1** were reported (Figure 4.1.).[135] The analogues presented in Scheme 4.4. also have biological behaviors for contraceptives therapy **4.2** and as anti-HIV drug **4.3.**[136]



4.1 **4.2** **4.3 Efavirenz (SUSTIVA)**

Figure 4.1. Silver-catalysed reaction with CO_2

In spite of the importance of the benzoxazine-2-one components, the methods for their synthesis have been limited. Several preparative reactions employing phosgene, carbon monoxide, carbonyldiimidazole or hypervalent iodine compound were reported.[129,137] In 2013, one report presented the use of carbon dioxide as an appealing

---

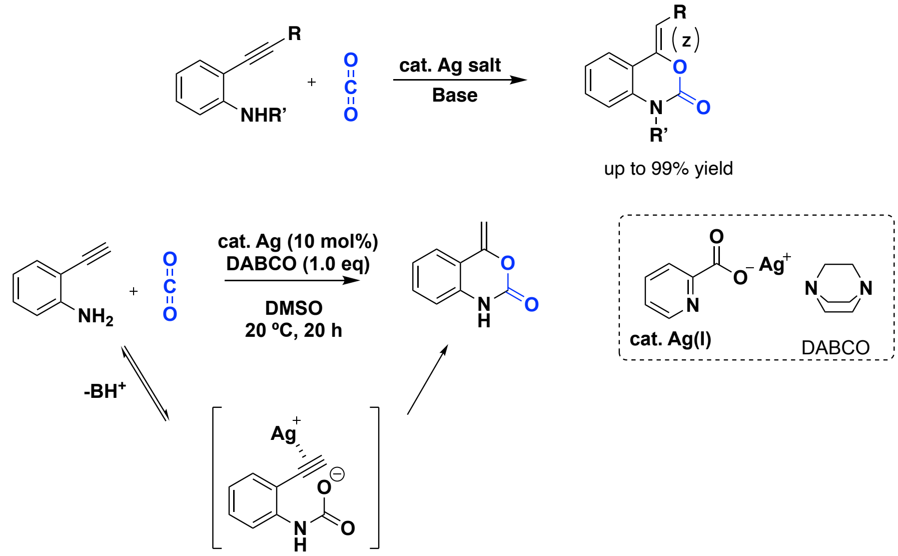
[134] a) L. Zhang, Z. Hou, *Chem. Sci.* **2013**, 4, 3395-3403; b) Y. Tsuji, T. Fujihara, *Chem. Commun*, **2012**, 48, 9956-9964

[135] M. Nakatsuka, S. Okada, K. Shimano, S. Watanabe, Y. Suzuki, F. Nishikaku, Sumitomo Pharmaceuticals Co., Ltd. PCT Int. Appl. WO98/42688, **1998**

[136] a) P. Chang, E. A. Terefenko, J. Wrobel, Z. Zhang, Y. Zhu, J. Cohen, K. B. Marschke, D. Mais, *Bioorg. Med. Chem. Lett.* **2001**, 11, 2747-2750; *J. Med. Chem.* **2002**, 45, 4379-4382; b) M. Patel, S. S. Ko, R. J. McHugh, J. A. Markwalder, A. S. Srivasta, B. C. Cordova, R. M. Klabe, S. Erickson-Viitanen, G. L. Trainor, S. P. Seitz, *Bioorg. Med. Chem. Lett.* **1999,** 9, 2805-2810

[137] a) E. Tresta, L. Fontanella, *Farmaco Ed. Sci* **1966**, 21, 549-557; b) E. Hernández, J. M. Vélez, C. P. Vlaar, *Tetrahedron Lett.* **2007**, 48, 8972-8975

C1 resource and alternative to the use of toxic chemical reagents for the synthesis of benzoxazine-2-one derivatives synthesis (Scheme 4.4.).[138] In this reaction, the silver



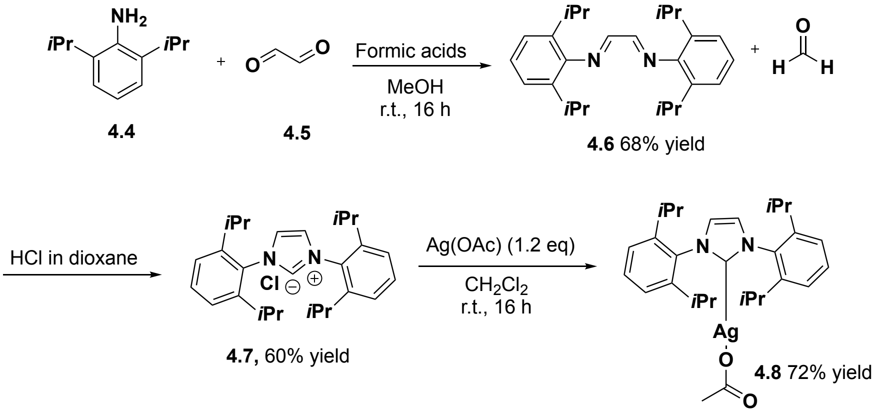
Scheme 4.4. *Silver-catalysed incorporation of CO_2 into o-alkynylaniline and reported mechanism.*[137a]

In line with our research interest, we sought to develop a sustainable route to benzoxazine-2-one derivatives. Thus, silver(I)-based N-heterocyclic carbene and further pyrene-tagged Ag(I) complex were explored in CO_2 conversion to benzoxazine-2-one derivatives.

4.2 Results and discussion

4.2.1 Synthesis and characterization of NHC-silver(I) complexes

First, NHC-Silver(I) complex, [IPr(AgOAc)] **4.8**, was synthesized and fully characterized following existing reports starting from diisopropylaniline **4.4** (Scheme 4.5.).[139]



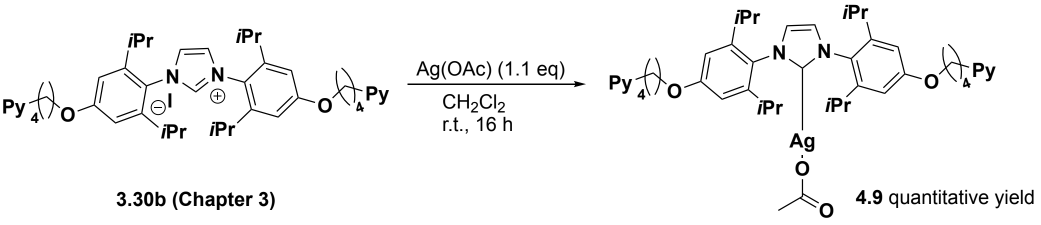
Scheme 4.5. *Synthesis of [IPr(AgOAc)]* ***4.8***

---

[138] a) T. Ishida, S. Kikuchi, T. Tsubo, T. Yamada, *Org. Lett.* **2013**, 15, 848-851; b) C. Ruan, L. Yang, Y. Yuan, Y. Ju, H. Wang, *Comput. Theor. Chem.* **2015**, 1058, 34-40

[139] a) K. Yamashita, S. Hase, Y. Kayaki, T. Ikariya, *Org. Lett.* **2015**, 17, 2334−2337; b) V. H. L. Wong, S. V. C. Vummaleti, L. Cavallo, A. J. P. White, S. P. Nolan, K. K. Hii, *Chem. Eur. J.* **2016**, 22, 13320−13327

Following the same procedure, pyrene-tagged NHC-silver(I) was synthesized and obtained in quantitative yield (Scheme 4.6). (The synthesis of the imidazolium salt is presented in Chapter 3)



Scheme 4.6. *Synthesis of pyrene tag [Ag(I)]* ***4.9***

The formation of the pyrene-tagged silver complex was clearly confirmed by ^{1}H NMR analysis due to the disappearance of the acidic N*C*HN signal corresponding to the imidazolium ring and the signal of the acetate protons at 1.8 ppm (Figure 4.2.).

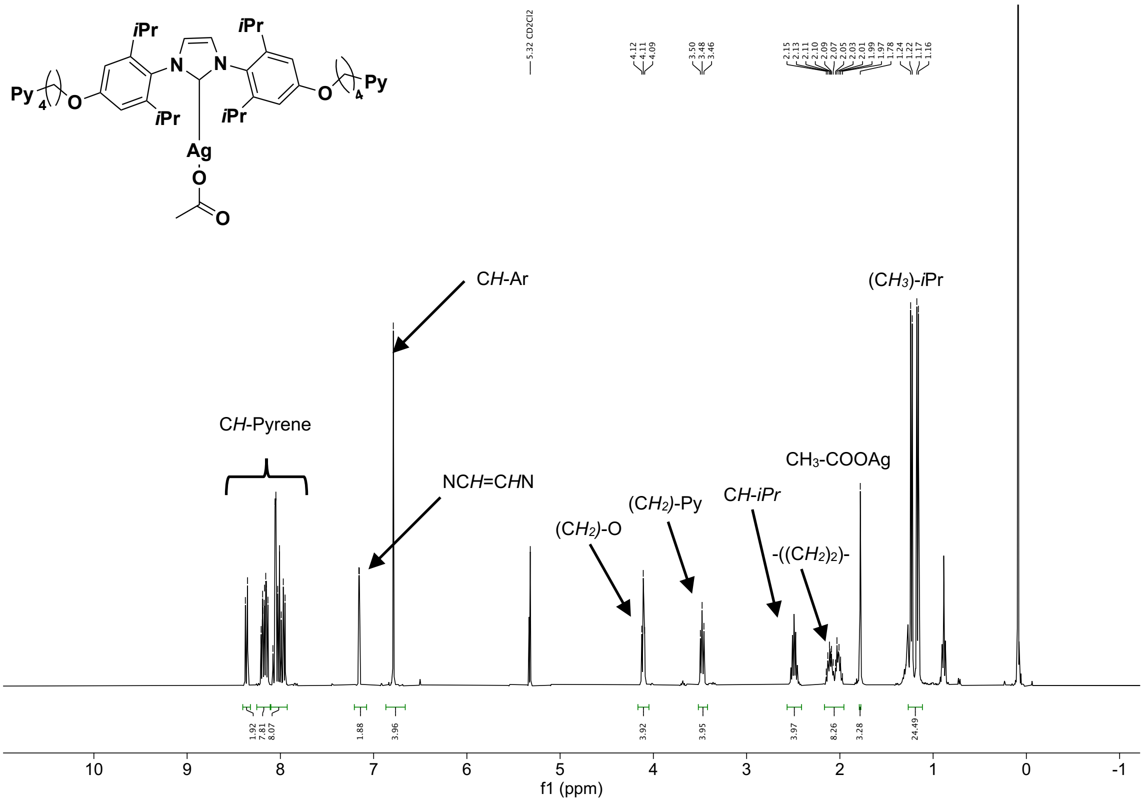
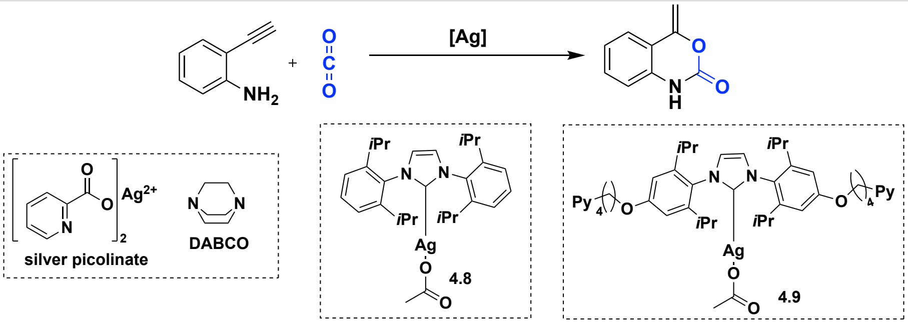


Figure 4.2. *^{1}HNMR spectrum of complex* ***4.9 in*** *CD_2Cl_2*

4.2.2 Proof of concept using pyrene-tagged NHC-silver(I) complexes

When the non-pyrene-tagged NHC Ag(I) complex **4.8** was tested in the incorporation of CO_2 into *o*-ethynylaniline, the corresponding benzoxazine-2-one was obtained in 68% yield at room temperature under free solvent conditions (Table 4.1., entry 2). The yield obtained is similar to the reported result using DABCO as a base to deprotonate the substrate and silver (II) picolinate which activates the C-C triple bond to promote the carboxy-cyclization (Table 4.1., entry 1). Thus, no effect that might be attributed to the NHC ligand is observed in this reaction. Next, the pyrene-tagged Ag(I) complex was evaluated and the desired product was obtained in 72% yield following the same reaction conditions (Table 4.1., entry 3). We can therefore conclude that NHC-Ag(I) complex are active for the incorporation of CO_2 into *o*-ethynylaniline. Moreover, pyrene moiety does not affect the catalytic performance of the corresponding Ag(I) catalyst. Therefore, its stability and reusability for the synthesis of benzoxazine-2-one derivatives was further studied.

Table 4.1. New pyrene-tagged silver(I) complex **4.9** catalytic activity in the incorporation of CO_2 into *o*-ethynylaniline



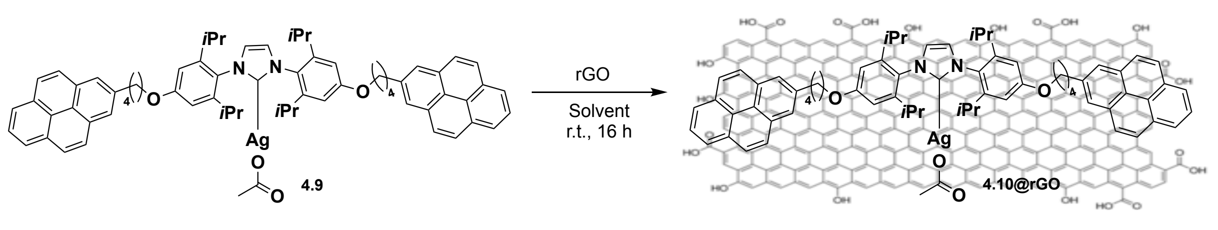
Entry	[Ag]	Additives	Solvent	Yield (%) [c]
1[a]	Silver(II) picolinate (10 mol%)	DABCO (0.2 equiv)	DMSO	75[138a]
2[b]	NHC-Ag(I) (2.5 mol%)	-	Neat	68
3[b]	Pyrene-tagged NHC-Ag(I) (2.5 mol%)	-	Neat	72

[a] 0.125 mmol of substrate, DMSO (1.0 mL), P(CO_2)= 1 MPa, T= 25 ºC, 16h. [b] 2.5 mol% of NHC-Ag(I) and Pyrene-tagged NHC-Ag(I), neat. [c] Isolated yield after silicagel purification chromatography

4.2.3 Immobilization of the pyrene tagged NHC silver(I) complex

At this stage, the immobilization of pyrene-tagged Ag(I) complex **4.9** onto reduced graphene oxide (rGO) *via* π-π stacking interaction was achieved following the same procedure reported in Chapter 3, Figure 3.8. The hybrid material was obtained in a very straightforward manner by simply stirring a solution of the corresponding pyre-functionnalized Ag(I) complex in the presence of a suspension of rGO. After 16 hours, the hybrid material was recovered by filtration. The influence of the solvent on the catalyst immobilization onto rGO was evaluated (Table 4.2.). Using dichloromethane (CH_2Cl_2) and ethyl acetate (ACOEt) as solvent, the suspension was stirred at room temperature for 16 hours and resulted in a hybrid material containing 8.5% weight and 8.6% weight of Ag(I) complex **4.9** respectively, as measured by inductively coupled plasma-mass spectrometry (ICP-MS) (Table 4.2., entries 1-2). When Ag(I) complex **4.9**, was stirred in the presence of rGO in THF, a 11.7% weight of the latter complex was encountered in the corresponding hybrid material (Table 4.2., entry 3).

Table 4.2. Solvents evaluation in the immobilization of **4.9** onto reduced graphene oxide



Entry	Solvent	Ag(wt%)[b]
1	ACOEt	8.5
2	CH_2Cl_2	8.6
3	THF	11.7

[a] Reaction conditions: Commercial rGO were dispersed in CH_2Cl_2 or AcOEt or THF and sonicated for 1h. The pyrene-tagged silver(I) complex was then added to the suspension and stir 16 h at r.t., A ratio of 1:3 of rGO:Ag(I) (wt/wt) [b] determined by ICP-MS analysis of the solid after filtration

The TGA analysis of the hybrid material **4.10@rGO** also revealed the incorporation of Ag(I) complex onto rGO *via* the observation of a clean loss of the ligand between 400 °C and 700 ºC (Figure 4.4.).

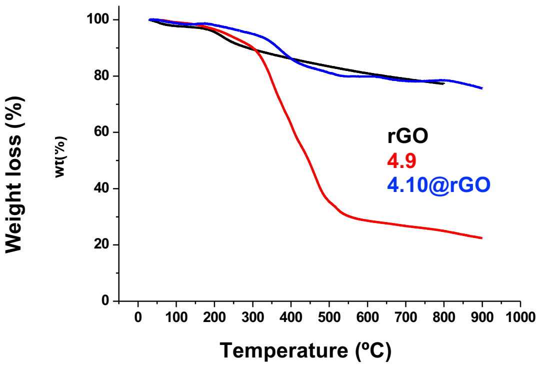
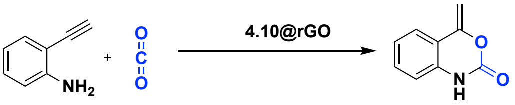


Figure 4.4. *TGA analysis of hybrid material* ***4.10@rGO***

4.2.4 Evaluation of heterogenized Ag(I) complex **4.10** in the carboxy-cyclization of o-alkynylanilines and CO_2

In order to gain insight on the catalytic potential of the heterogenized complex presented above, it was tested under batch conditions in the carboxy-cyclisation of *o*-ethynyaniline into the corresponding benzoxazine-2-one (Table 4.3.). In a first test, the heterogenized Ag(I) **4.10@rGO** was used under free solvent conditions and no conversion was observed at room temperature. An easy explanation for this result could be the poor “contact” between the substrate and the silver(I) catalyst. Next, in THF, conversion of *o*-ethynylaniline was observed (Table 4.3., entry 2). When the temperature was increased to 40 ºC, a moderate yield of the desired product was obtained (Table 4.3., entry 3).

Table 4.3. Hybrid material **4.10@rGO** activity in the incorporation of CO_2 into *o*-ethynylaniline

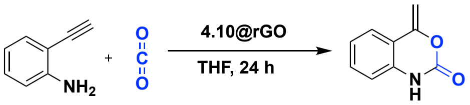


Entry	Temperature	Solvent	Yield (%) [b]
1	r.t.	Neat	No conversion
2	r.t.	THF	37
3	40 °C	THF	55

[a] 1.5 mol% of Pyrene-tagged NHC-Ag(I) **4.10@rGO**, $P(CO_2)$= 1 MPa, 24 h. [b] Isolated yield after silicagel purification chromatography

At this point, recycling experiments were performed to probe the robustness of the catalyst **4.10@rGO**. The pyrene tag silver(I) catalyst was recycled by filtration of the reaction mixture. The solid residue was washed with EtOAc and then directly used as catalyst in the subsequent runs. As shown in Table 4.4., the catalytic activity of **4.10@rGO** was maintained at 50% yield of the desired benzoxazine-2-one in the 2nd run. However, a drop in activity was observed in the 3rd run and no conversion was observed in the 4th run. Taking all these results together, we believe that the decrease in activity may be due to the partial loss of catalysts during the recovering process whereas the complete loss of activity can be explained by the loss of the acetate which acts as a base to drive the conversion to the desired benzoxazine-2-one derivative.

