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Kinetic and mechanistic studies on the transformation of
carbon dioxide by molecular catalysts.

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A mes parents,

A ma famille,

A mes amis,

A tous les gens que j'aime,

This is a breathtaking pace, and such a pace cannot help but create new ills as it dispels old, new ignorance, new problems, new dangers. [...]

We choose to go to the moon. We choose to go to the moon in this decade and do the other things, not because they are easy, but because they are hard, because that goal will serve to organize and measure the best of our energies and skills, because that challenge is one that we are willing to accept, one we are unwilling to postpone, and one which we intend to win, and the others, too. [...]

Many years ago the great British explorer George Mallory, who was to die on Mount Everest, was asked why did he want to climb it. He said, "Because it is there." Well, space is there, and we're going to climb it, and the moon and the planets are there, and new hopes for knowledge and peace are there.

John F. Kennedy, Address at Rice University on the Nation's Space Effort – September 12th, 1962

I don't want to demystify the events that take place [...]. But it is, by far, the "truest" book I've written, in terms of the majority of events that happened. It's up to each reader to decide how much [...] actually occurred.

*Brest Easton Ellis – Interview about **Lunar Park***

The truth is that I never really thought we'd make it

Here we are

Lene Marlin – Here we are

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Abbreviations

| | |
|-----------------|---|
| ARS | asymmetric ring stretching |
| CO ₂ | carbon dioxide |
| COD | 1,5- <i>cis</i> -cyclooctadiene |
| DABCO | 1,4-diazabicyclo[2.2.2]octane |
| dcpe | di-cyclohexylphosphino ethane |
| DMAP | 4-(dimethylamino)-pyridine |
| DMC | dimethyl carbonate |
| DPC | diphenyl carbonate |
| dtbpe | di- <i>tert</i> -butylphosphino ethane |
| EC | ethylene carbonate |
| FAB | fast atom bombardment |
| GC | gas chromatography |
| Gt | gigaton |
| IR | infrared |
| MS | mass spectroscopy |
| NMR | nuclear magnetic resonance |
| PO | propylene oxide |
| PC | propylene carbonate |
| ppm | parts per million |
| TBAB | tetra- <i>n</i> -butylammonium bromide |
| TBAC | tetra- <i>n</i> -butylammonium chloride |
| TBAI | tetra- <i>n</i> -butylammonium iodide |
| TBD | triazabicyclodecene |
| TOF | turn over frequency |

Index

| | | |
|----------|---|-----------|
| 1 | INTRODUCTION..... | 1 |
| 1.1 | GENERALITIES ABOUT CARBON DIOXIDE | 1 |
| 1.1.1 | <i>CO₂ in the atmosphere</i> | <i>1</i> |
| 1.2 | INDUSTRIAL REACTIONS INVOLVING CO ₂ | 3 |
| 1.3 | CHEMICALS PROPERTIES OF CARBON DIOXIDE | 5 |
| 1.4 | REACTIVITY OF CO ₂ WITH TRANSITION METALS | 7 |
| 1.4.1 | <i>Activation of CO₂ by transition metals</i> | <i>7</i> |
| 1.4.2 | <i>Insertion of CO₂ into M-L bond.....</i> | <i>10</i> |
| 1.5 | THE FORMATION OF CARBONATES FROM CO ₂ | 12 |
| 1.6 | OBJECTIVES OF THIS WORK | 15 |
| 2 | FORMATION OF PROPYLENE CARBONATE FROM PROPYLENE OXIDE AND CARBON DIOXIDE WITH METAL HALIDES UNDER MILD CONDITIONS | 17 |
| 2.1 | INTRODUCTION | 17 |
| 2.2 | SCREENING OF CATALYSTS AND CO-CATALYSTS | 19 |
| 2.2.1 | <i>Screening of metals halides</i> | <i>19</i> |
| 2.2.2 | <i>Screening of nucleophiles.....</i> | <i>21</i> |
| 2.3 | BEHAVIOR AT MILD CONDITIONS AND WITH OTHER EPOXIDES..... | 22 |
| 2.3.1 | <i>Behavior at low pressure and room temperature.....</i> | <i>22</i> |
| 2.3.2 | <i>Reaction with other epoxides.....</i> | <i>23</i> |
| 2.4 | INFLUENCE OF DIFFERENT PARAMETERS ON THE FORMATION OF PROPYLENE CARBONATE | 25 |
| 2.4.1 | <i>Influence of carbon dioxide pressure</i> | <i>25</i> |
| 2.4.2 | <i>Influence of the concentration of NbCl₅.....</i> | <i>26</i> |
| 2.4.3 | <i>Influence of the concentration of DMAP.....</i> | <i>27</i> |
| 2.5 | CONCLUSION | 29 |
| 3 | MECHANISTIC STUDY ON THE FORMATION OF PROPYLENE CARBONATE FROM PROPYLENE OXIDE AND CARBON DIOXIDE USING THE CATALYTIC SYSTEM NBCL₅/DMAP | 31 |
| 3.1 | INTRODUCTION | 31 |
| 3.2 | DESCRIPTION OF THE OBSERVATIONS | 33 |
| 3.2.1 | <i>Observations with a 1:1 NbCl₅:DMAP ratio.....</i> | <i>33</i> |
| 3.2.2 | <i>Observations with a 1.5:1 NbCl₅:DMAP ratio.....</i> | <i>35</i> |
| 3.3 | STUDY OF THE FORMATION OF THE SPECIE WITH A CHARACTERISTIC BAND AT 1621 CM ⁻¹ | 36 |
| 3.3.1 | <i>Control experiment</i> | <i>36</i> |