Table 4.4. Hybrid material **4.10@rGO** catalytic activity in the incorporation of CO_2 into *o*-ethynylaniline



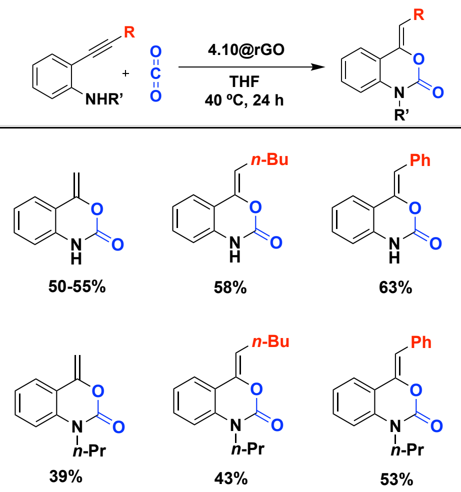
Run	Yield (%) [b]	Ag lost %[c]
1	55	7
2	50	69
3	17	31
4	0	n.d.

[a] 1.5 mol% of Pyrene-tagged NHC-Ag(I), $P(CO_2)$= 1 MPa, 24 h, 40 °C. [b] Isolated yield after silicagel purification chromatography [c] determined by ICP-MS analysis of the solid after filtration

4.2.5 Synthesis of various benzoxazine-2-one derivatives under the optimized conditions

To investigate the applicability of **4.10@rGO** in the carboxy-cyclization reaction, a variety of *o*-alkynylanilines were examined under standard conditions: 1MPa of carbon dioxide in THF at 40 ºC during 24 h. As shown in table 4.5., the present catalytic system was successfully applied for the synthesis of benzoxazine-2-one derivatives When, the reaction of the *o*-alkynyaniline substituted with trimethylsilylacetylenyl (TMS) was carried out, the corresponding benzoxazine-2-one was obtained without the TMS group in ca. 50 % yield (Table 4.5.). Overall, the carboxy-cyclization reaction proceeded without any side product formation.

Table 4.5. Evaluation of the substrate scope under standard reaction conditions



[a] 1.5 mol% of pyrene-tagged NHC-Ag(I) **4.10@rGO**, P(CO_2)= 1 MPa, 24 h. [b] Isolated yield after silicagel purification chromatography

4.3 Conclusions

From the study described in this chapter, the following conclusion can be extracted:

i) NHC-silver(I) **4.8** and pyrene-tagged NHC-silver(I) salts **4.9** were synthesized and fully characterized successfully completed.

ii) The pyrene-tagged NHC-silver(I) and the non-pyrene-tagged NHC silver(I) complexes were evaluated in the synthesis of benzoxazine-2-ones under neat and mild reaction conditions. Similar results than those reported using a base (DABCO) and silver catalysts were obtained thus, we conclude that NHC-silver catalysts can successfully be applied to this reaction and that the pyrene moiety has no effect in the performance of the catalyst.

iii) The pyrene-tagged silver(I) complex **4.9** was successfully immobilized onto reduced graphene oxide using tetrahydrofuran as a solvent which was analyzed by TGA and ICP-MS

iv) The Ag(I)-catalyzed the incorporation of carbon dioxide into *o*-ethynylaniline provided no conversion under neat conditions. By adding solvent and increasing the temperature, moderate yields were obtained.

v) Preliminary study on the recycling of the hybrid materials **4.10@rGO** in batch showed that the catalysts can only be successfully recycled once. From the 3rd run on words, a rapid drop on activity is observed.

4.4 Experimental part

General considerations

All operations were carried out under inert atmosphere using Schlenk tube or glovebox. Anhydrous solvents were collected from a Braun MB SPS-800 system except for EtOAc, which was dried with CaH_2 and stored under inert atmosphere. The chemicals were purchased in analytic quality from SigmaAldrich, AlfaAesar and AcrosOrganics and used as received. rGO (SBET = 500-400 m^2/g) were purchased from Graphenea.

Solution Nuclear Magnetic Resonance (NMR). ^1H and ^{13}C NMR spectra were recorded using a Varian Mercury VX 400 MHz spectrometer. Chemical shift values(δ) are reported in ppm relative to TMS (^1H and $^{13}C\{^1H\}$) and coupling constants are reported in Hertz. High-resolution mass spectra (HRMS) were recorded on an Agilent Time-of-Flight 6210 using ESI-TOF (electrospray ionization-time of flight). Samples were introduced to the mass spectrometer ion source by direct injection using a syringe pump and were externally calibrated using sodium formate.

Thermogravimetric analysis (TGA). It was carried out using a Mettler Toledo TGA/DSC 1 microbalance. Analyses were performed in N2 (50 NmL min^{-1}) ramping the temperature from room temperature to 900 °C at 10 °C min^{-1}.

Synthesis of 4.6

2,6 diisopropylaniline **4.4** (11g, 0.056mol) was dissolved in methanol (112 mL), treated with aqueous glyoxal solution **4.5** (3.23 mL, 0.028 mol) and three drops of formic acid. The reaction mixture was stirred for 16 h at room temperature. The yellow solid was filtered off, washed with cold methanol and dried in vacuum; yield: 7.9 g (68% yield). ^{1}HNMR (^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 2 H), 7.1 - 7.25 (m, 12 H), 2.94 (m, 4H), 1.21 (d, 24 H, *J*= 6.9 Hz). Spectroscopic data are in agreement with the reported in the literature.[140]

Synthesis of 4.7

Diazabutadiene **4.6** (10 g, 0.027 mol) was dissolved in anhydrous THF (150 mL) under an atmosphere of Ar. A solution of paraformaldehyde (1g, 0.033 mol) in HCl in dioxane (10 mL, 0.04 mol) was prepared and added to the diimine solution at 0 ºC *via* syringe. The reaction mixture was stirred at room temperature for 16 h to observe the formation of a white precipitate. The precipitate was filtered off and washed with THF (3 X 50 mL); yield: 6.69 g (60% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.13 (s, 4H), 7.83 (d, 2H), 7.55 (t, 2H, *J*= 7.7 Hz), 2.43 (m, 4H),1.29 (d, 12H, *J*= 6.9 Hz), 1.21 (d, 2H, *J*= 6.9 Hz). Spectroscopic data are in agreement with the reported in the literature.[138]

---

[140] A.J. Arduengo, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, 55, 14523–14534.

Synthesis of 4.8

A Schlenk flask was charged with **4.7** (500 mg, 1.28 mmol, 1.0 equiv.), AgOAc (257 mg, 1.54 mmol, 1.2 equiv.) and anhydrous DCM (10 mL). The reaction mixture was stirred overnight at room temperature. The resulting suspension was filtered off and the filtrate partially evaporated under reduced pressure. Pentane was added resulting in the formation of precipitated product which was subsequently washed with pentane, dried under reduced pressure to afford a light brown solid; yield: 511 mg (72% yield): ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.51 (t, *J*= 7.8 Hz, 2H), 7.31 (d, *J*= 7.8 Hz, 4H), 7.23 (d, *J*= 2.0 Hz, 2H), 2.57 (sept, *J*= 6.9, 4H), 1.86 (s, 3H), 1.31 (d, *J*= 6.9 Hz, 12H), 1.24 (d, *J*= 6.9 Hz, 12H). Spectroscopic data are in agreement with the reported in the literature.[139]

Synthesis of 4.9

A Schlenk flask was charged with **3.30b** (500 mg, 0.47 mmol, 1.0 equiv.), AgOAc (95 mg, 0.57 mmol, 1.2 equiv.) and anhydrous DCM (10 mL). The reaction mixture was stirred overnight at room temperature. The resulting suspension was filtered off and the filtrate partially evaporated under reduced pressure. Pentane was added resulting in the formation of precipitated product which was subsequently washed with pentane, dried under reduced pressure to afford a light brown solid; yield: 505 mg (97% yield): ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.36 (d, *J* = 9.3 Hz, 2H), 8.25 – 8.10 (m, 8H), 8.11 – 7.93 (m, 8H), 7.16 (d, *J* = 1.9 Hz, 2H), 6.79 (s, 4H), 4.11 (t, *J* = 7.6 Hz, 4H), 3.48 (t, *J* = 7.6 Hz, 4H), 2.49 (m, 4H), 2.17 – 1.96 (m, 8H), 1.78 (s, 3H), 1.20 (dd, *J* = 26.4, 6.9 Hz, 24H).; ^{13}C NMR (100 MHz, CD_2Cl_2): δ 184.15, 177.40, 161.99, 148.85, 138.10, 131.95, 130.35, 129.20, 128.35, 128.07, 127.69, 125.54, 125.47, 125.36, 125.23, 124.12, 110.28, 68.42, 33.67, 29.63, 24.92, 24.05.

Immobilisation of 4.9 onto reduced graphene oxide

In a Schlenk flask, 300 mg of carbon support was added under argon to a solution of anhydrous solvent (10 mL). The mixture was then sonicated in an ultrasound bath for 30 min in order to disperse the support, where after the silver(I) complex **4.9** (100 mg) in anhydrous solvent (5 mL) was added to the suspension and the reaction left stirring at room temperature for 16 h until the solution become clear. The black solid was filtrated, washed with the corresponding solvent (3 X 5mL) and dried under vacuum, affording the resulting product as a black solid.

General Procedure for the incorporation of CO_2 into *o*-alkynylaniline.

In a typical experiment, a 25 mL stainless steel autoclave equipped with a magnetic stirrer was charged with the corresponding quantities of silver(I) catalyst or supported homogeneous catalyst and the substrate dissolve in anhydrous THF. Then, the autoclave was sealed, purged with CO_2 0.3 MPa for three times, heat to the desired temperature and subsequently pressurized with 1MPa of CO_2 for 24 h with a stirring speed of 500 rpm. The autoclave was cooled in a liquid nitrogen bath below 0ºC and the CO_2 was slowly liberated from the vessel. The residue was purified by silica gel chromatography to obtain the corresponding product

Recycling experiments: After completion of each run, the black powder was washed thoroughly with THF, dried and reused as such in the following run.

4-methylene-1,4-dihydro-2H-3,1-benzoxazine-2-one was obtained in 55% yield (g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 4.97 (d, *J* = 2.9 Hz, 1H), 4.86 (d, *J* = 2.9 Hz, 1H). Peaks are in agreement with reports in the literature.[138]

4-pentylidene-1,4-dihydro-2H-3,1-benzoxazine-2-one was obtained in 58% yield (g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.37 (t, *J* = 7.6 Hz, 1H), 2.35 (q, *J* = 7.3 Hz, 2H), 1.35-1.49 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H). Peaks are in agreement with reports in the literature. [138]

4-benzylidene-1,4-dihydro-2H-3,1-benzoxazine-2-one was obtained in 63% yield (g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.28-7.41 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.26 (s, 1H),. Peaks are in agreement with reports in the literature.[138]

4-methylene-1-propyl-1,4-dihydro-2H-3,1-benzoxazine-2-one was obtained in 39% yield (g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 1.3 Hz, 7.9 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz,1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.92 (d, *J* = 2.7 Hz, 1H), 4.81 (d, *J* = 2.9 Hz, 1H), 3.88 (t, *J* =7.9 Hz, 2H), 1.70-1.80 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). Peaks are in agreement with reports in the literature.[138]

4-pentylidene-1-propyl-1,4-dihydro-2H-3,1-benzoxazine-2-one was obtained in 43% yield (g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 7.28 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.31 (t, *J* = 7.5 Hz, 1H), 3.86 (t, *J* = 7.9 Hz, 2H), 2.34 (q, *J* = 7.3 Hz, 2H), 1.74 (td, *J* = 7.7 Hz, 15.3 Hz, 2H), 1.37-1.45 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H). Peaks are in agreement with reports in the literature.[138]

4-benzylidene-1-propyl-1,4-dihydro-2H-3,1-benzoxazine-2-one was obtained in 53% yield (g) following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.32-7.40 (m, 3H), 7.24 (t, *J* = 6.3 Hz,1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.20 (s, 1H), 3.91 (t, *J* = 7.6 Hz, 2H), 1.77 (td, *J* =

7.6 Hz, 15.2 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H). Peaks are in agreement with reports in the literature.[138]

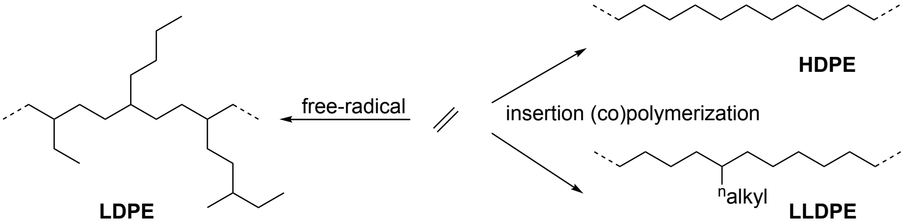
Chapter 5

“Pyrene-tagged α-diimine Pd-complexes. Synthesis, characterization and application in the copolymerization of ethylene and methyl acrylate”

5.1 Introduction

5.1.1 From polyolefins to polar functionalized polyolefins

Polyolefins, namely polyethylene and polypropylene, are amongst the most important classes of materials, with a wide range of applications ranging from simple plastic bags to high strength fibers.[141] For the preparation of polyethylene, ethylene can be polymerized by a free-radical or an insertion polymerization mechanism. The free-radical process is generally performed at high pressure and temperature leading to highly branched low-density polyethene (LDPE).[142] These conditions are however industrially unattractive.[143] Nowadays, the largest commercialized volume of these polyolefins is linear high-density polyethylene (HDPE) and its copolymers with 1-alkenes linear low-density polyethylene (LLDPE). They are all prepared by insertion polymerization using transition-metal catalysts [144] (Scheme 5.1.).



Scheme 5.1. *Synthesis of low-density polyethylene (LDPE), high density polyethylene (HDPE) and linear low-density polyethylene (LLDPE)*

As polyethene and polypropene consist essentially of very long alkane molecules, these materials are very apolar and lipophilic. Although polyolefins serve a wide range of applications, their apolar nature limits their properties in certain areas, with respect to their barrier properties, permeability, dyeability, printability, and compatibility with more polar materials (such as glass fiber for reinforcement).[145] It therefore would be desirable for certain applications to modify the polymer by introducing polar functional groups, with retention of the other favorable properties, like modulus, strength, solvent resistance, etc…[146] Currently, commercial processes for functionalized polyolefins production are

---

[141] a) D. B. Malpass *Introduction to Industrial Polyethylene*, Eds.: Wiley, Hoboken, NJ, USA, **2010**, 85-97; b) G. Hilken, *Kunstsoffe* **2005**, *10*, 34-40; b) R. G. Harvan, *Chem. Ind.* **1997**, 212; c) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, 100, 1169-1204; d) H. Knuuttila, A. Lehtinen, A. Nummila-Pakarinen, *Adv. Polym. Sci.* **2004**, 169, 13-28

[142] *Ullmann's Encyclopedia of Industrial Chemistry* **2005**, Wiley-VCH, Weinheim

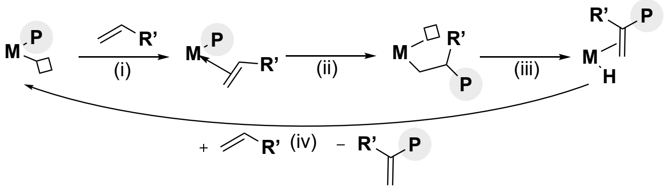
[143] R. A. Hines, W. M. D. Bryant, A. W. Larchar, D. C. Pease, *Ind. Eng. Chem.* **1957**, 49, 1071-1074

[144] a) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, 67, 541-547; b) Natta, G. *Angew. Chem.* **1956**, 68, 393-403

[145] a) A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.* **2009**, 109, 5215-5244; b) A. Berkefeld, S. Mecking, *Angew. Chem.* **2008**, 120, 2572-2576; *Angew. Chem.* **2008**, 47, 2538-2542; c) A. Sen, S. Borkar, *J. Organomet. Chem.* **2007**, 692, 3291-3299; d) J.-Y Dong, Y. Hu, *Coord. Chem. Rev.* **2006**, 250, 47-65; e) L. S. Boffa, B. M. Noval, *Chem. Rev.* **2000**, 100, 1479-1494; e) K. Nozaki, *Chem. Rec.* **2010**, 10, 315-325

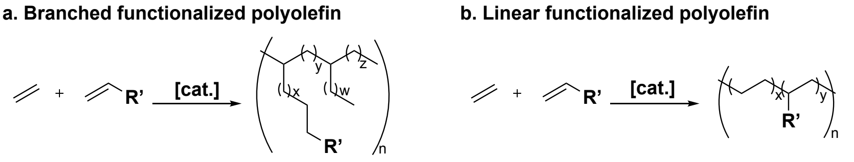
[146] a) K. Takemoto, R. M. Ottenbrite, M. Kamachi, Functional Monomers and polymers; Marcel Dekker, Inc.: New York; **1997**; b) T. Simonazzi, A. D. Nicola, M. Aglietto, G. Ruggeri, Comprehensive Polymer Science, Pergamon Press, New York, **1992**; c) L. S. Boffa, B. M. Novak, *Chem. Rev.* **2000**, 100, 1479-1493

based on radical polymerization and post-polymerization functionalization. These two technologies suffer from high energy consumption, low cost-efficiency and poor control over the polymer microstructure. Thus, limiting the variety of available materials, polymers architectures and properties,[5a] Alternatively, transition-metal catalyzed copolymerization of olefins with polar monomers is a direct and economic route. It proceeds on metal alkyl species via a reaction sequence known as the Cossee-Arlman mechanism (Scheme 5.2.).[147] It is a two steps mechanism where the first step consists of the coordination of the olefin to the metallic site (i). followed by the migratory insertion reaction of the coordinated monomer into the metal-carbon bond (ii). These steps are repeated many times leading to the growing of the polymer chain, until chain transfer occurs. The latter typically proceeds via a reversible β-hydride elimination (β-H) (iii). The complex obtained may undergo hydride reinsertion to continue polymerization along the same polymer chain, or the olefin-terminated polymer chain may be displaced by another olefin to release the polymer chain and begin the polymerization process (iv).



Scheme 5.2. *Cossee-Arlman mechanism. (i) coordination, (ii) insertion, (iii) β-H elimination, (iv) chain transfer*

The direct, controlled, homogeneously catalyzed copolymerization of ethylene and polar vinyl monomers (Scheme 5.3) represents the most powerful and environmentally friendly approach for the incorporation of polar functionalities in the polyolefin backbone. However, it has been recognized as one of the major unsolved problems in the field of polymer synthesis. Therefore, in the last two decades, enormous efforts have been addressed to the discovery of homogeneous catalysts active in this target reaction under milder conditions and allowing a better control on polymer microstructure compared to radical polymerization.



Scheme 5.3. *Homogeneous catalyzed copolymerization of ethylene and polar vinyl monomers*

5.1.2 A brief history on polyolefins synthesis

---

[147] a) P. Cossee, *J. Catal.* **1964**, 3, 80–88; b) E.J. Arlman, P. Cossee, *J. Catal*. **1964**, 3, 99-104.

Historically, polyolefins were produced using highly active heterogeneous catalysts prepared from supported groups 4 or 6 halides, activated by aluminum alkyls. In the 1950s, the first olefin polymerization catalysts were reported by Phillips and are constituted essentially of Cr/silica or Cr/silica–alumina (Figure 5.1.).[148] In 1963, Ziegler and Natta discovered that ethene and propene can be effectively polymerized by heterogeneous catalysts generated from combinations of titanium halides and alkyl aluminum compounds on $MgCl_2$ (Figure 5.1.). This group 4 metal has been the mainstay of industrial polyolefin production.[149] However, the multi-site nature of those catalysts makes them difficult to study and the produced polymers are complex mixtures of different kinds of polymer chains.