| | | |
|----------|---|-----------|
| 3.3.2 | <i>Synthesis of the DMAP-NbCl₅ species</i> | 37 |
| 3.4 | STUDY OF THE FORMATION OF THE SPECIE WITH A CHARACTERISTIC BAND AT 1654 CM ⁻¹ | 38 |
| 3.4.1 | <i>Isolation of the species</i> | 38 |
| 3.4.2 | <i>Characterization of complex 4</i> | 39 |
| 3.5 | NMR STUDY OF THE EQUILIBRIUM BETWEEN UNBOUNDED DMAP, 3 AND 6..... | 42 |
| 3.6 | COMPOUND 6 AS AN INTERMEDIATE IN THE FORMATION OF PROPYLENE CARBONATE FROM PROPYLENE OXIDE AND CO ₂ | 44 |
| 3.7 | FORMATION OF A NEW INTERMEDIATE WITH CO ₂ | 46 |
| 3.7.1 | <i>Formation of a new intermediate with CO₂</i> | 46 |
| 3.7.2 | <i>NMR experiment with ¹³CO₂</i> | 48 |
| 3.7.3 | <i>Control experiment with species 3</i> | 52 |
| 3.8 | THE ROLE OF FREE DMAP | 52 |
| 3.9 | PROPOSED CATALYTIC CYCLE | 56 |
| 3.10 | INFLUENCE OF DIFFERENT PARAMETERS OVER THE STARTING RATE OF FORMATION OF PROPYLENE CARBONATE | 57 |
| 3.10.1 | <i>Influence of carbon dioxide pressure</i> | 57 |
| 3.10.2 | <i>Influence of the propylene oxide concentration</i> | 58 |
| 3.11 | CONCLUSION | 59 |
| 4 | PALLADIUM (0) COMPLEXES BEARING PHOSPHINE OR NHC LIGANDS AS PRECURSORS FOR REACTIONS INVOLVING CARBON DIOXIDE | 61 |
| 4.1 | INTRODUCTION | 61 |
| 4.1.1 | <i>Interaction of palladium (0) complexes with CO₂</i> | 61 |
| 4.1.2 | <i>Formation of metallalactones from ethylene and CO₂</i> | 62 |
| 4.2 | SYNTHESIS OF PALLADIUM(0) PRECURSORS | 63 |
| 4.2.1 | <i>Synthesis of Pd(IMes)₂ and of Pd(Idipp)₂</i> | 64 |
| 4.2.2 | <i>Synthesis of Pd(PtBu₃)₂ and of Pd(PCy₃)₂</i> | 66 |
| 4.3 | REACTION OF PALLADIUM (0) COMPLEXES 9A AND 9B WITH CO ₂ | 67 |
| 4.4 | FORMATION OF PALLADIUM (II) COMPLEXES BY REACTION OF PALLADIUM (0) COMPOUNDS WITH CH ₃ I AND THEIR REACTION WITH CO ₂ | 69 |
| 4.4.1 | <i>Reaction of Pd(IMes)₂ and Pd(PCy₃)₂ with CH₃I</i> | 69 |
| 4.4.2 | <i>Reaction of Pd(IMes)₂(CH₃)(I) and Pd(PCy₃)₂(CH₃)(I) with CO₂</i> | 72 |
| 4.5 | REACTION OF Pd(IMES) ₂ WITH HCL AND ITS REACTION WITH CO ₂ | 72 |
| 4.5.1 | <i>Reaction of Pd(IMes)₂ with HCl</i> | 72 |
| 4.5.2 | <i>Reaction of Pd(IMes)₂(H)(Cl) with CO₂</i> | 73 |
| 4.6 | REACTION OF Pd(IMES) ₂ WITH HCOOH | 73 |
| 4.7 | REACTION OF 9A AND 9B WITH GASES: H ₂ AND O ₂ | 76 |
| 4.7.1 | <i>Reaction of Pd(Idipp)₂ with H₂</i> | 76 |
| 4.7.2 | <i>Reaction of Pd(IMes)₂ with O₂ and epoxidation of cyclooctene</i> | 77 |