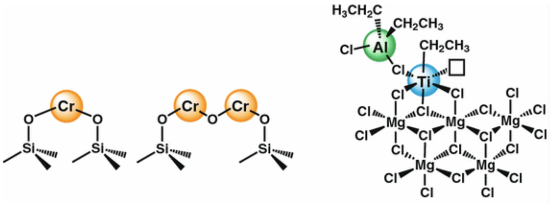


Figure 5.1. *Proposed structures for Phillips and Zielgler-Natta catalysts*

The subsequent development of soluble, well-defined single-site catalysts also focused initially on the group 4 metals, especially titanium and zirconium based metallocene catalysts.[150] They consist of a metal ion sandwiched between two parallel π-carbocyclic ligands such as cyclopentadienyl, fluorenyl, indenyl or their substituted structures (Figure 5.2.). They are effective in the presence of a methylaluminoxane (MAO) cocatalyst which was found to act as an activator of the metallocene catalysts. The effect of the substituents on the metallocene ligands is one of the most important aspects of the catalyst systems and it has been extensively studied in the literature.[151] In contrast to the conventional Ziegler-Natta catalysts, these polymers are uniform in terms of molar mass, microstructure and chemical composition.

---

[148] a) M.P. McDaniel, *Adv. Catal.* **2010**, 53, 123-606; b) A. Zecchina, E. Groppo, A. Damin, C. Prestipino, *Top Organomet Chem* **2005**, 16,1-35.

[149] a) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, 67, 541-636; b) K. Ziegler, *Angew. Chem.* **1964**, 76, 545-620; c) G. Natta, *Angew. Chem.* **1956**, 68, 393-424 d) G. Natta, *Angew. Chem.* 1964, 76, 553-566

[150] a) G. W. Coates, R. M. Waymouth, *Science* **1995**, 267, 217-219; b) X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, 116, 10015-10031; c) E. B. Coughlin, J. E. Bercaw, *J. Am. Chem. Soc.* **1992**, 114, 7606-7607; d) X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc*. **1994**, 116, 10015-10031; e) H. G. Alt et al. Chem. Rev. 2000, 100, 1205-1222

[151] a) A. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G. H. Fredrickson, E. J. Kramer, Y.-W. Shin, F. Shimizu, A. E. Cherian, P. D. Hustad, J. M. Rose, G.W. Coates, *Proc. Natl. Acad. Sci.* U. S. A. **2006**, 103, 15327-15332; b) D. H. Camacho, E. V. Salo, Z. Guan, J. W. Ziller, *Organometallics* **2005**, 24, 4933-4939; c) Z. Zhang, C. Guo, N. Cui, Y. Ke, Y. Hu, *J. Appl. Polym. Sci.* **2004**, 94, 1690-1696; d) M. De Fatima, V. Marques, A. Conte, *J. Appl. Polym. Sci.* **2002**, 86, 2054-2061; e) C.-H. Lin, C.-Y. Sheu, *Macromol. Rapid Commun.* **2000**, 21, 1058-1062

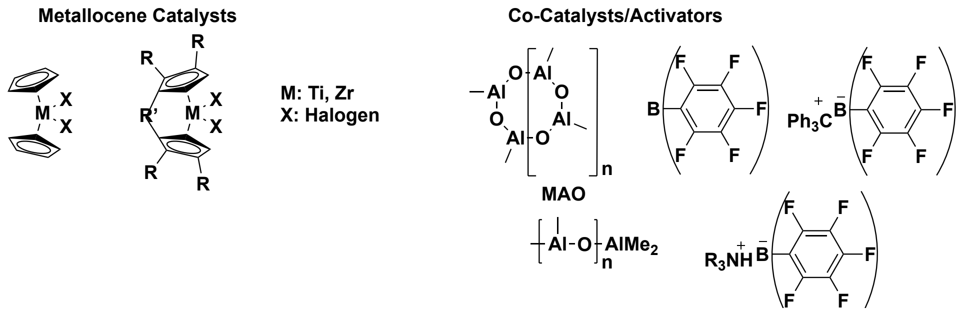
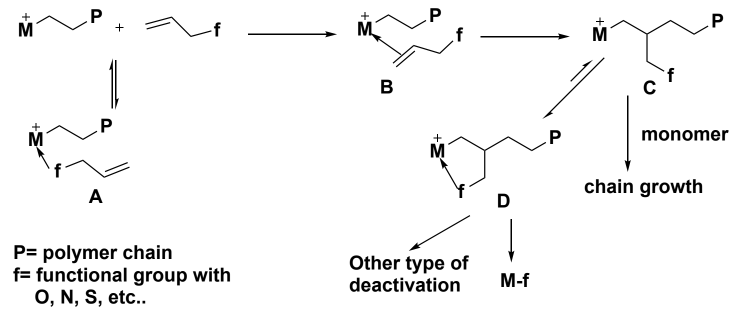


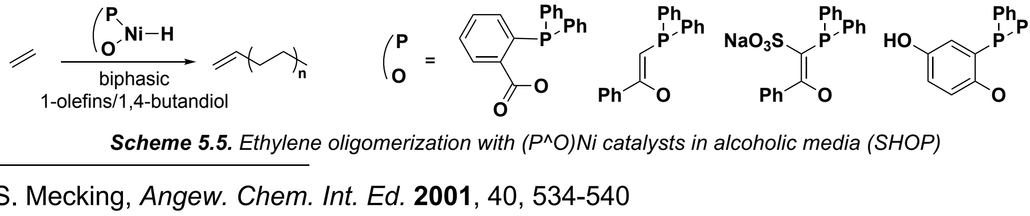
Figure 5.2. *The generic structure of titanium and zirconium metallocene catalysts and selected examples of activating cocatalysts*

The copolymerization of ethylene with polar monomers is not feasible using these early transition metal catalysts based on Ti, Zr, Cr or V. They are electropositive, hard Lewis acidic and oxophilic which cause irreversible coordination and further reactions of the functional group to the catalytically active metal center thus, blocking the catalyst for incoming monomers to coordinate via the double bond and subsequently insert (Scheme 5.4.)



Scheme 5.4. *Irreversible coordination and further reactions of functional group to the highly oxophilic active metal center*

In contrast to the highly oxophilic early transition metal catalysts, late transition metal show reduced affinity towards polar groups leading to a greater functional-group tolerance.[152] The first important development in late transition-metal catalysts for ethylene polymerization was the discovery by Keim and coworkers in the late 1970s that neutral Ni complexes of certain [P,O]-chelating ligands are excellent catalysts for the oligomerization of ethylene to short-chain α-olefins (Scheme 5.5.).[153] These catalysts comprise a component of the Shell Higher Olefin Process (SHOP), a multi-stage industrial process for the production of C_{11-15} terminal alcohols for various industrial uses, such as detergents.[154]



Scheme 5.5. *Ethylene oligomerization with (P^O)Ni catalysts in alcoholic media (SHOP)*

---

[152] a) S. Mecking, *Angew. Chem. Int. Ed.* **2001**, 40, 534-540

[153] a) W. Keim, F. H. Kowaldt, R. Goddard, C. Kruger, *Angew. Chem., Int. Ed.* **1978**, 6, 466-467; b) K. Hirose, W. Keim, *J. Mol. Cat.* **1992**, 73, 271-276

[154] a) W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. H. Kowaldt, U. Kurschner, B. Limbacker, F. P. Sistig, *Organometallics* **1986**, 5, 2356-2359. b) B. Reuben, H. Wittcoff, *J. Chem. Ed.* **1988**, 65, 605-607

Despite being both tolerant to the presence of polar functionality and active for ethylene polymerization, [P,O]-chelated Ni complexes are not active in the copolymerization of ethylene with vinyl-functionalized olefins such as methyl methacrylate or vinyl acetate.[140] This is attributed to a deactivation mechanism involving hydrogen transfer from substrate to Ni complex.[155] Other "non metallocene" catalysts were subsequently reported such as phenoxyiminato Ti, Zr and Hf complexes by Fujita and coworkers and phenoxyiminato Ni complexes by Grubbs and coworkers.[156]

5.2 Pd and Ni Catalysts in the copolymerization reaction of olefins with polar monomers

5.2.1 Cationic Pd and Ni α-Diimine catalysts

Despite decades of research and the development of hundreds of catalysts for olefin polymerization, systems that can address the polar monomer problem remain scarce. In 1995, a milestone discovery was made by Brookhart and co-workers, wherein cationic nickel and palladium diimine complexes (Figure 5.3.) were shown to be active in ethylene polymerization.[145]

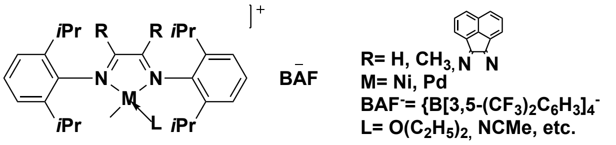
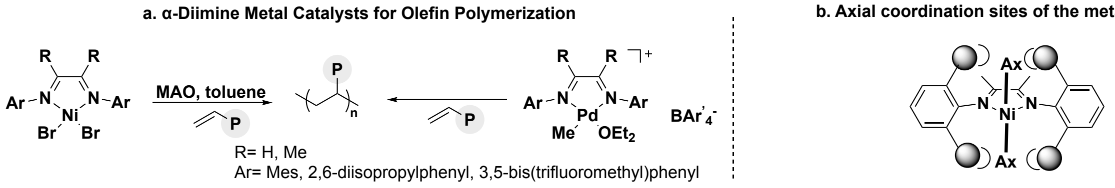


Figure 5.3. *The cationic alpha-diimine Ni and Pd catalysts [(N^N)ML][BAF]*

By applying bulky α-diimine ligands around the metal center, Ni and Pd complexes were reported to afford high molecular weight polymers.[157] This was attributed to the steric hindrance of the aryl groups on the rate of chain transfer to monomer (Scheme 5.6.a.). Indeed, the presence of substituents situated above and below the square planar Ni or Pd coordination center block the axial approach of monomer to the metal as illustrated in Scheme 5.6 b.



Scheme 5.6. *Brookhart's Ni and Pd α-diimine-based precatalysts*

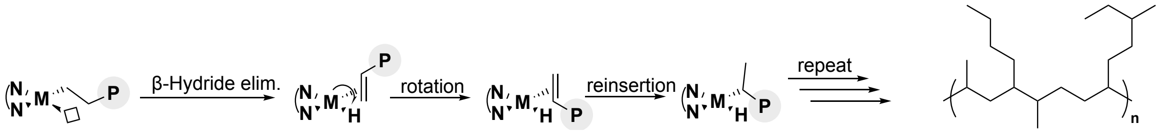
---

[155] A. W. Waltman, T. R. Younkin, R. H. Grubbs, *Organometallics* **2004**, 23, 5121-5123

[156] a) T. Matsugi, T, Fujita *Chem Soc Rev* **2008**, 37, 1264-1277; b) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs *Organometallics* **1998**, 17, 3149-3151; c) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben *Science* **2000**, 287, 460-462

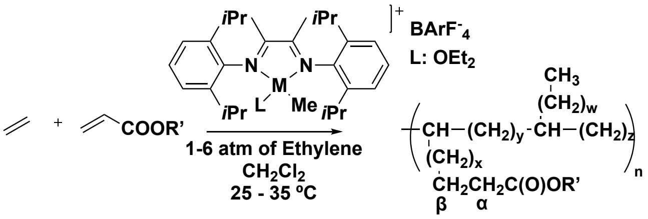
[157] L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, 117, 6414-6415

Moreover, the produced polymers have a high degree of branching directly related to the β-hydride elimination. Indeed, multiple β-H elimination and reinsertion events, with intervening olefin rotation causes the branching (Scheme 5.7.). However, there is a significant difference in the degree of branching obtained by Ni and Pd complexes. When Pd catalysts are used, extensive branching is almost always observed (~100 branches per 1000 carbon atoms), with long branches and even branches on branches.[158] This branching is indicative of frequent β-hydride elimination by Pd α-diimine catalysts. Nickel catalysts allow for more control over branching (from 1-100 branches per 1000 carbon atoms) through variation of polymerization conditions (temperature and ethylene pressure).[157]



Scheme 5.7. **"**Chain running", leads to branched polymer

The Brookhart palladium catalyst is able to incorporate the vinyl functionalized comonomer methyl acrylate (MA) (Scheme 5.8.).[159] The copolymers obtained are highly branched (100 branches per 1000 carbon atoms) and contain up to 25 mol% of incorporated acrylate. The high branching and the fact that acrylates are predominantly incorporated at the end of the branches are attributed to a sequence of β-hydride elimination, followed by olefin rotation and re-insertion.



Scheme 5.8. *Copolymerization of ethylene and acrylates with cationic palladium diimine catalysts*

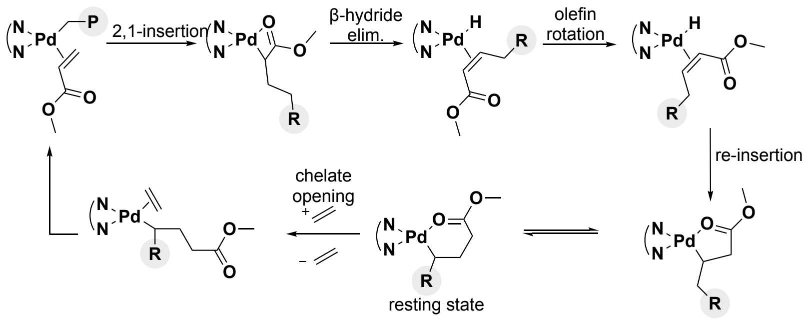
Scheme 5.9 shows the mechanism of insertion and chain walking for ethylene co-polymerization with methyl acrylate. The insertion proceeds in a 2,1-fashion forming a 4-membered chelate. This chelate isomerizes via a 5-membered palladacycle to a stable 6-membered metallacycle which was found to be the catalyst resting state since further insertions require opening of this κ -O chelate.[157, 160] The chelate structure can be opened in the presence of ethylene binding insertion. With fast chain walking after ethylene insertion, the majority of the polar groups are located at the end of the branches in the resulting copolymers.

---

[158] Z. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science* **1999**, 283, 2059-2062.

[159] L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, 118, 267-268.

[160] a) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, 120, 888-899.



Scheme 5.9. Chain walking mechanism after acrylate insertion

The success of co-polymerizations of ethene and propene with acrylates encourages more attempts to copolymerize other vinyl polar comonomers using α-diimine Ni or Pd catalysts. However, the polar monomers scope is limited to acrylates, vinyl ketones, aryl silyl and many others (Figure 5.4.).[161] Vinyl acetate, acrylamide and acrylonitrile polar monomers were found to inhibit the polymerization completely.

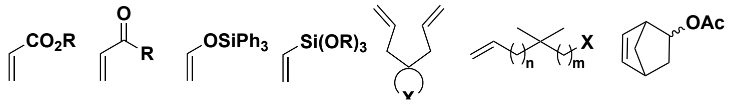


Figure 5.4. Suitable polar comonomers for Brookhart catalysts

5.2.2 Neutral Pd and Ni-based catalysts

In 2002, Drent and co-workers reported a phosphino-sulfonate palladium catalyst for ethylene-alkyl acrylate copolymerization.[162] It is applicable to a variety of polar comonomers (Figure 5.5.) and in contrast to the Brookhart catalysts, highly linear copolymers with in-chain comonomers incorporation were obtained.[163]

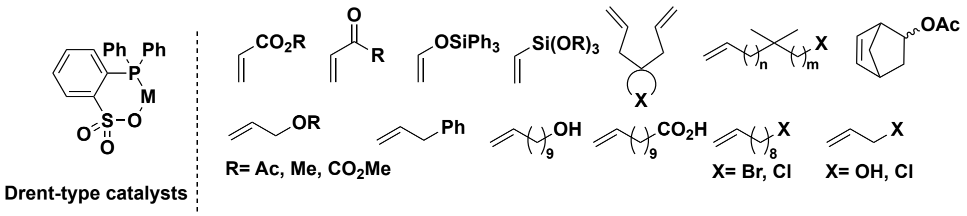


Figure 5.5. Drent-type catalysts and suitable polar comonomers

---

[161] a) E. Y. X. Chen, *Chem. Rev*. **2009**, 109, 5157-5214; b) S. Luo, R. F. Jordan, *J. Am. Chem. Soc.* **2006**, 128, 12072-12073; c) C. L. Chen, S. Luo, R. F. Jordan, *J. Am. Chem. Soc*. **2010**, 132, 5273-5284; d) Y. Chen, L. Wang, H. Yu, Y. Zhao, R. Sun, G. Jing, J. Huang, H. Khalid, N. M. Abbasi, M. Akram, *Prog. Polym. Sci*. **2015**, 45, 23-43; e) Z. Dong, Z. Ye, *Polym. Chem*. **2012**, 3, 286-301; f) D. Takeuchi, *Polym. J.* **2012**, 44, 919-928; g) D. Takeuchi, K. Osakada, *Polymer* **2016**, 82, 392-405; h) Z. Chen, W. Liu, O. Daugulis, M. Brookhart, *J. Am. Chem. Soc*. **2016**, 138, 16120-16129; i) Z. Chen, M. D. Leatherman, O. Daugulis, M. Brookhart, *J. Am. Chem. Soc*. **2017**, 139, 16013-16022 ; j) S. X. Zhou, C. L. Chen, *Sci. Bull.* **2018**, 63, 441-445; k) J. Kiesewetter, W. Kaminsky, *Chem. Eur. J.* **2003**, 9, 1750-1758.

[162] E. Drent, R. van Dijk, R. van Ginkel, B. van Oort, R. I. Pugh, *Chem. Commun*. **2002**, 744-745.

[163] a) S. Ito, *Bull. Chem. Soc. Jpn.* **2018**, 91, 251-261; b) K. Nozaki et al. Acc. Chem. Res. 2013, 46, 1438-1449.

Despite the universal capabilities of the Drent-type phosphino-sulfonate palladium catalysts in copolymerization, the nickel counterparts showed undesirable reactivities when used with polar monomers.[164,5a] Indeed, reports using phosphino-sulfonate nickel catalysts having biaryl substituents on the phosphorous atom and substituents on the *ortho*-position of the sulfonate group were applied to the copolymerization of ethylene with various co-monomers (Figure 5.6.).[165] However, in contrast to vinylalkoxysilane most of the polar comonomers caused termination or provided no comonomer incorporation.[166]

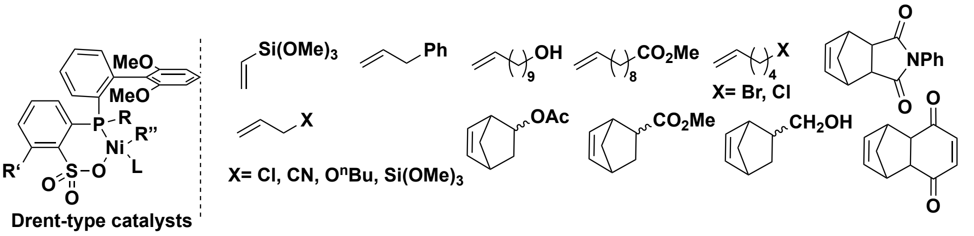


Figure 5.6. Drent-type catalysts and suitable polar comonomers

Another notable advance in the field was made by Grubbs and co-workers in 2000. They showed that neutral salicylaldimine nickel catalysts were capable of copolymerizing ethylene with polar-substituted norbornene (Figure 5.7.). [17c] Subsequently, a few other special polar monomers[167] were successfully copolymerized with ethylene using this type of nickel catalyst.

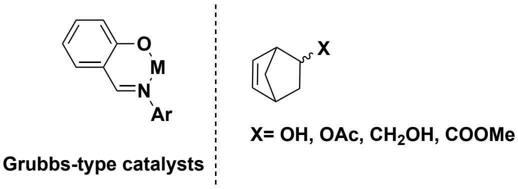


Figure 5.7. *Grubbs-type catalysts and suitable polar-substituted norbornene comonomers*

5.3 Supported organometallic chemistry for olefin copolymerization with polar monomers

5.3.1 Covalent immobilization of transition-metal catalysts

Recently, single-site organometallic catalysts supported on solid or organic substrates are making an important contribution to heterogeneous catalysis. Indeed,

---

[164] S. Ito, Y. Ota, K. Nozaki, *Dalton Trans.* **2012**, 41, 13807-13809.