| | | |
|----------|---|------------|
| 4.8 | REACTION OF Pd(PtBu ₃) ₂ , Pd(PCy ₃) ₂ AND Pd(PPh ₃) ₄ WITH ETHYLENE AND CO ₂ | 78 |
| 4.9 | CONCLUSION | 80 |
| 5 | SYNTHESIS OF PLATINUM (II)- AND PALLADIUM (II)-METHYL COMPLEXES BEARING BISPHOSPHINE OR BIS-NHC LIGANDS AND THEIR REACTION WITH CARBON DIOXIDE | 83 |
| 5.1 | INTRODUCTION | 83 |
| 5.2 | SYNTHESIS OF Pt(BIS-PHOSPHINE)Me ₂ COMPLEXES AND THEIR REACTION WITH CO ₂ | 84 |
| 5.2.1 | <i>Synthesis of Pt(dcpe)Me₂ and Pt(dtbpe)Me₂.....</i> | 84 |
| 5.2.2 | <i>Reactivity of Pt(dcpe)Me₂ and Pt(dtbpe)Me₂ with CO₂.....</i> | 86 |
| 5.3 | SYNTHESIS OF Pt(BIS-PHOSPHINE)H ₂ COMPLEXES AND THEIR REACTION WITH CO ₂ | 87 |
| 5.3.1 | <i>Synthesis of Pt(bis-phosphine)H₂ complexes.....</i> | 87 |
| 5.3.2 | <i>The reactions of Pt(bis-phosphino)H₂ complexes with CO₂.....</i> | 88 |
| 5.4 | SYNTHESIS OF Pd(BIS-NHC)Br ₂ COMPLEXES | 89 |
| 5.4.1 | <i>Synthesis of bis-imidazolium salts.....</i> | 89 |
| 5.4.2 | <i>Synthesis of Pd(bis-NHC)Br₂ complexes</i> | 91 |
| 5.5 | SYNTHESIS OF Pd(BIS-NHC)Me ₂ COMPLEXES | 91 |
| 5.5.1 | <i>Synthesis from the reaction of Pd(bis-carbene)Br₂ with MeLi.....</i> | 91 |
| 5.5.2 | <i>Synthesis from the formation of the free carbene</i> | 92 |
| 5.6 | SYNTHESIS OF Pd(BIS-NHC) HYDRIDE COMPLEXES | 93 |
| 5.6.1 | <i>Synthesis of Pd(bis-NHC)H₂ complexes.....</i> | 93 |
| 5.6.2 | <i>Synthesis of Pd(bis-NHC) hydride complexes</i> | 93 |
| 5.7 | CONCLUSION | 95 |
| 6 | SYNTHESIS OF PALLADIUM (II)-METHYL COMPLEXES WITH CNC PINCER LIGANDS AND THEIR REACTION WITH CARBON DIOXIDE | 97 |
| 6.1 | INTRODUCTION | 97 |
| 6.2 | SYNTHESIS OF PALLADIUM(II)-METHYL COMPLEXES..... | 99 |
| 6.2.1 | <i>Synthesis of the CNC ligands</i> | 99 |
| 6.2.2 | <i>Synthesis of the palladium precursor</i> | 99 |
| 6.2.3 | <i>Synthesis of the palladium(II) complexes</i> | 100 |
| 6.3 | REACTION OF 34A AND 34B WITH CARBON DIOXIDE | 101 |
| 6.4 | CONCLUSION | 104 |
| 7 | EXPERIMENTAL SECTION | 105 |
| 7.1 | GENERAL PROCEDURES | 105 |
| 7.1.1 | <i>Inert gas atmosphere</i> | 105 |
| 7.1.2 | <i>Solvents.....</i> | 105 |
| 7.1.3 | <i>Characterization Methods</i> | 105 |
| 7.2 | CHAPTER 2..... | 106 |