[165] a) M. Chen, C. L. Chen, *ACS Catal*. **2017**, 7, 1308-1312; b) G. Z. Song, W. M. Pang, W. M. Li, M. Chen, *Polym. Chem*. **2017**, 8, 7400-7405; c) B. P. Yang, S. Y. Xiong, C. L. Chen, *Polym. Chem*. **2017**, 8, 6272-6276.

[166] T. Liang, C. L. Chen, *Inorg. Chem*. **2018**, 57, 14913-14919.

[167] a) E. F. Connor, T. R. Younkin, J. I. Henderson, S. Hwang, R. H. Grubbs, W. P. Roberts, J. J. Litzau, *J. Polym. Sci.* Part A **2002**, 40, 2842-2859; b) M. R. Radlauer, A. K. Buckley, L. M. Henling, T. Agapie, *J. Am. Chem. Soc*. **2013**, 135, 3784-3787; c) D. Takeuchi, Y. Chiba, S. Takano, K. Osakada, *Angew. Chem. Int. Ed.* **2013**, 52, 12536-12540; *Angew. Chem.* **2013**, 125, 12768-12772; d) M. P. Weberski, C. L. Chen, M. Delferro, T. Marks, *Chem. Eur. J.* **2012**, 18, 10715-10732.

their heterogenization serves for gas slurry phase olefin polymerization to control the morphology of the resulting polymer and to avoid reactor fouling.[168] Early transition metal-based catalysts in particular were extensively studied for olefin polymerization, leading to the commercialization of many systems (Figure 5.8).[169] They are mostly prepared by molecular-level anchoring/chemisorption in which a molecular precursor undergoes reaction with the surface while maintaining most of the ligand sphere of the parent molecule.

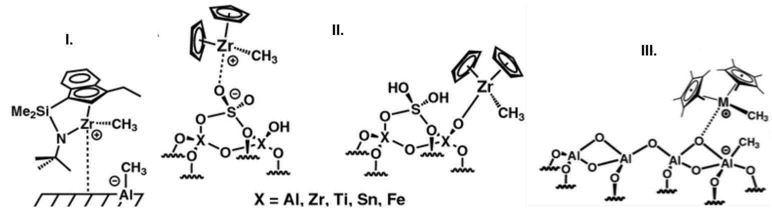


Figure 5.8. I. Zirconoceum catalyst supported on sulfated metal oxides; **II.** Zirconocenium complex supported on sulfated metal oxides; **III.** Neutrally charged u-oxo organometallic complex supported on gamma-alumina

The corresponding studies using late-transition-metal catalysts, especially for the purpose of polar monomer copolymerization, have remained largely unexplored. In 2014, Mecking and co-workers reported the covalent immobilization of phosphine-sulfonate palladium catalysts onto inorganic substrates and polystyrene,[170] and studied their properties in ethylene polymerization and copolymerization with methyl acrylate. They found that covalent binding of neutral phosphino-sulfonato Pd(II) complex to polystyrene has a strong influence on activity which decreases by ~1 order of magnitude compared to the homogeneous Pd-catalyst. Furthermore, lower electrophilicity of the metal center may causes the insertion of the ethylene in the polymer growing chain less effective. Therefore, following studies focused on the development of cationic Pd and Ni complexes having weaker link with the surface to increase catalyst accessibility, mobility, and electrophilic character. Conely and co-workers described the immobilization of α-diimine nickel and palladium catalysts on sulfated zirconium oxide partially dehydroxylated through electrostatic interactions.[171] It resulted in a higher activity compared to the Pd(II) complex covalently bond onto polystyrene which shows that the nature of the active single-site species is advantageous retained upon supporting. However, lower activities than those obtained with solution catalysts are observed and prolonged reaction times lead to a steady decrease in catalyst activity suggesting deactivation overtime.

---

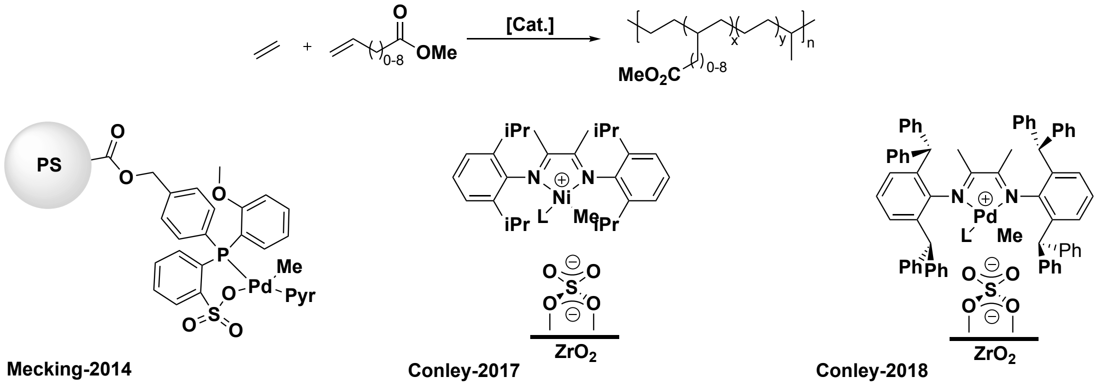
[168] a) G. G. Hlatky, *Chem. Rev.* **2000**, 100, 1347-1376; b) J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, 105, 4073-4147.

[169] a) M. M. Stalzer, M. Delferro, T. J. Marks, *Catal. Lett.* **2015**, 145, 3–14; b) M. C. Baier, M. A. Zuideveld, S. Mecking, *Angew. Chem. Int. Ed*. **2014**, 53, 9722-9744; *Angew. Chem*. **2014**, 126, 9878–9902.

[170] P. Wucher, J. B. Schwaderer, S. Mecking, *ACS Catal*. **2014**, 4, 2672-2679.

[171] a) H. Tafazolian, D. B. Culver, M. P. Conley, *Organometallics* **2017**, 36, 2385-2388; b) D. B. Culver, H. Tafazolian, M. P. Conley, *Organometallics* **2018**, 37, 1001-1006.

Table 5.1. *Examples of supported Pd and Ni catalysts and application in olefins copolymerization with acrylates comonomers*



Entry	T ºC	$P_{Ethylene}$ (psi)	Solvent	Reaction time	XMA (mol%)	Mn (kg/mol)	D	B	Ref.
Mecking-2014[a]	90	-	Toluene	15 mins	2.5	3.7	-	-	170
Conley-2017[b]	60	45	Toluene	15 mins	0.4	23.6	4.15	72	171a
Conley-2018[c]	60	80	Toluene	15 h	0.4	16	2.3	39	171b

Reaction conditions: [a] Molecular weight and MA incorporation determined by ^{1}HNMR at 130 ºC in $C_2D_2Cl_4$; [b] and [c] Molecular weight determined by GPC at 140 ºC in trichlorobenzene; XMA: Methyl acrylate incorporation; D: dispersity; B: Number of branches per 1000 carbons

5.3.2 Non-covalent immobilization of α-diimines Palladium catalysts

The results obtained are currently being included in a patent application and will not be described in the public version of this thesis.

Chapter 6

"Biphasic Catalytic system for the Telomerization of 1,3 butadiene and CO_2"

6.1 Introduction

A major challenge for chemists today when developing new products or more economic routes to existing products is minimizing the impact on the environment. Indeed, catalyzed reactions often deal with potentially toxic and/or costly metal complexes, thus, the search for recoverable catalyst has become a major concern of modern chemistry.[172] In this context, various methods and strategies for the recycling and reuse of homogeneous catalysts have been reported,[173] including biphasic catalysis, that represents one of the best ways of improving the environmental efficiency of a chemical process as it allows the separation of the catalyst from the product by simple decantation.

6.2 Liquid-liquid biphasic systems

Biphasic processes that lead to simple recovery and recycling have been successfully applied in the chemical industry in processes such as Shell High Olefin Polymerization,[174] Ruhrchemie/Rhône-poulenc oxoprocess[175] and the Difasol process[176]. In such processes, the reaction media consists of two immiscible solvent systems (organic/organic or organic/aqueous) where usually one dissolves the catalyst and the other dissolves substrates and products, allowing an easy catalyst recovery and reuse by means of phase separation.

6.2.1 Aqueous biphasic systems

One of the most successful approaches to separate homogeneous transition metal catalysts from the product mixture is the application of water-soluble catalysts in aqueous biphasic systems (Figure 6.1.). In such catalytic systems the solubility of the catalyst in water is usually achieved by introducing highly polar substituents such as -SO_3H, -COOH, -OH, or - NH_2, (or their salts) on the ligands,[177] while the substrates and products remain in the organic layer. The advantages of highly active and selective homogeneous catalysts are combined with an easy separation by decantation.

---

[172] M. Benaglia, Recoverable and Recyclable Catalysts, John Wiley & Sons, Chichester UK, **2009**

[173] a) J. A. Gladysz, *Chem. Rev.*, **2002**, 102, 10, 3215-3216; b) D. J. Cole-Hamilton, *Science*, **2003**, 299, 1702-1706; c) D.J. Cole-Hamilton, R.P. Tooze, Catalyst Separation, Recovery and Recycling: Chemistry and Process Design, Eds. Springer, Dordrecht, The Netherlands, **2006**.

[174] a) W. Keim, *Angew. Chem. Int. Ed.*, **1990**, 29, 235-244; b) W. Keim, *Green Chem.*, **2003**, 5, 105-111

[175] A) W. A. Hermann, C. W. Kohlpainher, *Angew. Chem.*, **1993**, 105, 1588-1609; b) E. Weibus, B. Cornils, *Chem. Ing. Tech.*, **1994**, 66, 916-923; c) C. W. Kohlpaintner, R. W. Fisher, B. Cornils, *Appl. Catal. A*, **2001**, 221, 219-225; d) E. Kuntz, Rhône-Poulenc Industries, Paris, DE2627354 A1, **1976**; e) B. Cornils, W. Konkol, H. Bach, G. Daembkes, W. Gick, E. Wiebus, H. Bahrmann, DE3415968 A1, **1985.**

[176] a) Y. Chauvin, B. Gilbert, I. Guibard, Journal of the Chemical Society, Chem. Communications, 1990, 1715-1716; b) H. Oliver, *J. Mol. Catal A-Chem.*, **1999**, 146, 285-289.

[177] a) J. Manassen, Catalysis: Progress in Research, F. Basolo, L. Burwell Eds., Plenium Press, London, UK, **1973**; b) T. G. Southern, *Polyhedron*, **1989**, 8, 407-441; c) P. Kalck, F. Monteil, Adv. Organomet. Chem., **1992**, 34, 219-284; d) W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed.*, **1993**, 32, 1524-1544; e) F. Mercier, F. Mathey, J. *Organomet. Chem.*, **1993**, 462, 103-106.

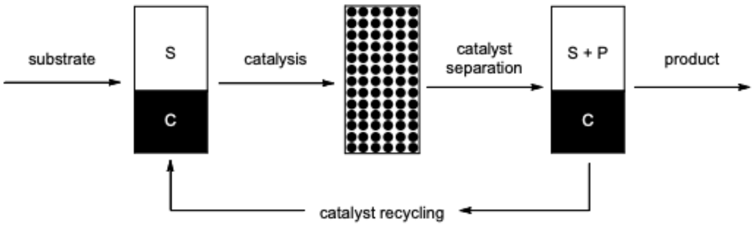
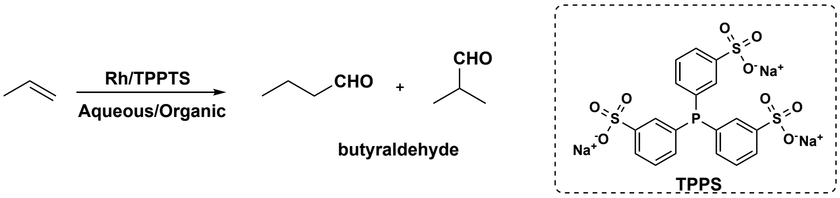


Figure 6.1. *Schematic representation of water/organic phase biphasic catalysis with subsequent catalyst separation and recycle. S= substrate, C= catalysts and P= product*

With the advent of green chemistry, aqueous biphasic catalysis has attracted great attention and led to numerous industrial applications.[178] Aqueous biphasic catalysis has found application in the fine and bulk chemical industry for the Pd-catalyzed C-C coupling for the production of vitamin precursors.[179] An early success of aqueous biphasic systems is the commercialization in 1984 of the Ruhrchemie/Rhone-Poulenc hydroformylation process for the production of 1-butanal (Scheme 6.1.).[180] A rhodium-based catalyst is used in combination with a water-soluble triphenyl phosphine trisulphonate ligand to produce more than 450 000 tones of aldehyde per year using four plants.



Scheme 6.1. *Biphasic hydroformylation for the manufacture of n-butyraldehyde by the RCH/RP process*

Other reactions that have been reported using this strategy include hydrogenations,[181] Heck reactions,[182] and oligomerizations.[183] The use of aqueous biphasic catalysis, however, is limited to substrates that are at least slightly soluble in water, and several reports in literature deal with these solubility limitations: 1) addition of solvents and/or co-solvents,[184] 2) addition of surfactants,[181,185] and/or 3) the application

---

[178] B. Cornils, W. A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, Eds., Wiley-VCH, Weinheim, Germany, **2002**.

[179] C. Mercier, P. Chabardes, *Chem. Ind. Catal. Org. React.*, **1995**, 62, 213.

[180] a) G. Fremy, Y. Castanet, R. Grzybek, E. Monflier, A. Montreux, A. M. Trzeciak, J. J. Ziolkowski, *J. Organomet. Chem.*, **1995**, 505, 11-16; b) E. Monflier, G. Fremy, Y. Castanet, A. Montreux, *Angew. Chem. Int. Ed.*, **1995**, 34, 2269-2271.

[181] a) J. M. Grosselin, C. Mercier, G. Allmang, F. Grass, *Organometallics*, **1991**, 10, 2126-2133; b) V. Kotzabasakis, E. Georgopoulou, M. Pitsikalis, N. Hadjichristidis, G. Papadogianakis, *J. Mol. Catal. A: Chem.*, **2005**, 231, 93-101.

[182] J. kiji, T. Okano, T. Hasegawa, *J. Mol. Catal. A: Chem.*, **1995**, 97, 73-77

[183] W. Baidossi, N. Goren, J. Blum, *J. Mol. Catal. A: Chem.*, **1993**, 85, 153-162

[184] R. M. Deshpande, S. S. Divekar, B. M. Bhanage, R. V. Chaudhari, *J. Mol. Catal.*, **1992**, 75, L19.

[185] a) M. Giménez-Pedrós, A. Aghmiz, C. Claver, A. M. Masdeu-Bultó, D. Sinou, *J. Mol. Catal. A: Chemical* **2003**, 200, 157-163; b) E. V. Dehmlow, Phase Transfer Catalysis, S. S. Dehmlow Eds., Wiley-VCH, Weinheim, Germany, **1993**.

of amphiphilic catalysts.[186] In addition, aqueous media cannot be used for chemical systems in which one of the components undergoes undesired chemical reactions with water. Although aqueous biphasic systems seem appealing because of the "green" image of water, they generally lead to large amounts of dilute aqueous organic waste streams, which are particularly difficult to process.[187] This environmental concern, together with already addressed other limitations has stimulated the development of new strategies involving non-aqueous biphasic catalysis.

6.2.2 Fluorous biphasic systems

In the 1990s Horvath and Rabai introduced a new concept called "fluorous biphasic catalysis" (FBC) in which fluorocarbons are used as solvent for homogeneous catalysis.[188] The fluorous phase usually consists of perfluorinated alkanes, ethers, or tertiary amines in which all hydrogens atoms have been replaced by fluorinated atoms-(Figure 6.2.).[189] Their miscibility with common organic solvents such as toluene, acetone and alcohols are negligible at room temperature.

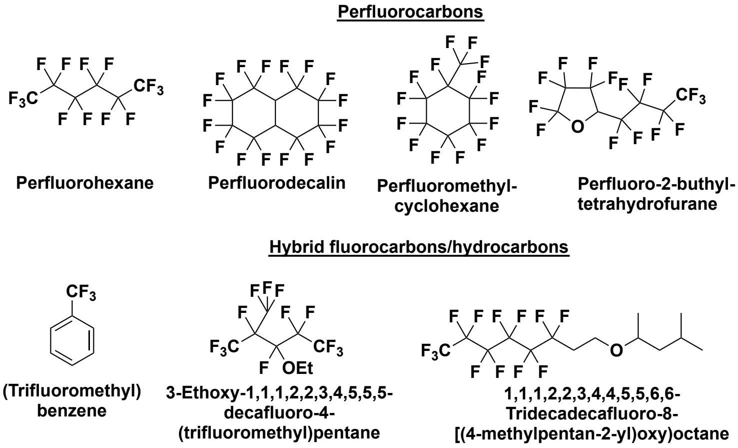


Figure 6.2. *Examples of fluorinated solvents applied in Fluorous Biphasic Catalysis (FBC)*

A fluorous biphasic reaction could proceed either in the fluorous phase or at the interface of the two phases depending on the solubility of the reactants in the fluorous phase. Moreover, at elevated temperatures the biphasic mixture containing catalyst and substrates transforms in a single phase, giving rise to effective homogeneous catalytic reactions (Figure 6.3.). After completion of the reaction the system can be cooled down to give phase separation, thus recovering the catalyst. Fluorous-modified ligand have been successfully applied in several catalytic reactions such as allylic substitutions,[190]

---

[186] J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, Rhodium Catalyzed Hydroformylation, Ch. 3, P. W. N. M. van Leeuwen, C. Claver Eds., Kluwer Academic Publishers, **2000**.

[187] R. T. Baker, W. Tumas, *Science* **1999**, *284*, 1477-1479

[188] I. T. Horvath, J. Rabai, *Science*, **1994**, 266, 72-75

[189] D.-W. Zhu, *Synthesis* **1993**, 10, 953-954

[190] R. Kling, D. Sinou, G. Pozzi, A. Choplin, F. Quignard, S. Busch, S. Kainz, D. Koch, W. Leitner, *Tetrahedron Lett.*, **1998**, 39, 9439-9442.

cross-coupling reactions,[191] Diels-Alder reactions,[192] epoxidation of olefins,[193] Friedel-Crafts acylation,[197] Heck reaction,[194] hydrogenation,[195] and hydroformylation in a biphasic system. [192a,198, 196]

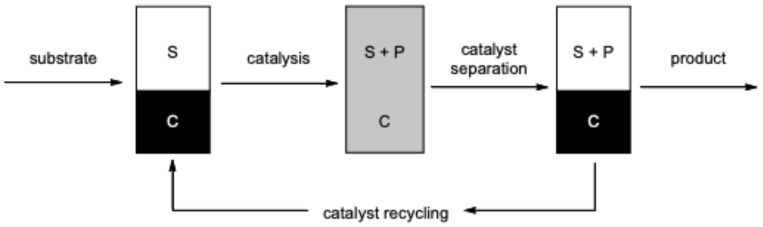


Figure 6.3. *General concept of fluorous biphasic catalysis. The black area is the fluorous phase, the white area is the organic phase and the grey area is the homogeneous mixture at high temperature. S= subtrate, C= Catalyst and P= product*

Further optimization of this system, by the use of heavier fluorous solvents and longer fluoroalkyl chains on the ligands, is necessary to minimize the significant leaching of catalyst and fluorous solvent in the product mixture.[179, 181] Currently the commercialization of such biphasic systems are prohibited by these leaching issues and the high costs of fluorinated solvents.

6.2.3 Supercritical fluids

Supercritical fluids (SCFs) have received considerable attention as new reaction media for chemical syntheses.[197] By definition, they are substances heated above their critical temperature T_c and compressed above their critical pressure p_c. Such phase dissolves many low- to medium-polarity organic molecules which become fully miscible with permanent gases.

$scCO_2$ is by far the most widely used supercritical fluid due to its mild critical constants (p_c = 73.75 bar, T_c = 31.0 ºC) (Figure 6.4.). Moreover, technical aspects such

---

[191] B. Betzemeier, P. Knochel, *Angew. Chem. Int. Ed.*, **1997**, 36, 2623

[192] J. Nishikido, H. Nakajima, T. Saeki, A. Ishii, K. Mikami, *Synlett*, **1998**, 1347

[193] a) G. Pozzi, F. Montanari, S. Quici, *Chem. Commun.*, **1997**, 69-70; b) I. Klement, H. Lutjens, P. Knochel, *Angew. Chem. Int. Ed.*, **1997**, 36, 1454; c) J.-M. Vincent, A. Rabion, V. K. Yachandra, R. H. Fish, *Angew. Chem. Int. Ed.*, **1997**, 36, 2346; d) B. Betzemeier, F. Lhermitte, P. Knochel, *Synlett*, **1999**, 489.

[194] L. K. Yeung, R. M. Crooks, *Nano Lett.*, **2001**, 1, 14-17

[195] a) D. Rutherford, J. J. J. Juliette, C. Rocaboy, I. T. Horvat, J. A. Gladysz, *Catal. Today*, **1998**, 42, 381; b) E. G. Hope, R. D. W. Kemmitt, D. R. Paige, A. M. Stuart, *J. Fluorine Chem.*, **1999**, 95, 125; c) B. Richter, E. De Wolf, G. van Koten, B.-J. Deelman, *J. Org. Chem.*, **2000**, 65, 3885; d) V. Chechik, R. M. Crooks, *J. Am. Chem. Soc.*, **2000**, 122, 1243; e) D. Sinou, D. Maillard, A. Aghmiz, A. M. Masdeu-Bultó, *Adv. Synth. Catal.* **2003**, 345, 603-611

[196] a) I. T. Horvat, G. Kiss, R. A. Crook, J. E. Bond, P. A. Stevens, J. Rabai, E. J. Mozelski, *J. Am. Chem. Soc.*, **1998**, 120, 3133; b) W. Chen, L. Xu, J. Xiao, *Chem. Commun.*, **2000**, 839.

[197] a) P. G. Jessop, W. Leitner, Chemical Syntheses Using Supercritical Fluids, Eds., Wiley-VCH, Weinheim, Germany, **1999**; b) W. Leitner, *Acc. Chem. Res.*, **2002**, 35, 746

as its nontoxicity, nonflammability, low cost and possible utilization on industrial scales favor supercritical CO_2 ($scCO_2$) as an alternative to conventional solvents.[179,181, 198]

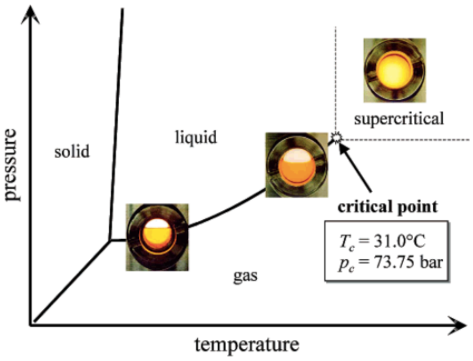
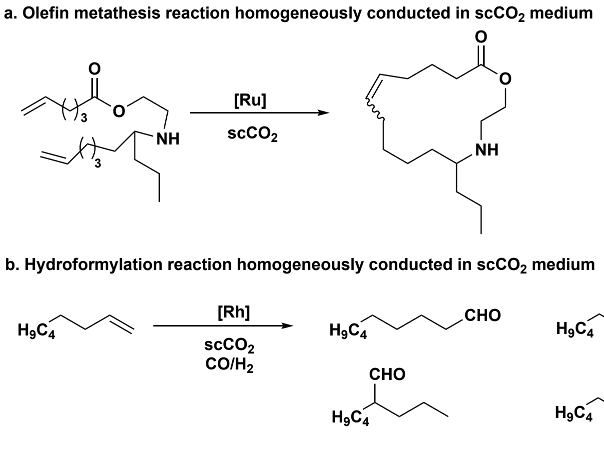


Figure 6.4. *Schematic phase diagram of CO_2 with snapshots of the transition from liquid/gas region to the supercritical region (bright orange "CO_2-philic" rhodium complex was added for better contrast and to illustrate the solvent properties of the liquid and the supercritical phase).*

Rathke and Klingler were the first to report $scCO_2$ as a solvent for the homogeneous hydroformylation of propene using $[Co_2(CO)_8]$ as a catalyst precursor. However, it suffers from high reaction temperatures (>90 ºC) and high catalyst loading.[199] Following this work, Leitner *et al.* presented ruthenium-catalyzed ring-closing olefin metathesis (RCM) and rhodium-catalyzed hydroformylation homogeneously conducted in $scCO_2$ (Scheme 6.2.). By working in $scCO_2$, the scope of the olefin metathesis reaction was extended to substrates (with NH groups) generally not tolerated in conventional solvents and higher rates in the hydroformylation reaction were obtained than in the conventional solvents. Post-reaction product isolation was achieved through CO_2-density's adjustement (= variation of pressure and/or temperature), thus allowing selective extraction while leaving the catalyst in the reactor for recycling.[200]



Scheme 6.2. *Ruthenium-catalyzed RCM of acyclic diene and Rhodium-catalyzed hydroformylation of 1-octene in $scCO_2$*

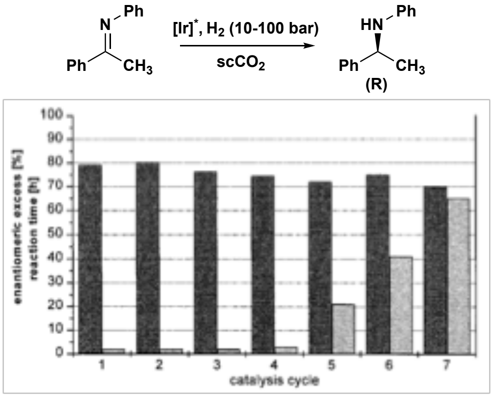
---

[198] a) K. Zosel, *Angew. Chem., Int. Ed.* **1978**, 17, 702-702; b) M. A. McHugh and V. J. Krukonis. Supercritical Fluid Extraction: Principles and Practice, 2nd ed., Butterworth-Heinemann, Oxford, **1994**; c) S. L. Wells, J. DeSimone. *Angew. Chem., Int. Ed.* **2001**, 40, 519-527.

[199] J. W. Rathke; R. J. Klingler, T. R. Krause, *Organometallics* **1991**, 10, 1350-1355.

[200] a) A. Fürstner, D. Koch, K. Langemann, W. Leitner, C. Six, *Angew. Chem. Int. Ed. Engl.*, **1997**, 36, 2466-2469; b) D. Koch, W. Leitner, *J. Am. Chem. Soc.* **1998**, 120, 13398-13404

A special case of catalysis and extraction using $scCO_2$ is the asymmetric hydrogenation of imines with chiral iridium catalyst. After consumption of all the substrates, the catalyst precipitates without need of density variation. Again, product extraction with $scCO_2$ allows reuse of the chiral metal complex without substantial decrease in enantioselectivity until the 5th cycle (Scheme 6.3.).



Scheme 6.3. *Catalyst recycling in the enantioselective hydrogenation of imines in $scCO_2$. The dark bars indicate the enantiomeric excess, and the light gray bars show the time required for quantitative conversion.*

Several other homogeneously catalyzed reactions have been successfully performed in $scCO_2$ such as hydrosilylation, metathesis, oxidations, and various C–C coupling reactions in which temperature and pressure swings are used to precipitate the catalyst selectively and the product can be recovered by decompression.[201]

6.2.4 Non-aqueous ionic liquids

An important and rapidly growing area of non-aqueous biphasic catalysis is based on the application of ionic liquids as catalyst phase.[202] Ionic liquids (ILs) are molten salts that are liquid at temperature below 100 ºC. They consist of a typical combination of cations and anions (Figure 6.5.).

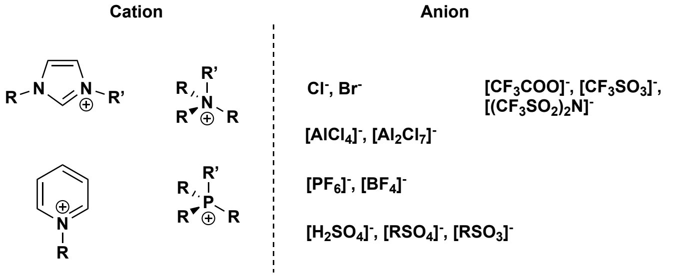


Figure 6.5. *Typical cation and anion that fomed ionic liquids*

The first application as solvent for transition metal catalysis was described in 1990 by Chauvin[203] and Carlin[204] in the nickel catalyzed dimerization of propene and in the

---

[201] P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.*, **1999**, 99, 475

[202] K. R. Seddon, *J. Chem. Technol. Biotechnol.*, **1997**, 68, 351.

[203] Y. Chauvin, B. Gilbert, I. Guibard, *J. Chem. Soc.*, *Chem. Commun.*, **1990**, 1715

[204] R. T. Carlin, R. A. Osteryoung, *J. Mol. Catal.*, **1990**, 63,125.

Ziegler-Natta catalyzed ethene polymerization, respectively. Within the biphasic reaction system, the ionic liquid chosen exhibited a good solubility for the catalysts thus, giving rise to a straightforward recovery of the homogeneous transition metal catalyst from the product mixture. In addition, ionic liquids have practically no vapor pressure, which also facilitate separation of the catalyst from the product *via* distillation.[205] Various examples are present in literature on the use of ionic liquids as solvent for transition metal catalysis,[206] including hydrogenations, oxidations, hydroformylations, and C-C coupling reactions, mainly involving ionic liquids based on imidazolium salts.[179, 207]

6.3 Liquid-Supercritical Fluid Biphasic systems

In contrast with the classical liquid-liquid biphasic systems for homogeneous catalysis, liquid/SCF biphasic systems are truly integrated strategies. Reaction and separation can be run in a single unit operation due to the gas-like properties of the SCF phase separation that takes place inside the reactor.

6.3.1 Water/scCO$_2$

The feasibility of homogeneous catalysis in H_2O/scCO$_2$ systems is possible due to the low solubility of H_2O in scCO$_2$. It allows to process hydrophilic substrates placed in the water phase (or mobile phase) whereas the catalyst is present in the scCO$_2$ phase (or stationary phase) (Figure 6.6.).

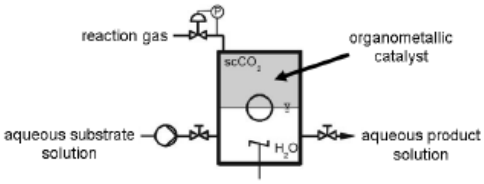


Figure 6.6. *H_2O/scCO$_2$ system.* [215a]

This approach was successfully demonstrated in the rhodium-catalyzed hydroformylation and enantioselective C=C hydrogenations using CO$_2$-philic catalyst bearing fluorinated phosphine ligands.[208] Catalyst recycling could be performed without the need of decompressing the SCF for 9 cycles with high rates (TOF> 200 h^{-1}) and selectivities (up to 99% ee) and low levels of leaching.

6.3.2 PEG/scCO$_2$

---

[205] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.*, **2000**, 39, 3772.

[206] a) F. H. Hurtley, U.S. Patent, 2.466.331, **1948**; b) F. H. Hurltey, *Chem. Abstr.*, **1949**, 43, P7645b; c) S. E. Fry, N. J. Pienta, *J. Am. Chem. Soc.*, **1985**, 107, 6399; d) J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.*, **1986**, 51, 480

[207] V. I. Parvulescu, C. Hardacre, *Chem. Rev.*, **2007**, 107, 2615.

[208] a) K. Burgemeister, G. Franciò, V. Gego, L. Greiner, H. Hugl, W. Leitner, *Chem. Eur. J.* **2007**, 13, 2798-2804; b) M. McCarthy, H. Stemmer, W. Leitner, *Green Chem.* **2002**, 4, 501-504

The combination of liquid polymers such as polyethylene glycols (PEGs) as a catalyst phase and $scCO_2$ as a mobile phase offers a "green" possibility of recovering expensive metal catalysts and running the metal-mediated chemical reactions under continuous flow conditions. Indeed, PEGs are inexpensive, non-volatile and environmentally benign solvents that are relatively insoluble in $scCO_2$.[216a] For example, the biphasic system of PEG-1500/$scCO_2$ has been used for the immobilization of Wilkinson's catalyst in the hydrogenation of styrene and for the ruthenium-catalyzed enantioselective hydrogenation of tiglic acid (Figure 6.7.).[209] Product isolation by intermittent $scCO_2$ extraction and batch-wise catalyst recycling with stable selectivity (average 83% ee) was demonstrated for the latter reaction.

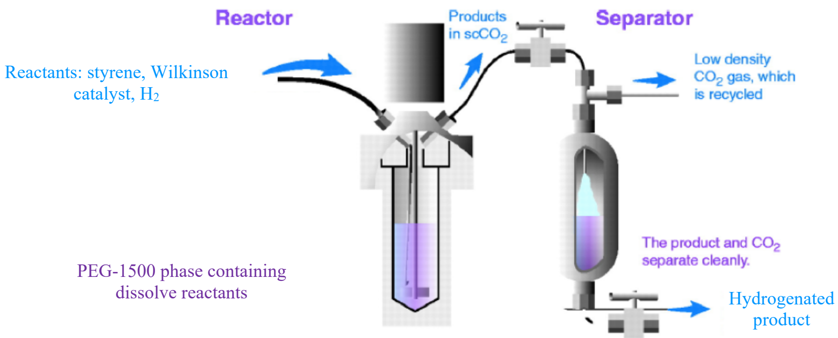


Figure 6.7. *Styrene hydrogenation in PEG/$scCO_2$ system*

Examples of continuous flow catalysis using $scCO_2$ with PEG-based systems have also been demonstrated. Highly selective oxidative dehydrogenation of a range of light alcohols with O_2 catalyzed by palladium nanoparticles embedded in PEG-1000 has been conducted with $scCO_2$ flow. Over 40 hours of stable catalysis were demonstrated whereby agglomeration of the nanoparticles to inactive Pd-black was prevented.

6.3.3 IL/$scCO_2$

Inspired by the utility of ILs for organometallics catalysis[210] and the highly attractive phase behavior of ILs with CO_2[211] a number of homogeneously catalysed reactions have successfully been transferred into IL/CO_2 biphasic systems. Given the ionic nature of ILs, their solubility in CO_2 is even lower than that of PEG or water, offering an almost ideal stationary catalyst phase for flow systems. Early reports on C=C hydrogenations with batch-wise catalyst recycling (achiral, rhodium-catalyzed[212] and

---

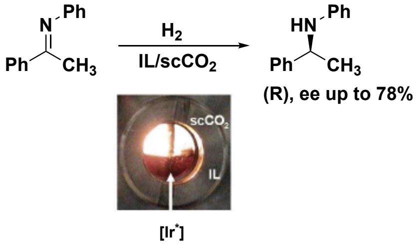
[209] a) D. J. Heldebrant, P. G. Jessop, *J. Am. Chem. Soc.* **2003**, 125, 5600-5601; b) D. J. Heldebrant, H. N. Witt, S. M. Walsh, T. Ellis, J. Rauscher, P. G. Jessop, *Green Chem.* **2006**, 8, 807-815

[210] a) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 3772-2789; b) T. Welton, *Coord. Chem. Rev.* **2004**, 248, 2459-2477; c) V. I. Parvulescu, C. Hardacre, *Chem. Rev.* **2007**, 107, 2615-2665

[211] a) L. A. Blanchard, D. Hancu, E. J. Bekman, J. F. Brennecke, *Nature* **1999**, 399, 28-29 b) L. A. Blanchard, J. F. Brennecke, *Ind. Eng. Chem. Res.* **2001**, 40, 287-292

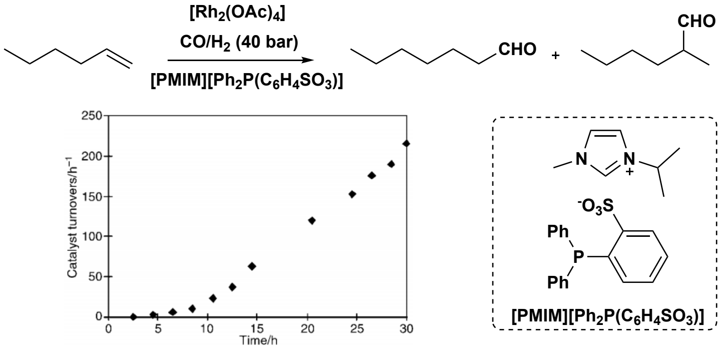
[212] F. Liu, M. B. Abrams, R. T. Baker, W. Tumas, *Chem. Commun.* **2001**, 433-434

enantioselective ruthenium-catalyzed[213]) proved the feasibility of the concept: excellent separation could be achieved by $scCO_2$ extraction of products leaving the catalyst-IL solutions active for reuse. Oxidative catalysis, such as Wacker-oxidation of 1-hexene[214] and propylene carbonate synthesis[215], has also been demonstrated in IL/$scCO_2$. The potential of IL/$scCO_2$ reaction media was demonstrated in the iridium-catalyzed asymmetric imine hydrogenation (Scheme 6.4.).[216] Indeed, the precursor was activated in the IL by anion exchange and the catalyst was found to be more stable towards air when dissolved in IL. Moreover, the catalysis was more rapid when conducted in the presence of $scCO_2$ due to enhance availability of H_2 in the IL phase and the products were readily isolated from the catalyst solution by CO_2 extraction.



Scheme 6.4. *Imine hydrogenation in IL/$scCO_2$ system.*[223]

A pioneering example of successful continuous application using an IL/$scCO_2$ biphasic system was the hydroformylation of long-chain olefins with rhodium complexes (Scheme 6.5.). Sulfonated triphenylphosphine ligands were used to match the requirements of the stationary ionic environments. The reaction proceeded with high stability over more than 30 hours at metal leaching < 1 ppm.[217] In subsequent studies the system was studied in detail and further improved to TOFs of 500 h^{-1} at stability over several weeks and rhodium leaching down to 0.01 ppm.[218]



Scheme 6.5. *Hydroformylation in IL/$scCO_2$ system*

---

[213] R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert,C. L. Liotta, P. G. Jessop, *J. Am. Chem. Soc.* **2001**, 123, 1254-1255

[214] Z. Hou, B. Han, L. Gao, T. Jiang, Z. Liu, Y. Chang, X. Zhang, J. He, *N. J. Chem.* **2002**, 26, 1246-1248

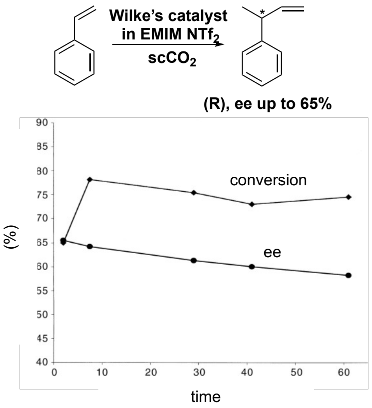
[215] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* **2003**, 896-897

[216] M. Solinas, A. Pfaltz, P. G. Cozzi, W. Leitner, *J. Am. Chem. Soc.* **2004**, 126, 16142-16147

[217] Murielle F. Sellin, Paul B. Webb, David J. Cole-Hamilton, *Chem. Commun.*, **2001**, 781-782

[218] a) P. B. Webb, M. F. Sellin, T. E. Kunene. S. Williamson, A. M. Z. Slawin, D. J. Cole-Hamilton, *J. Am. Chem. Soc.* **2003**, 125, 15577-15588; b) P. B. Webb, T. E. Kunene, D. J. Cole-Hamilton, *Green Chem.* **2005**, 7, 373-379

Another example demonstrating the importance of matching catalyst and separation strategy is the nickel-catalysed asymmetric hydrovinylation of styrene in IL/CO_2 where the active species is formed in situ through halide abstraction from the catalyst precursor by the IL.[219] Continuous operation afforded the additional advantage of preventing catalyst starvation: while during batch-wise recycling the complex progressively deactivated due to temporary absence of substrate, sustaining reaction conditions in continuous flow mode yielded stable enantioselective catalysis over more than 60 hours (Scheme 6.6.).