| | | |
|----------|------------------------|------------|
| 7.3 | CHAPTER 3..... | 111 |
| 7.4 | CHAPTER 4..... | 114 |
| 7.5 | CHAPTER 5..... | 119 |
| 7.6 | CHAPTER 6..... | 124 |
| 8 | SUMMARY..... | 127 |
| 9 | REFERENCES..... | 133 |

1 Introduction

1.1 Generalities about carbon dioxide

1.1.1 CO₂ in the atmosphere

Carbon dioxide (CO₂) has gained much attention in the mass media recently as it is playing an important role as a greenhouse gas in the Earth's global warming.^[1]

CO₂ is naturally present as a gas in the atmosphere at a concentration of 0.0395 % by volume in 2012^[2] (corresponding to 395 ppm by volume) which represents around 3,100 Gigatons (Gt) of CO₂. Nature is able to recycle some 200 Gt of carbon dioxide each year through the natural carbon cycle,^[3] in particular through photosynthesis: plants, algae and cyanobacteria absorb carbon dioxide, light and water to produce carbohydrate energy and release oxygen as a waste product. CO₂ is a fundamental element of the Earth's atmosphere as a greenhouse gas: it transmits visible light from the Sun but absorbs strongly the heat radiated by the Earth in the infrared and near-infrared, before slowly re-radiating it back to the Earth. Without this greenhouse effect, the estimated average Earth's surface temperature would be - 19 °C, much colder than the conditions that actually exist (around 14 °C).^[4]

The carbon cycle has been very efficient over centuries, keeping the CO₂ level at a medium value of 275-284 ppm,^[5] however since the middle of the 1850s, the CO₂ level in the atmosphere is rising and nature has proven to be unable to recycle the excess of CO₂ (Figure 1.1.). From 1960 to 2005, the annual average growth of CO₂ in the atmosphere is of 1.4 ppm, which represents around 11 Gt of CO₂ per year. The speed of the rise has even been increasing in the last years: during the decade 1995-2005, it has been of 1.9 ppm per year. The main origin of this massive rise of the CO₂ concentration in the atmosphere comes from anthropogenic (man-made) emissions of CO₂, mostly from the use of carbon-based fossil fuels. Moreover, as 85 % of the global energy production comprises oil, coal and gas and as the overall demand on energy keeps on increasing, an increase in the emission of CO₂ is expected.