Scheme 6.6. *Asymmetric hydrovinylation of styrene in IL/$scCO_2$ system*

6.4 Biphasic system for the telomerization reaction of butadiene with CO_2

Our group aims at developing cleaner synthetic routes in a manner which maximizes efficiency and minimize waste. Apart from surface organometallic chemistry (SOMC) that promotes catalyst recycling, biphasic catalysis represents a more sustainable method for the separation of transition metal (TM) catalyst and product. Thus, in the following section the telomerization reaction of 1,3-butadiene and CO_2 to produce δ-lactone in a biphasic catalytic system is presented. The main purpose being the study of catalyst recycling and product extraction without any cross-contamination. This part of the thesis was carried out in the group of Prof. Dr. W. Leitner at RWTH Aachen University.

6.4.1 Background

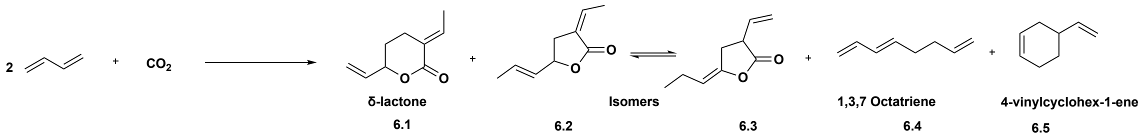
The telomerization reaction is a 100% atom-efficient reaction.[220] The added value of this reaction is increased by using cheap and easily available feedstocks such as carbon dioxide (CO_2). Typical side reactions are palladium-catalyzed dimerization to

---

[219] A. Bösmann, G. Franciò, E. Janssen, M. Solinas, W. Leitner, P. Wasserscheid, *Angew. Chem. Int. Ed.* **2001**, 40, 2697-2699

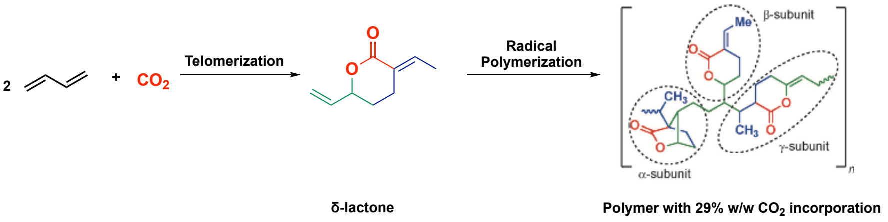
[220] T. A. Faßbach, A. J. Vorholt, W. Leitner, *ChemCatChem* **2019**, 11, 1153-1166

1,3,7 octatriene **6.4** and the non-catalyzed Diels-alder (DA) to 4-vinylcyclohexene **6.5** (Scheme 6.7.).[221]



Scheme 6.7. *Telomerization of 1,3-butadiene with carbon dioxide and dimerization side reactions*

The catalytic reaction of 1,3-butadiene and CO_2 was first mentioned in the 1970s,[222] with process concepts and subsequent applications being developed later on, especially by Behr *et al.*[223] Recently, investigations on this telomerization reaction is due to the possible application of the reaction product in the synthesis of polymers that will incorporate CO_2 (Scheme 6.8.).[224]



Scheme 6.8. *Telomerization of 1,3-butadiene with carbon dioxide and subsequent polymerization*

The accepted mechanism of this telomerization reaction is illustrated in scheme 6.9 and is based on detail investigations by Behr *et al.*[225] It involves a monophosphine-ligated to palladium(0) complexes as active catalyst specie. After the oxidative coupling of two butadienes coordinated to the Pd^0, an n^3-allyl palladium complex **6.A** is formed. Such complex can follow two different paths. First, as a side reaction, protonation and β-hydride elimination which lead to the formation of the dimer octatriene. Second, complex **6.A** contains a highly nucleophilic σ-Pd-carbon bond that is able to insert CO_2 to give the key intermediate **6.B**. Complex **6.B** can then undergo an intramolecular cyclization to yield the five- or six-membered ring lactones which are convertible into each other while, β-hydride elimination from **6.B** and subsequent telomerization can form esters and related isomers.

---

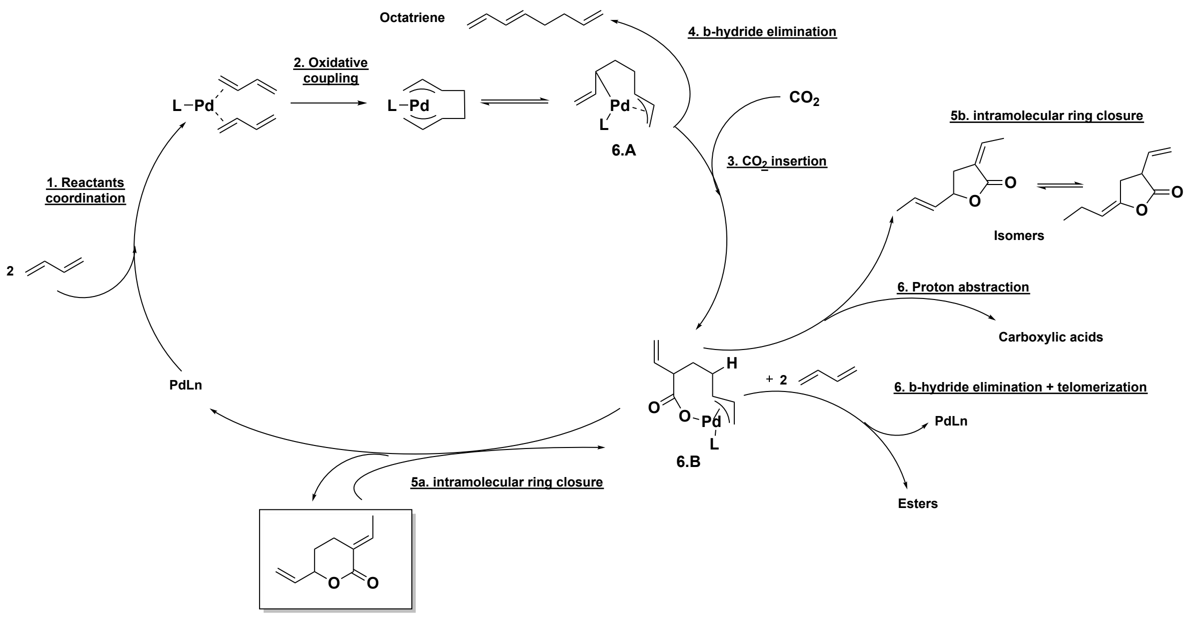
[221] a) A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski, S. Reyer, *Angew. Chem. Int. Ed.* **2009**, 48, 3598-3614; *Angew. Chem. Int. Ed.* **2009**, 121, 3652-3669

[222] a) Y. Sasaki, Y. Inoue and H. Hashimoto, *J. Chem. Soc.*, *Chem. Commun.*, **1976**, 605-606; b) Y. Inoue, Y. Sasaki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **1978**, 51, 2375-2378; c) A. Musco, C. Perego and V. Tartiari, *Inorg. Chim. Acta*, **1978**, 28, L147; d) A. Musco, R. Santi, G. P. Chiusoli, US Patent 4167513A; *Chem. Abstr.*, **1979**, 90, 186403

[223] a) A. Behr, M. Heite, *Chem. Eng. Technol.* **2000**, 23, 952-955; b) A. Behr, G. Henze, *Green. Chem.* **2011**, 13, 25-39; c) A. Behr, P. Bahke, B. Klinger, M. Becker, *J. Mol. Catal. A* **2007**, 267, 149-156; d) A. Behr, V. A. Brehme, *J. Mol. Catal. A* **2002**, 187, 69-80

[224] R. Nakano, S. Ito, K. Nozaki, *Nat. Chem.* **2014**, 6, 325-331

[225] A. Behr, R. He, K.-D. Juszak, C. Krüger, Y.-H. Tsay, *Chem. Ber.* **1986**, 119, 991-1015



Scheme 6.9. *Accepted mechanism for the telomerization of 1,3-butadiene with* CO_2

Behr and co-workers established the use of more basic phosphine and acetonitrile as solvent to obtained δ-lactone with high yields and selectivies.[226] Therefore, among the catalytic system tested, Pd(acac)$_2$/tricyclohexylphosphine is considered to be best catalytic system for this transformation. Although, low catalyst turnover numbers (up to 350) and yields up to 45% are obtained.[227] In 2012, catalysts containing P,N-bidentate ligands were found to be useful in order to increase the turnover numbers and obtain more active catalysts.[228] Later on, Beller *et al.* reported the utilization methoxy-functionalised triphenylphosphine ligand that increase the electron density on the metal center, resulting in catalysts that were more active (Scheme 6.10.).[229] One year later, a combination of palladium acetate and tris(p-methoxyphenyl)phosphine as a catalyst in acetonitrile with *p*-hydroquinone and N,N-diiso-propylethylamine gave catalytic system three times more active[230] (Scheme 6.10.).

---

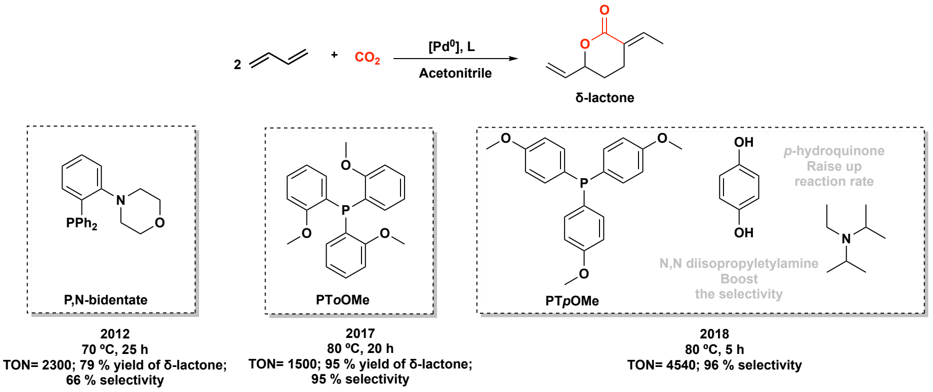
[226] a) A. Behr, G. V. Ilsemann, *J. Organomet. Chem.*, **1983**, 255, 77-79; b) A. Behr, Carbon Dioxide Activation by Metal Complexes, VCH, Weinheim, **1988**; c) P. Braunstein, D. matt, D. Nobel, *Chem. Rev.* **1988**, 88, 747-764; d) A. Behr, M. heite, *Chem. Eng. Technol.* **2000**, 23, 952-955; e) S. Pitter and E. Dinjus, *J. Mol. Catal. A*, **1997**, 125, 39-45

[227] a) A. Musco, C. Perego, V. Tartiari, *Inorg. Chim. Acta* **1978**, 28, L147; b) A. Behr, K.-D. Juzak, W. Keim, *Synthesis* **1983**, 574

[228] Y. Dai, X. Feng, B. Wang, R. He, M. Bao, *J. Organomet. Chem.* **2012**, 696, 4309-4314

[229] M. Sharif, R. Jackstell, S. dastgir, B. Al-Shihi, M. Beller, *ChemCatChem* **2017**, 9, 542-546

[230] J. M. Balbino, J. Dupont, J. C. Bayón, *ChemCatChem* **2018**, 10, 206-210



Scheme 6.10. *Different reaction conditions for the production of δ-lactone*[235, 236, 237]

6.4.2 Reaction concept

The biphasic catalytic system studied here is a combination of ionic liquids (ILs) and supercritical carbon dioxide ($scCO_2$). Ionic liquids are excellent solvents for transition metal catalysts. Mainly due to their widely tunable properties, high thermal stability and lack of noticeable vapor pressure.[231] $scCO_2$ is also of increasing interest as it combines environmentally benign character with favorable physico-chemical properties (high volatility and low polarity) that makes it an interesting solvent partner with the nonvolatile and polar ILs.[232] Moreover, the system IL/$scCO_2$ constitutes a close-to-ideal solvent combination for biphasic molecular catalysis because of the extreme differences in polarity, volatility and mutual miscibility of the two components.[233] The focus will be on the synthesis of δ-lactone in high yield and selectivity in the IL/$scCO_2$ biphasic system. The key point of this concept would be that the catalyst is strictly kept in the ionic liquid phase, the product is extracted into the supercritical CO_2 phase in a continuous-flow manner thus, pure recovery of δ-lactone would be straightforward without the need of any downstream separation.

6.4.3 Results and discussion

Starting with reaction conditions based on literature reports, the influence of the different parameters (ratio of catalyst to reactant, ratio of 1,3 butadiene to CO_2, CO_2 pressure, ratio of ILs to reactant) were studied in order to find the optimum combination for a successful transfer to the later intended continuous process.

6.4.3.1 Telomerization reaction in a single system catalysis

---

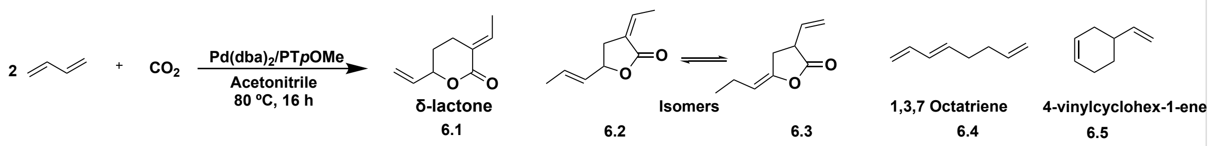
[231] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, 112, 3926-3945

[232] P. G. Jessop, W. Leitner, Chemical Synthesis Using Supercritical Fluids, Eds. Wiley-VCH, Weinheim, **1999**

[233] F. Jutz, J.-M. Andanson, A. Baiker, *Chem. Rev.* **2011**, 111, 322-353

As a first approach, reactions using a classical homogeneous system were performed. These experiments were performed to validate the procedure and have references of catalytic activity and selectivity of the studied reaction performed in the lab apparatus. Catalytic screening tests were performed in dry and degassed acetonitrile while varying the molar ratio of catalyst to 1,3-butadiene in a 10 mL stainless steel window autoclave (Table 6.1.). The amount of 1,3-butadiene and carbon dioxide used was quantified by weighting the autoclave at room temperature. By varying the Pd loading, similar performances were obtained. Nevertheless, a selectivity close to the published results was achieved at 0.08 mol% of [Pd(dba)$_2$] and 1.5 ratio of CO$_2$/1,3-butadiene (Table 6.1., entry 2)

Table 6.1. Validated procedure for the Telomerization reaction



Entry	Pd (mol%)	Ratio CO_2/1,3 But	CO_2 (mmol)	Overall yield (%)	6.1 Yield (%)	6.2+6.3 Yield (%)	6.4 Yield (%)	6.5 Yield (%)	Sel. (%)
1	0.04	1.04	0.040	58	43[b]	13[b]	0 [b] (<2) [c]	0 b] [c]	64
2	0.08	1.5	0.059	65	58[b]	7[b]	0 [b] (0) [c]	0 b] [c]	85
3	0.17	1.89	0.080	59	47[b]	4[b]	0 [b] (8) [c]	0 b] [c]	80
4[d]	0.05	1.40	0.080	/	67 [b]	/	/	/	95
5[e]	0.01	/	30 bar	/	22 [c]	<1[c]	<1[c]	<1[c]	96

[a] General Conditions: Phosphine: 3 equiv of [Pd(dba)$_2$]; 1,3-butadiene ~ 2 g (0,037 mol); (x mol) of CO$_2$, acetonitrile: 6 mL, T= 80 ºC, 16 h. [b] Yields were determined after purification by column chromatography. [c] Results obtained from GC analysis with diglyme as internal standard. [d] Beller's group results.[236] [e] Dupont's group results.[237]

6.4.3.2 Telomerization reaction transfer into a biphasic system catalysis (IL/scCO$_2$)

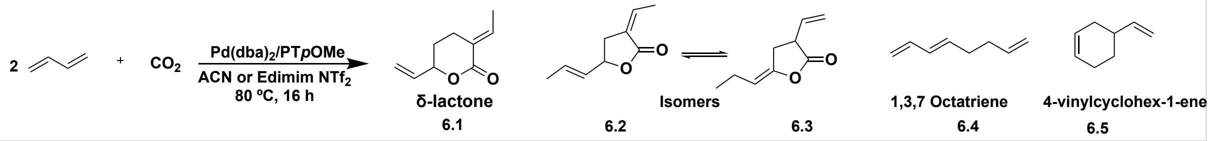
Based on this established procedure, the biphasic system combining [Edimim] [NTf$_2$] (Table 6.2) and scCO$_2$ was evaluated by modifying the catalyst concentration. An imidazolium-based ionic liquid, substituted at C2 position, was chosen for this Pd-catalyzed telomerization reaction, as it is well known that their parents non-substituted at the C2 position lead to the deactivation of the catalyst by the formation of a highly stable Pd-imidazolylidene complexes.[234] As shown in table 6.2., the telomerization reaction was successful in this biphasic catalytic system. However, the yield and selectivity towards δ-lactone are about 5-10% lower compared to the homogeneous system at similar conditions (Table 6.2., entries 1-2). Interestingly, under higher

---

[234] a) W. Keim, *Green Chem.* **2003**, 5, 105-111; b) B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, Multiphase Homogeneous Catalysis, Wiley-VCH Verlag GmbH, Weinheim, Germany, **2005**

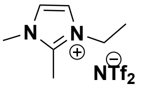
palladium loading, the yield towards δ-lactone decreases which can be explained by increased formation of palladium black (Table 6.2., entries 2, 4). The highest yield and selectivity towards δ-lactone in the biphasic system used is obtained at 0.17mol% of Pd (Table 6.2. entry 2).

Table 6.2. Telomerization reaction in a biphasic system IL/ScCO₂



Entry	"Solvent"	Pd (mol%)	Ratio CO_2/1,3 But	CO_2 (mmol)	Overall yield (%)	6.1 Yield (%)	6.2+6.3 Yield (%)	6.4 Yield (%)	6.5 Yield (%)	Sel. (%)
1	ACN	0.08	1.5	0.059	65	58[b]	7[b]	0[b] (0) [c]	0[c]	85
2	[Edimim][NTf₂]	0.08	1.00	0.037	47	37[b]	7[c]	3 [c]	0[c]	79
3	[Edimim][NTf₂]	0.17	1.40	0.053	42	35[b] 42[c]	0[c]	0[c]	0[c]	100
4	[Edimim][NTf₂]	0.51	2.36	0.071	18	16[c]	2[c]	0[c]	0[c]	89

[a] General Conditions: phosphine: 3 equiv of [Pd(dba)₂]; 1,3 butadiene ~ 2 g (0,037 mol); (x mol) of CO₂, acetonitrile: 6 mL, ILs: 2 mL, T= 80 ºC, 16 h. [b] Yields were determined after purification by column chromatography. [c] Results obtained from GC analysis with diglyme as internal standard.



[Edimim] [NTf₂]

Furthermore, Table 6.2 illustrates that an increase amount of CO_2 negatively affects the outcome of the reaction (Table 6.2, entries 3-4). This is in agreement with reported results on the effect of CO_2 pressure on reaction rates in the biphasic IL/CO_2 reaction systems.[235] Therefore, a study on the effect of CO_2 pressure on the telomerization reaction was conducted at constant loading of ionic liquid, substrate and catalyst while varying CO_2 pressure. As shown in Figure 6.8. the yield toward δ-lactone decreases with increasing CO_2 pressure while the selectivity on the telomerization is maintained. This observation is concomitant with reports on CO_2 dissolution in the IL-phase thus leading to a dramatical decrease in catalyst and reactants concentration thereby affecting the conversion.

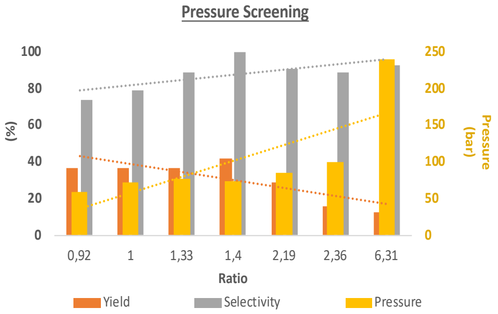


Figure 6.8. *Effect of the ratio CO_2/1,3-btadiene on the telomerization reaction in a biphasic catalytic system*

---

[235] A. Ahosseini, W. Ren, A. M. Scurto, *Ind. Eng. Chem. Res.* **2009**, *48*, 4254-4265

However, increasing CO_2 pressure up to a certain value, increases the conversion and selectivity toward δ-lactone (Figure 6.8.). Indeed, looking at the conversion and selectivity as function of CO_2 pressure, "optimum reaction conditions" for the telomerization reaction were extracted (Figure 6.9.). After this optimum value (PCO_2 = 74 bar, 1.4 molar ratio CO_2/1,3-butadiene), an increase of CO_2 pressure causes a decrease in conversion which can be explained by a lower content of catalyst and reactants in the IL phase due to a higher solubility of CO_2 in the IL-phase.

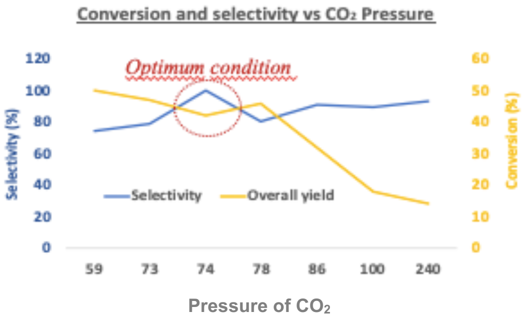
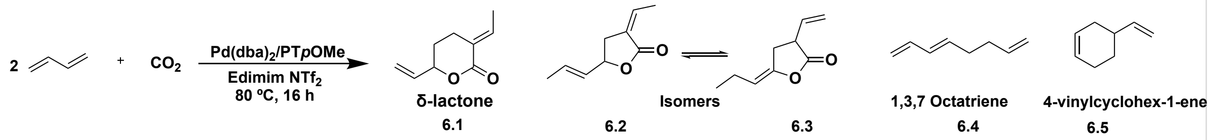


Figure 6.9. *Effect of PCO_2 on the conversion and selectivity of the telomerization reaction*

Next, the telomerization reaction was carried out at a constant pressure of carbon dioxide (~80 bar) while varying the ionic liquid amount, the molar ratio CO_2/1,3-butadiene and the reaction time. Table 6.3 reveals that by increasing the molar ratio CO_2/1,3-butadiene, there is a decrease in the overall yield of the reaction which confirmed the results above (Table 6.3., entries 1, 2, 3). The amount of ionic liquid (Table 6.3, entries 1-2, 1, 3) nor does the reaction time (Table 6.3, entries 3-4) significantly affect the reaction outcome. We can therefore conclude that the telomerization reaction is mostly dependent on the molar ratio CO_2/1,3-butadiene.

Table 6.3. Evaluation of the ILs amount, time reaction and CO_2/1,3 butadiene ratio at same PCO_2



Entry	IL	Ratio CO_2/1,3 But	P (bar)	Time (h)	Overall yield[c] (%)	6.1 Yield (%)	6.2+6.3 Yield (%)	6.4 Yield (%)	6.5 Yield (%)	Sel. (%)
1	2 mL	1.4	74	2	42	35[b] 42[c]	0	0[b] (0) [c]	0	100
2	1 mL	1.34	86	2	43	38[b]	5[b]	0	0	93
3	2 mL	1.71	86	2	35	31[b]	4	0	0	95
4	1 mL	2.19	82	16	32	29[b]	3	0	0	91

[a] General Conditions: Phosphine: 3 equiv of $[Pd(dba)_2]$; 1,3 butadiene ~ 2 g (0,037 mol); (x mol) of CO_2, IL: 2 mL, T= 80 ºC, 16 h. [b] Yields were determined after purification by column chromatography. [c] Results obtained from GC analysis with diglyme as internal standard.

From these experiments, the reaction conditions that give δ-lactone with high yield and selectivity in the telomerization reaction of 1,3 butadiene and CO_2 are at a pressure of CO_2 comprises between 74 < PCO_2 < 86 bar and a molar ratio CO_2/1,3-butadiene between 1,33 < r < 1,5. However the yield of the reaction seems to be blocked at a value of 42% conversion in 2h. For a better understanding of the telomerization reaction, we examined the pressure-time profile of the reaction. As shown in Figure 6.10. the reaction initially exhibits a steep drop in pressure but after ~ 2 h, a constant pressure is maintained. Thus, we assume a deactivation of the organometallic complex overtime.

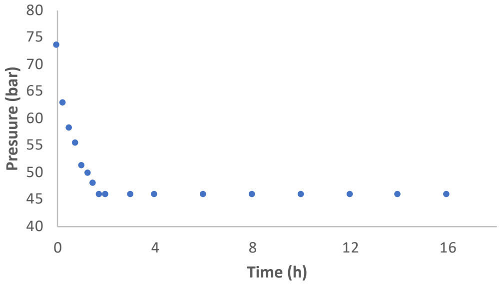
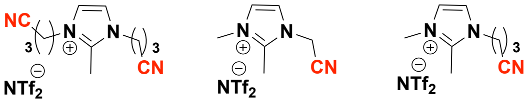


Figure 6.10. *Telomerization reaction profile at 74 bar initial total pressure*

In an attempt to improve the δ-lactone yield of the telomerization reaction in this biphasic catalytic system, synthesis of ionic liquid bearing nitrile group was envisioned (Figure 6.11.). Indeed, Studies on the catalytic cycle of this reaction have established acetonitrile as the best solvent regarding yield and selectivity. This is due to a so-called "nitrile effect" where unstable but active catalytic intermediates are stabilized through interaction of the nitrile pendant group with the metal center.[236] These task specific ILs are expected to interact with Pd-active intermediates and thus improve their stability.



6.14 **6.15** **6.16**

Figure 6.11. *Nitrile functionalized ILs synthesized*

6.4.3.3 Telomerization reaction in a biphasic system catalysis using "task-specific" ILs

a. Task specific ionic liquids synthesis

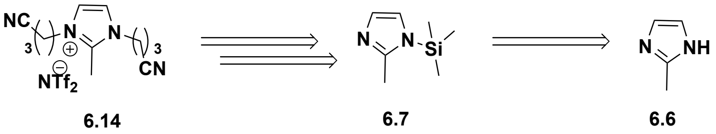
In this Pd-catalyzed telomerization reaction, the ionic liquid used as reaction media is an imidazolium-based ionic liquid substituted at C2 position. Thus, nitrile-functionalized ILs substituted at C2 position (single-armed as well as double-armed) were prepared with modifications of literature procedures for the synthesis of the related 1-alkyl-3-methylimidazolium salts.[237]

---

[236] A. Behr, M. Becker, *Dalton Trans.,* **2006**, 4607-4613

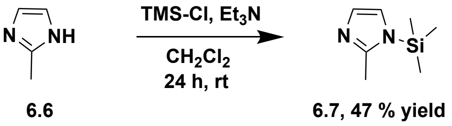
[237] a) Q. Zhang, Z. Li, J. Zhang, S. Zhang, L. Zhu, J. Yang, X. Zhang, Y. Deng, *J. Phys. Chem. B.* **2007**, 111, 2864-2872; b) T. K. Carlisle, J. E. Bara, C. J. Gabriel, R. D. Noble, D. L. Gin, *Ind. Eng. Chem. Res.* **2008**, 47, No. 18, 8496-8498; c) T. Alammar, A. V. Mudring, *ChemsusChem* **2011**, 4, 1796-1804

1,3-Bis(3-cyanopropyl)-2-methylimidazoliumbis(trifluoro- methyl sulfonyl) imide **6.14** was prepared in 3 steps from 2-methylimidazole **6.6** (Scheme 6.12.).



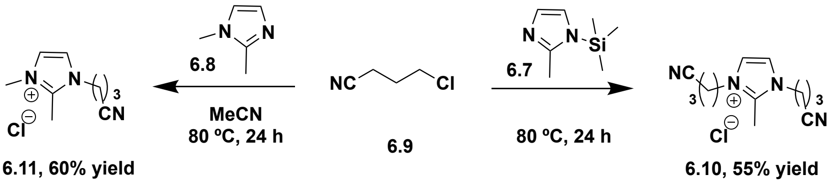
Scheme 6.12. *Retrosynthetic scheme for **6.14** synthesis, NTf₂: bis(trifluoromethane)sulfonimide*

Compound **6.7** was prepared on a 0.12 mol scale by mixing equimolar amounts of trimethyl silyl chloride and 2-methylimidazole **6.6** in the presence of excess triethylamine.[238] The reaction mixture was stirred at room temperature until the reaction was complete as determined by ^{1}HNMR. The product purified by distillation was obtained in 47 % yield as a colorless liquid which is subsequently used in the next step (Scheme 6.13.).



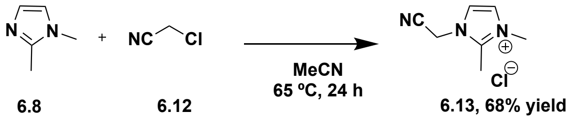
Scheme 6.13. *Synthesis of the precursor of N,N-bisfunctionalized-imidazolium salts*

The next step was a quaternization reaction providing the corresponding imidazolium halides. Thus, reactions of **6.7** and 1,2 dimethyl imidazole **6.8** with 4-chlorobutyronitrile **6.9** were respectively carried out at 80 °C during 24 h. Compounds **6.10** was obtained as a light brown solid in 55 % yield and compound **6.11** as a white solid in 60 % yield (Scheme 6.14.).



Scheme 6.14. *Quaternization step to the imidazolium halides*

1-Cyanomethyl 2,3-dimethyl imidazolium chloride **6.13** was obtained as a light-yellow powder in 68 % yield following the same procedure with chloroacetontrile **6.12** at 65 °C for 24 h (Scheme 6.15.).

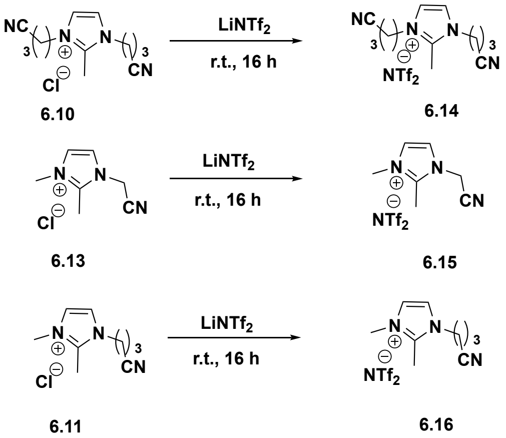


Scheme 6.15. *Nitrile functionalized imidazolium salt synthesis*

---

[238] A. F. Jayzeng, G. N. Lypka, R. E. Wasylishen, *Can. J. Chem.* **1980**, 58, 60-64

The nitrile functionalized ILs with NTf_2 as anions **6.14-6.16** were obtained in quantitative yield *via* anion metathesis reaction (Scheme 6.16.). After synthesis, they were washed several times with deionized water in order to remove the lithium chloride formed during the anion exchange reaction. In addition, a silver nitrate test for residual halides was performed on the aqueous phase until no formation of AgCl precipitate was observed.[239]

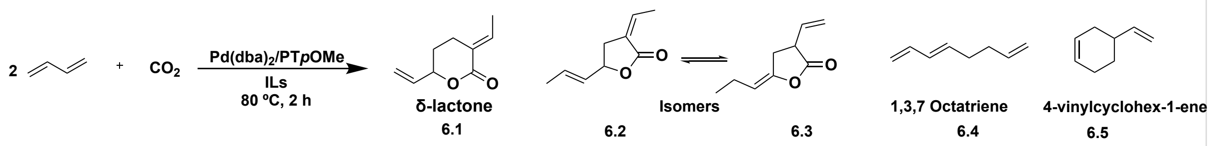


Scheme 6.16. *Anion exchange step*

b. Application of the task specific ionic liquids in the telomerization reaction

The nitrile functionalized ionic liquids were tested as reaction media in the telomerization reaction of 1,3-butadiene with CO_2. The procedure described above was followed and the results summarized in Table 6.4.

Table 6.4. Nitrile functionalized ILs applied in the Telomerization reaction



Entry	IL	Ratio CO_2/1,3 But	P (bar)	Overall yield[c] (%)	6.1 Yield (%)	6.2+6.3 Yield (%)	6.4 Yield (%)	6.5 Yield (%)	Sel. (%)
1	$EdimimNTf_2$	1.4	74	42	35[b] 42[c]	0	0[b] (0) [c]	0	100
2	**6.15**	1.61	86	-	-	-	-	-	-
3	**6.16**	2.1	95	25	13[b] (16)[c]	9[b] (9)[c]	0	0	64
4	**6.14**	1.4	90	32	6[b] (7)[c]	1[b] (<1)[c]	0	0	86

[a] General Conditions: Phosphine: 3 equiv of $[Pd(dba)_2]$; 1,3 butadiene ~ 2 g (0,037 mol); (x mol) of CO_2, IL: 2 mL, T= 80 ºC, 2 h. [b] Yields were determined after purification by column chromatography. [c] Results obtained from GC analysis with diglyme as internal standard.

The incorporation of a nitrile functionality to the ILs was expected to prevent the catalyst deactivation. However, as illustrates in table 6.4, the telomerization did not proceed in these nitrile functionalized ILs. NC-C_1dmim NTf_2 **6.15** is a solid at room temperature and

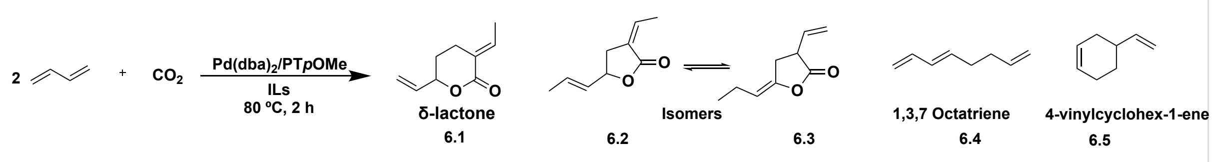
---

[239] T. V. Hoogerstraete, S. Jamar, S. Wellens, K. Binnemans, *Anal. Chem.* **2014**, 86, 3931-3938

becomes a sticky oil at 80 ºC where no stirring of the reaction mixture was observed (Table 6.4., entry 2). The high viscosity of the double armed nitrile functionalized IL **6.14** is accountable for a reduced mass transfer and thus lower reaction rate (Table 6.4., entry 4). It has been noticed before that an intensive stirring is important for the reactants to be converted. In the case of NC-C_3dmim NTf_2 **6.16**, δ-lactone is obtained in low yield (13%) and precipitation of Pd-black was observed (Table 6.4., entry 3).

To avoid the viscosity problem while taking advantage of the nitrile functionalized ILs ability to stabilize the Pd-actives species, the telomerization reaction was carried out by mixing non-functionalized and nitrile functionalized ILs. The data collected in Table 6.5. show that by mixing ILs, there is an improvement in catalyst activity. Also, a reduced amount of Pd-black is noted. However, a high decrease in selectivity is also observed (Table 6.5., entries 2-3).

Table 6.5. Mixing ILs in the Telomerization reaction



Entry	IL	Ratio CO_2/1,3 But	P (bar)	Overall yield[c] (%)	6.1 Yield (%)	6.2+6.3 Yield (%)	6.4 Yield (%)	6.5 Yield (%)	Sel. (%)
1	EdimimNTf_2	1.4	74	42	35[b] 42[c]	0	0[b] (0) [c]	0	100
2	EdimimNTf_2/**6.8**	1.66	80	47	25[c]	15[c]	7[c]	0[c]	53
3	EdimimNTf_2/**6.6**	1.75	78	5	3[c]	0[c]	0[c]	0[c]	60

[a] General Conditions: Phosphine: 3 equiv of Pd(dba)$_2$; 1,3 butadiene ~ 2 g (0,037 mol); (x mol) of CO_2, IL: 2 mL, T= 80 ºC, 2 h. [b] Yields were determined after purification by column chromatography. [c] Results obtained from GC analysis with diglyme as internal standard.

In view of the results obtained, we can conclude that the telomerization reaction of 1,3-butadiene and CO_2 is possible in a biphasic system consisting of Edimim NTf_2 and supercritical CO_2. Moreover, optimum reactions conditions to perform this reaction with 100% selectivity toward the desired lactone were found. In addition, ionic liquids bearing nitrile group were synthesized and employed with Edimim NTf_2 in the telomerization reaction. By mixing ionic liquids, higher overall yield was obtained however the selectivity toward δ-lactone decreased.

6.4.3.4 Realization of a continuous reaction system for supercritical fluid processing

a. δ-lactone phase behavior study in compressed carbon dioxide

At this stage and due to limited time, we focused our efforts on the concept of continuous equilibrium displacement where δ-lactone will be extracted from the IL phase by scCO_2. Therefore, the miscibility of δ-lactone in CO_2 was checked in a window autoclave by increasing the pressure of CO_2 at a fixed amount of 1,3-butadiene and temperature.

In this study, visual monitoring revealed 3 different stages. The first stage was a two-phase system where δ-lactone (liquid phase) is in contact with the gas phase (CO_2) at moderate pressure and 1,3-butadiene. Next, by increasing the pressure of CO_2, a dissolution of the gas into the liquid phase takes place (Figure 6.11.a). Further increasing of CO_2's pressure resulted in more gas dissolved causing a volumetric expansion of the liquid phase (Figure 6.11.b). Thus, this stage is named the expanded liquid phase. By continuing to increase CO_2's pressure, the density of the gas and liquid phase became more and more similar. When both phases had equal density and compositions, the mixture critical point is reached, and a single supercritical phase is formed (Figure 6.11.c).

c. Two phase system

b. Expanded liquid phase

a. Single supercritical phase

Figure 6.11. *Phase behavior of δ-lactone (0,5 g) with 1,3-butadiene (2 g) with increasing pressure of CO_2 at 80 ºC as observed in a 10 mL high-pressure autoclave*

A total system pressure of 200 bar at 80 ºC was established as an entry value for continuous process application.

b. Realization of a continuous flow extraction system with $scCO_2$

The aim of this studies was to prove that the homogeneous Pd-catalyzed telomerization of 1,3-butadiene and CO_2 can be performed in ILs followed by a continuous-flow extraction of the product with $scCO_2$. Therefore, the catalyst-containing IL phase which remains in the vessel can be reused without addition of further catalyst or ILs.