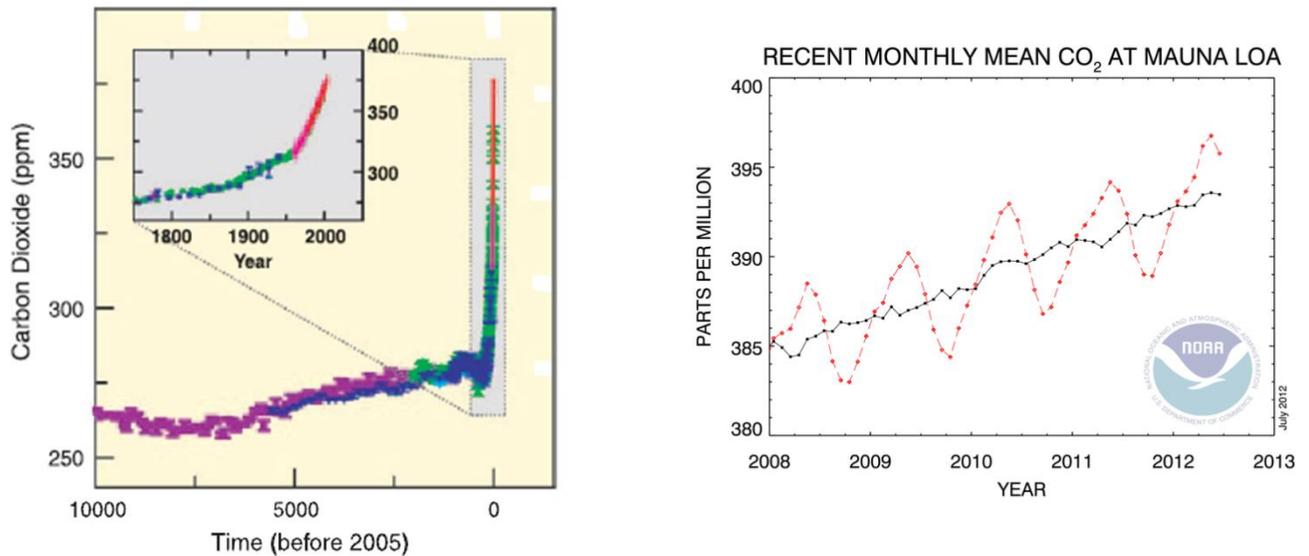


Figure 1.1. CO₂ level in the atmosphere over a 10 000 years period, with a zoom over the last 200 years(left)^[1] and over the last 5 years as measured at Mauna Loa, Hawaii(right)^[2]

On the right scheme, the red curves represent the monthly mean values, which have variations due to the seasonal cycle. The black line is an average with a correction for the average seasonal cycle.

This accumulation of CO₂ leads to an expansion of the greenhouse effect, and has potential effects on the climate change. Indeed, in the last years, the Earth's surface temperature has been rising at levels unseen before. As a consequence, the temperatures of the planet's water are rising, causing an important ice melting, and an increase of the water's level worldwide. Those changes can be devastating for population on coastal areas, as well as for species of plants and animals who would not be able to adapt to these new environmental conditions.

Another important concern is the long time required to stabilize the effects of the increased CO₂ concentration in the atmosphere. Even if mankind would stop releasing CO₂ today, it would take centuries to millenaries for Earth's temperature and sea water level to stabilize.^[7]

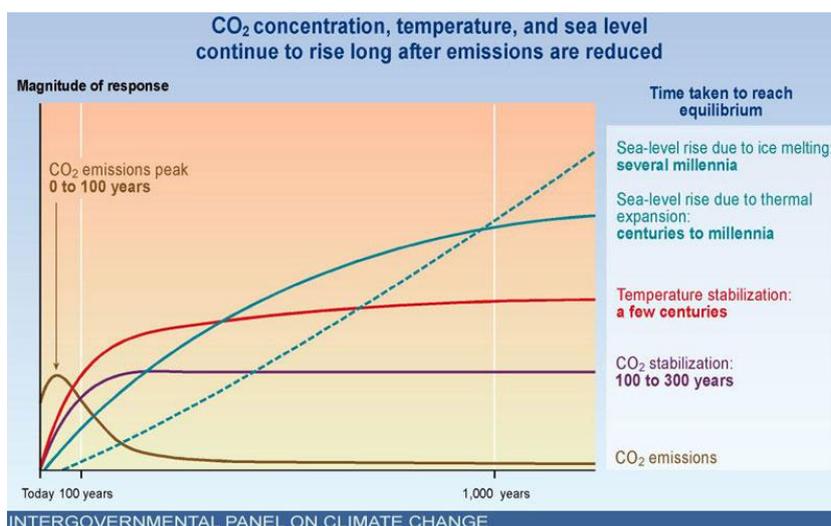


Figure 1.2. Estimated time for the CO₂ concentration, Earth's temperature and sea level to stabilize if CO₂ emissions reach a peak in 50 years^[7]

Therefore, it is vital for mankind to develop strategies to reduce the CO₂ emissions in the atmosphere. Areas of research such as carbon capture and storage^[8] have developed to use CO₂ as a chemical feedstock. An important one in which we have devoted our interest is the CO₂ utilization: It consists in incorporating CO₂ into value-added chemicals through the help of catalysts. Nevertheless, one has to keep in mind that the quantity of CO₂ consumed by chemicals is and will stay low when compared to the quantity released by anthropogenic uses. Moreover, the captured CO₂ is characterized by different degrees of purity according to its origin, and may require extensive purification for specific applications. In the case of several applications in the chemical industry, the presence of contaminants such as O₂, SO_x, or NO_y might cause poisoning effects on the catalysts.

1.2 Industrial reactions involving CO₂

Carbon dioxide is an inexpensive, abundant and non-toxic compound, which makes it a desirable starting material for high-scale syntheses. It is involved in an important number of reactions, some of them being industrialized. They are summarized by Sakakura et al.^[9]

Introduction

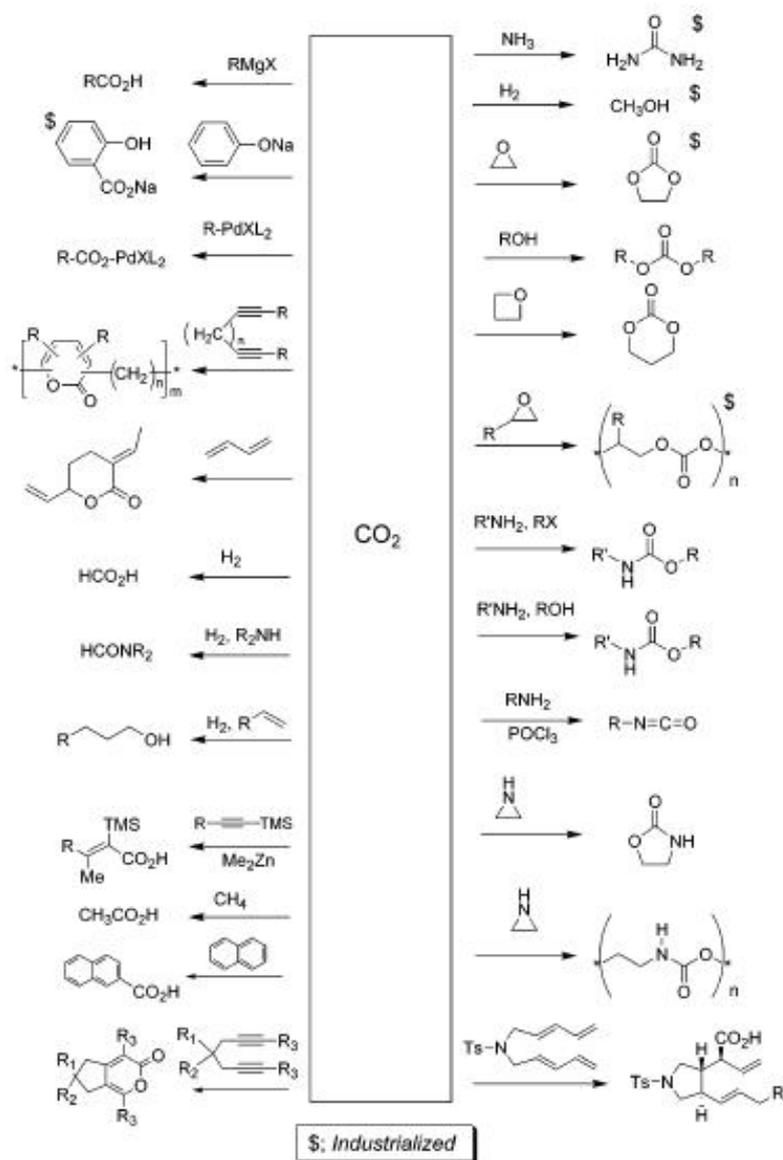
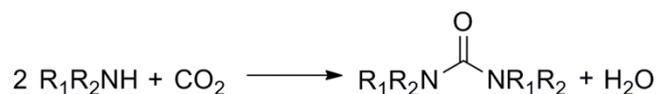


Figure 1.3. Reactions involving CO₂^[9]

The worldwide consumption of CO₂ through synthesis of chemicals is estimated at 110 Mtons/year.^[10] A large majority is used for the synthesis of urea (Scheme 1.1.), whose production is close to 90 Mtons/year.^[11] This synthesis has been commercialized since 1922 and is known as the Bosch-Meiser urea process.