The continuous experiments were performed in a window autoclave with a magnetic stirrer bar initially charged with a mixture of IL, $[Pd(dba)_2]$ and tris-(o-methoxyphenyl)-phosphine (TOMPP). The autoclave was then connected to the continuous CO_2 flow system through a dip tube, charged with 1,3-butadiene, heated to the working temperature and charged with CO_2 at the desired pressure. After 16 hours, the extraction process was run through an automated control system to ensure maximum safety. The flow scheme in Figure 6.12. illustrates the setup realized in the pilot plant hall of the ITMC.

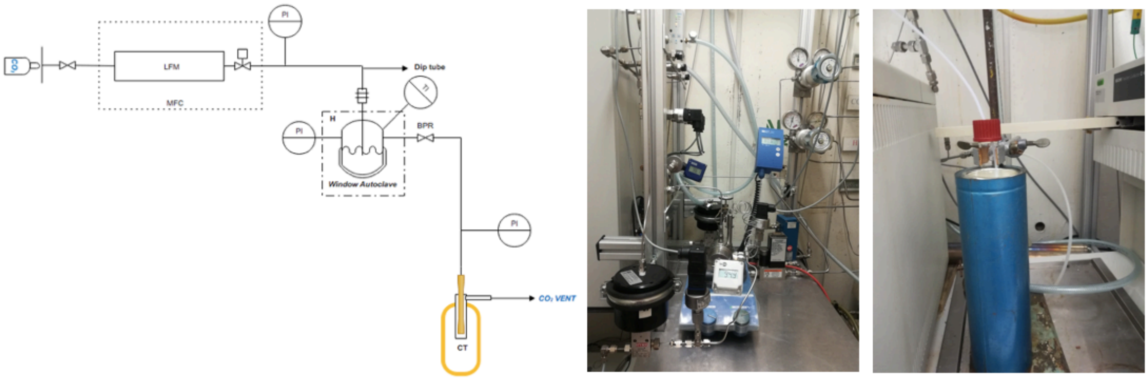


Figure 6.12. *Simplified flow scheme of the continuous extraction setup of δ-lactone, LFM = liquid flow meter, MFC= mass flow controller, PI= pressure indicator, TI= temperature indicator, H= heater, BPR= back pressure controller, CT= cooling trap*

The 1st extraction process was run from 80 to 200 bar for 1 hour. A light-yellow solution was recovered from the trap and analyzed by ^{1}HNMR. No contamination by the IL or metal catalyst was observed and δ-lactone was obtained with a selectivity of 85 %. The catalytic system was then depressurized, charged with 1,3-butadiene, heated to the desired temperature and charged with CO_2 for 48 hours. After 48 hours, the extraction was run for 3 hours to ensure complete extraction of the organic products. A slightly drop-in selectivity is observed, and IL is extracted with the product. The presence of the IL in this 2nd extract is explained by a poor control of the opening of the valve from which the product is released.

6.5 Conclusions

From the study described in this chapter, the following conclusions can be extracted:

(i) The telomerization reaction of 1,3 butadiene and CO_2 was possible in a biphasic catalytic system consisting of ionic liquid (C_2dmim NTf_2) and supercritical CO_2. The optimum conditions to perform this reaction with 100 % selectivity toward the desired δ-lactone were $74 < PCO_2 < 86$ bar and a molar ratio CO_2/1,3 butadiene between $1,33 < r < 1,5$

(ii) Nitrile functionalized ionic liquids were synthesized to be employed as reaction media and "stabilizer" of Pd-active species.

(iii) Promising results were obtained by mixing non-functionalized and functionalized ILs; however this system still needs improvement to obtain δ-lactone with high selectivity.

(iv) A total system pressure of 200 bar have been established to obtain a homogeneous supercritical phase that contained the desired product.

(v) The telomerization reaction of 1,3-butadiene and carbon dioxide with extraction of δ-lactone in a continuous-flow manner was performed. It resulted in an extraction of δ-lactone with a selectivity of 85 % without contamination by the IL and metal catalyst.

6.6 Experimental part

General considerations

All operations were carried out using Schlenk tubes or in a glovebox under inert atmosphere. Glassware was cleaned with acetone, consecutive immersion in ^{iso}propanol with KOH and aqueous HCl, and rinsing with deionized water. Pentane, DCM and toluene were purified by distillation and passing over activated alumina with argon in a centralized solvent purification system at the ITMC. Et_2O and THF were stored on KOH, distilled under argon and stored on dried molecular sieves 4Å. EtOH, MeOH and MeCN were distilled under argon and stored on dried molecular sieves 3A. Deionized water was taken from reverse -osmotic purification system (WERNER EASYPure II) and degassed by bubbling argon with a frit for 1 h. The chemicals were purchased in analytic quality from Iolitec, SigmaAldrich, AlfaAesar and AcrosOrganics and used as received. Functionalized ionic liquids **6.14-6.16**, were prepared with modifications of the reported procedures.[244]

Solution Nuclear Magnetic Resonance (NMR). ^{1}H and ^{13}C NMR spectra were recorded using a BRUCKER AV-600 MHz, AV-400 MHz or DPX-300 MHz spectrometers. Chemical shift values(δ) are reported in ppm relative to TMS (^{1}H and ^{13}C{^{1}H}) and coupling constants are reported in Hertz.

Gas Chromatography (GC-MS). GC analyses were performed on Agilent 7890A (column: Agilent 19091J-43; 325°C: 30m * 320 µm * 0.25 µm) using method: 50°C-260 °C-320 ºC.[240]

General procedure for the telomerization reaction

$Pd(dba)_2$ and ligand TOMPP were mixed in a Schlenk flask in dry MeCN (or dry MeCN and the corresponding ionic liquid) under argon for 40 mins. A 10 mL stainless steel window autoclave under argon was charged with the orange solution then, evacuated (to remove completely MeCN in the case the reaction is performed in the ionic liquid). The autoclave was weighted then, cooled to 0ºC using an ice bath and 1,3-butadiene was transferred from the bottle through a 3 ways valve into the autoclave. The amount of 1,3-butadiene was controlled by weighting again the autoclave at r.t. (in case the amount of 1,3-butadiene was superior to 2 g, the excess was evacuated at r.t.). CO_2 was then charged, the autoclave was weighted and heated for 16 h at 80 ºC. After completion, the

---

[240] T. Sakura, K. Kohno, *Chem. Commun.* **2009**, 1312-1330

autoclave was cooled to 0 ºC to release the remaining gases. A sample of the crude mixture was taken for GC and NMR analysis. Using ethyl acetate, the crude mixture was transferred to a weighted round bottom flask and the solvent was evaporated via a rotavapor. The amount weighted is used to calculate the overall yield of the reaction. The crude mixture is then purified by silica gel chromatography to yield a light-yellow oil. The yield of the δ-lactone was calculated based on the limited reactant.

Synthesis of the functionalized ionic liquids

Synthesis of 6.10

To a solution of 1,2-dimethylimidazolium **6.8** (8 g, 1.0 eq) in CH_3CN (1 mol.L^{-1}) at 80 ºC, $Cl(CH_2)_3CN$ **6.9** (8.7 mL, 1.1 eq) was added and the reaction was stirred for 24 h. The solvent was removed by rotary evaporation and the resulting viscous liquid was purified by recrystallization from ACN/Et_2O until the filtrate exiting the frit was colorless. After dried in a vacuum for 5 h, the product was obtained as a light brown solid (9.11 g, 55 %). ^{1}HNMR (300 MHz, CD_3CN) δ 7.50 (d, *J* = 2.1 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 4.29 - 4.16 (m, 2H), 3.73 (s, 3H), 2.60 - 2.50 (m, 5H), 2.12 (p, *J* = 7.3 Hz, 2H). Peaks are in agreement with report in the literature.[244]

Synthesis of 6.11

A mixture of 2-methylimidazolium **6.8** (10 g, 1.0 eq) and $Cl(CH_2)_3CN$ **6.9** (6.8 mL, 1.1 eq) was stirred at 90ºC for 24 h. The resulting brown solid was successively washed with diethyl ether (3 x 30 mL) and cold dichloromethane (30 mL). The product was obtained as a white solid which was dried in a vacuum for 16h (10.4 g, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 10.8, 2.1 Hz, 2H), 4.04 (t, *J* = 7.5 Hz, 2H), 3.79 (s, 3H), 2.60 (s, 3H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.66 (s, 3H), 1.37 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). Peaks are in agreement with report in the literature.[244]

Synthesis of 6.13

To a solution of 1,2-dimethylimidazolium **6.8** (8 g, 1.0 eq) in CH_3CN (1 mol.L^{-1}) at 65 ºC, chloroacetonitrile **6.12** (5.79 mL, 1.1 eq) was added and the reaction was stirred for 24 h. The resulting yellow powder was purified by recrystallization from ACN/Et_2O until the filtrate exiting the frit was colorless. After dried in a vacuum for 5 h, the product was obtained as a light yellow solid. Yield: 9.75 g, 68 %, MW: 171.63. ^{1}H NMR (300 MHz, CD_3CN) δ 7.82 (d, *J* = 2.2 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 5.71 (s, 2H), 3.74 (s, 3H), 2.66 (s, 3H). Peaks are in agreement with report in the literature.[244]

Typical procedure for the Synthesis of bis(trifluoromethanesulfonylimide)imide ILs

To a solution of the respective halide salt (1.0 eq) in deionized water (1mol.L^{-1}), $LiNTf_2$ (1.2 eq) was added under vigorous stirring at room temperature. After mixing 16 h (**6.10,**

6.11, 6.13) and 72 h (**Edimim Cl**), two phases were formed: the bottom phase was the bis(trifluoromethanesulfonylimide)imide IL and the top phase an aqueous solution of LiCl. After decanting, the bottom phase was dissolved with distilled EtOAc and washed several times with deionized water until a test with $AgNO_3$ for residual halide was negative (lack of AgBr or AgCl precipitate formation).[246] The remaining product was dried under high vacuum at 100ºC overnight to afford compounds **6.15** as a white solid; **6.14**, **6.16** and **Edimim NTf$_2$** as clear to pale yellow/brown oil.

Synthesis of 6.14

The product was obtained as an hydrophobic brown liquid at room temperature (5 g, 90 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.71 (s, 2H), 4.18 (t, *J* = 7.1 Hz, 4H), 2.63 (s, 3H), 2.59 (t, *J* = 7.3 Hz, 4H), 2.07 (p, *J* = 7.2 Hz, 4H). Peaks are in agreement with report in the literature.[244]

Synthesis of 6.15

The product was obtained as an hydrophobic brown liquid at room temperature (8.5 g, 72 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.65 (d, *J* = 2.1 Hz, 1H), 7.63 (d, *J* = 2.1 Hz, 1H), 4.17 (t, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 2.63 – 2.53 (m, 5H), 2.06 (p, *J* = 7.3 Hz, 2H). Peaks are in agreement with report in the literature.[244]

Synthesis of 6.16

The product was obtained as a white powder liquid at room temperature (10.4 g, 79 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.72 (d, *J* = 2.1 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 5.55 (s, 2H), 3.75 (s, 3H), 2.63 (s, 3H). Peaks are in agreement with report in the literature.[244]

Synthesis of Edimim NTf$_2$

The product was obtained as an hydrophobic pale yellow liquid at room temperature (7.0 g, 93 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 7.65 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 4.13 (q, *J* = 7.3 Hz, 2H), 3.74 (s, 3H). Peaks are in agreement with report in the literature.[244]

Chapter 7

“General Conclusions”

From the study of pyrene-tagged imidazolium carboxylate supported onto carbon materials carried out in Chapter 3, the following conclusions were extracted:

i) The synthesis of the pyrene-tagged imidazolium salts 3.- successfully completed.

ii) The corresponding pyrene-tagged imidazolium carboxylates **3.32a/3.32b** were synthesized in excellent yields.

iii) The pyrene-tagged imidazolium organocatalyst were applied in the homogeneous cycloaddition reaction of 1-hexene oxide. **3.32b** gives similar results than the classic imidazolium carboxylate adduct in term of activity in comparison to its analogue **3.32a**. Therefore, a clear effect of the linker length between the active site and the pyrene moiety was revealed to affect the activity of the resulting organocatalyst.

iv) The pyrene-tagged imidazolium carboxylate **3.32b** was successfully immobilized onto MWCNTs, rGO and CBs using EtOAc as solvent under mild conditions to afford the heterogenized catalysts **3.32a@MWCNTs**, **3.32a@rGO**, **3.32a@CBs**.

v) **3.32a@MWCNTs**, **3.32a@rGO**, **3.32a@CBs** were used in the cycloaddition reaction in batch. They proved to be effectives in the cycloaddition reaction.

vi) Recycling experiments with these hybrid materials were perform in a batch mode. The catalyst activity of **3.32a@MWCNTs** drop in the second run due to catalyst leaching. Less leaching was observed in the case of **3.32a@rGO** and **3.32a@CBs**. Among the heterogenized organocatalysts, **3.32a@rGO** hybrid material provided the best performance in term of robustness (recycle up to 5 runs).

vii) The heterogenized organocatalysts **3.32a@rGO** was successfully applied in the cycloaddition reaction of various epoxides under mild conditions (80 ºC, 5 h, 1 MPa of CO_2).

From the study of NHC-silver(I) complex applied to the incorporation of carbon dioxide into *o*-alkynylanilines for the synthesis of benzoxazine-2-ones derivatives described in Chapter 4, the following conclusion can be extracted:

i) The synthesis of the pyrene-tagged NHC-silver(I) salts **4.9** was successfully completed.

ii) The pyrene-tagged NHC-silver(I) and the non-pyrene-tagged NHC(I) silver complexes were evaluated in the synthesis of benzoxazine-2-ones under neat and mild reaction conditions. Similar results than those reported using a base (DABCO) and Ag(OAc) was obtained thus, we conclude that NHC-silver catalysts can successfully be applied to this reaction and that the pyrene moiety has no effect in the performance of the catalyst.

iii) The pyrene-tagged silver(I) complex **4.9** was successfully immobilized onto reduced graphene oxide using tetrahydrofuran as a solvent.

iv) The Ag-catalyzed the incorporation of carbon dioxide into *o*-ethynylaniline provided no conversion under neat conditions. By adding solvent and increasing the temperature, moderate yields were obtained.

v) Preliminary study on the recycling of the hybrid materials **4.10@rGO** in batch showed that the catalyst can be successfully recycled once. From the 3rd run on words, a rapid drop in activity is observed.

From the study in the copolymerization reaction of ethylene and methyl acrylate to yield functionalized polyolefins described in Chapter 5, the following conclusion can be extracted:

i) The synthesis of four pyrene-tagged α-diimine ligands were completed in good yields (55%-67%).

ii) Their corresponding neutral and monocationic Pd-complexes with pyrene-tagged ligands were successfully synthesized.

iii) The monocationic pyrene-tagged Pd-catalysts were successfully applied in the copolymerization of ethylene and methyl acrylate under mild reactions reaction conditions of temperature (35 ºC) and ethylene pressure (2.5 bar). Surprisingly, functionalized polyolefins with polar units into the main chain were obtained when TFE was the solvent. A mixture of units into the main chain and at the branch terminus were also observed with prevalence depending on the ligand's backbone and substitutions on the N-aryls *ortho*-position. When CH_2Cl_2 was the solvent, the four monocationic Pd-catalysts gave functionalized copolymers with units only at the end of the branches in agreement with previous reports on Brookhart type α-diimine Pd-catalysts.

iv) Depending on the solvent used in catalysis, the productivity of the Pd-catalysts is different, again, depending on the ligand's backbone and substitutions on the N-aryls *ortho*-position.

v) Attempted synthesis of two pyrene-tagged α-diimine ligands having a shorter spacer in between the pyrene and hydroxyl are presented.

vi) The synthesis of α-diimine ligands presenting a methoxy group at the N-aryls *para*-position is described.

From the study of the biphasic catalytic system consisting of ionic liquid and supercritical CO_2 to perform the telomerization reaction of 1,3 butadiene and CO_2 described in Chapter 5, the following conclusion can be extracted:

i) The telomerization reaction of 1,3 butadiene and CO_2 is possible in a biphasic catalytic system consisting of ionic liquid (C_2dmim NTf_2) and supercritical CO_2. The optimum condition to perform this reaction with 100 % selectivity toward the desired δ-lactone are $74 < PCO_2 < 86$ bar and a molar ratio CO_2/1,3 butadiene between 1,33 < r < 1,5

ii) Nitrile Functionalized ionic liquids were synthesized to be employed as reaction media and “stabilizer” of pd-active species.

iii) Promising results were obtained by mixing non-functionalized and functionalized ILs however, this system still needs improvement to obtain δ-lactone with high selectivity.

iv) A total system pressure of 200 bar have been established to obtain a homogeneous supercritical phase that contained the desired product.

v) The telomerization reaction of 1,3-butadiene and carbon dioxide with extraction of δ-lactone in a continuous-flow manner was performed. It resulted in an extraction of δ-lactone with a selectivity of 85 % without contamination by the IL and metal catalyst.

APPENDIX

Publications and patents

“Cooperative NHC-based Catalytic System Immobilised onto Carbon Materials for the Cycloaddition of CO_2 to Epoxides” M. Y. Souleymanou, F. El-Ouahabi, A. M. Masdeu-Bultò, C. Godard *Manuscript submitted*

“Cycloaddition of CO_2 using natural products as Catalysts” M. Y. Souleymanou, M. B. Yeamin, M. Reguero, C. Claver, C. Godard, A. M. Masdeu-Bultò *Review article under preparation*

“Catalysts for Olefin and Polar Monomers Copolymerization and Olefin Polymerization” C. Godard, M. Y. Souleymanou, B. Milani, A. Dall'Anese. *Patent submitted*

Conferences and Scientific Meetings

M. Y. Souleymanou, A. M. Masdeu-Bultó, C. Godard, C. Claver **“Heterogenization of new N-Heterocyclic Carbene ligands with Pyrene tags for the production of Fine Chemicals using Carbon Dioxide as a Reagent”** XXXIV Congress of the Organometallic Chemistry Specialized Group of the Real Sociedad Española de Química, Girona, Spain, September **2016**. Poster communication

M. Y. Souleymanou, A. M. Masdeu-Bultó, C. Godard, C. Claver **“Catalytic Conversion of Carbon Dioxide using New Immobilized N-Heterocyclic Carbene based Catalysts”** 1st Trans Pyrenean Meeting in Catalysis, Toulouse, France, October **2016**. Poster communication

M. Y. Souleymanou, A. M. Masdeu-Bultó, C. Godard, C. Claver **“Enabling CO_2 re-use for the Production of Organic Cyclic Carbonates”** 3rd EuCheMS Congress on Green and Sustainable Chemistry, York, United Kingdom, September **2017**. Poster communication

M. Y. Souleymanou, A. M. Masdeu-Bultó, C. Godard, G. Francio, W. Leitner **“δ-Lactone Production in Two-phase Catalysis with In-Situ Extraction”** 21st International Symposium on Homogeneous Catalysis ISHC XXI, Amsterdam, Netherlands, July **2018**. Poster communication

M. Y. Souleymanou, A. M. Masdeu-Bultó, C. Godard, C. Claver **“Enabling CO_2 re-use for the Production of Organic Cyclic Carbonates”** 11th CarLa Winter School, Heidelberg, Germany, February **2018**. Flash and Poster communication

M. Y. Souleymanou, A. M. Masdeu-Bultó, C. Godard, G. Francio, W. Leitner **“δ-Lactone Production in Two-phase Catalysis with In-Situ Extraction”** 2nd Trans Pyrenean Meeting in Catalysis, Tarragona, Spain, October **2018**. Poster communication

UNIVERSITAT
ROVIRA i VIRGILI