Scheme 1.1. Bosch-Meiser urea process

One major problem of employing CO₂ as a chemical feedstock is that the carbon atom of CO₂ is in its most oxidized state. It is therefore in a low energy level, which means high quantities of energy are required to transform it.^[9]

In this way, the use of CO₂ for the production of organic carbonates is promising. In organic carbonates, the four chemical bonds of the carbonyl carbon are connected to oxygen so the synthetic targets are highly oxidated too.^[12] Even if the production of organic carbonates is still limited, important research on this field is going on which might bring to the consumption of important quantities of CO₂ (see section 2.1. for a detailed discussion about this subject). Another approach which is thermodynamically favored consists in using high-energy starting materials, such as hydrogen or unsaturated compounds.^[13] For example, the industrial synthesis of methanol from CO₂ and H₂ has been intensively studied.^[14]

1.3 Chemicals properties of carbon dioxide

At normal temperature and pressure, carbon dioxide is an odorless non-toxic gas. The CO₂ molecule is linear and centrosymmetric, it is a 16 electrons molecule belonging to the D_{∞h} symmetry group. It is a non-polar molecule, containing two equivalent polar C=O bonds of lengths of 116.3 ppm. Those two bonds contain π electrons that can interact with d electrons of transition metals.

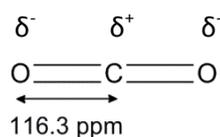


Figure 1.4. Carbon dioxide molecule

Introduction

The carbon atom (LUMO orbitals) has a Lewis acid character and can be described as an electrophilic center, whereas the oxygen atoms (HOMO orbitals) are weak Lewis bases and can be described as nucleophilic centers. Overall, CO₂ is a weak electrophile. The interaction of carbon dioxide with a metal induces the transfer of electrons from the metal to the LUMO orbital of CO₂. In this case, the lowest energy state of CO₂ corresponds to a bent geometry. So, the interaction of carbon dioxide with a metal induces a loss of linearity.^[3]

CO₂ and CO₂-containing molecules can be analyzed through NMR or IR spectroscopy. The ¹³C NMR spectrum of CO₂ dissolved in a non-polar solvent shows a resonance at 124 ppm, which is shifted up or down field when CO₂ is bonded to a metal center. As CO₂ has a center of symmetry, the asymmetric stretching (2349 cm⁻¹) and the degenerate bending modes (667 cm⁻¹) are IR-active and Raman-inactive, and the C=O symmetric stretching mode is IR-inactive. When CO₂ interacts with a metal, it provokes the bending of the molecule and often an increase in the C=O bond length. Those modifications are observed in the IR spectra: the anti-symmetric ν_a(C=O) stretching mode is lowered in the region 1500-2000 cm⁻¹, the symmetric ν_s(CO) stretching mode becomes IR-active and is observed in the region 1400-1100 cm⁻¹, the degenerate bending mode is shifted, and additional modes (metal-C and/or metal-O stretching modes, C=O out-of-plane bending mode) may appear between 300 and 800 cm⁻¹.^[3] The positions and intensities of these modes can provide some information on the bonding mode of CO₂ in the complex, together with an estimation of the O-C-O angle value.^[15]

Carbon dioxide is soluble in water, in which it forms an equilibrium with carbonic acid (H₂CO₃). The relative concentrations of CO₂, H₂CO₃, and the deprotonated forms HCO₃⁻ (bicarbonate) and CO₃²⁻ (carbonate) is pH-dependent.

Supercritical CO₂ has recently gained much attention as solvent for homogeneous and heterogeneous catalytic processes, polymerizations, green syntheses, and biocatalysis.^[16] CO₂ has accessible parameters (T_c = 304.12 K, P_c = 7.37 MPa), and has the advantages of being nonflammable and non-toxic. Another main advantage is that, when gaseous compounds are involved in the reaction, the reaction can be performed

under single-phase conditions, increasing greatly the solubility of the gases and accelerating the kinetic of the reaction.

1.4 Reactivity of CO₂ with transition metals

1.4.1 Activation of CO₂ by transition metals

The coordination of CO₂ to a metal center contributes in lowering its activation energy. CO₂ can bind to a metal center from four different basic modes (Figure 1.5.).

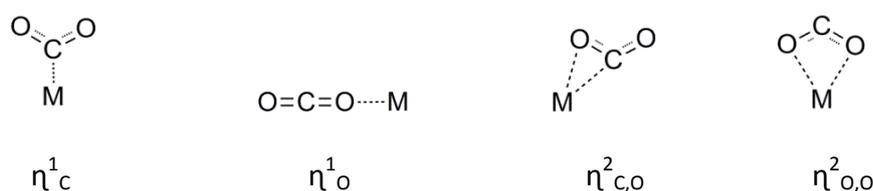
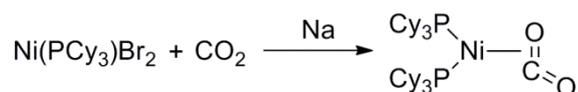


Figure 1.5. Possible bonding of CO₂ to a metal center

The first complex to be structurally characterized was a side-on $\eta^2(\text{C},\text{O})$ reported by Aresta et al. in 1975.^[17] By reduction of $(\text{PCy}_3)_2\text{NiBr}_2$ under a CO₂ atmosphere, the complex $(\text{PCy}_3)_2\text{Ni}(\text{CO}_2)$ could be isolated (Scheme 1.2.).



Scheme 1.2. Aresta's first synthesis of a coordinated CO₂ to a metal center^[17]

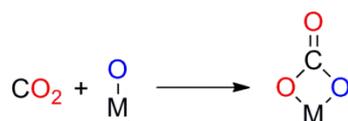
The Ni atom is coordinated to one CO₂ and two phosphine ligands in an almost planar environment. The coordinated CO₂ has two non-equivalent C=O bonds (1.17 and 1.22 Å), the one linked to the metal being lengthened. The CO₂ molecule is bent with an O-C-O angle of 133°. The complex $\text{Nb}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-CO}_2)$ synthesized by Lappert et al. exhibits comparable properties with C=O bonds slightly longer (1.21 and 1.28 Å) and the same O-C-O angle of 132°. ^[18] This side-on $\eta^2(\text{C},\text{O})$ has revealed to be common in the

activation of CO₂ by transition metal complexes. Numerous complexes have been isolated, mostly nickel^[19], molybdenum^[20], niobium^[21] and iron^[22] based. Examples are also found with rhodium^[23] and cobalt^[24] complexes; and with palladium, tungsten and titanium with the isolation of the complexes Pd(PMePh₂)₂(CO₂)^[25] W(CO)(η²-CO₂)(dppe)₂^[26] and Cp₂Ti(PMe₃)₂.^[27] Carmona et al. isolated and characterized in 1984 the complexes Mo(CO₂)₂(PMe₃)₄^[28] and Mo(CO₂)₂(PMe₃)₃(CNPr)^[20a], which were the first complexes with two CO₂ bonded by η²(C,O) mode to a single transition metal. In this η²(C,O) bonding mode, there is a double bonding scheme with a σ bond from the π orbital of CO₂ to an empty d_{z²} metal orbital, together with a “back-bonding” from a filled d_{xy} metal orbital to the empty π* CO₂ orbital. This coordination mode is favored by a high-energy d_σ-type orbital.^[29]

Another common binding mode of CO₂ to a metal center is the η¹_C coordination mode. In this mode, there is a strong charge transfer between a d_{z²} metal orbital and the anti-bonding π* orbital of CO₂.^[3] This bonding mode is preferred with electron-rich metals in low oxidation states.^[29] The first η¹_C coordinated complex to be structurally characterized was reported by Herskovitz et al.^[30]: Rh(diars)₂Cl(CO₂) whose C=O bonds have lengths of 1.20 and 1.25 Å and with an O-C-O angle of 126°. Different complexes of rhodium^[23], cobalt^[31], ruthenium^[32] and iridium^[33] have been isolated and characterized.

The η¹(O) end-on coordination mode remained a purely theoretic mode of bonding until the first such complex of uranium was isolated by Castro-Rodriguez et al. in 2004.^[34] The CO₂ molecule remains almost linear with an O-C-O angle of 178.0(3) °. The linearity is also kept with the uranium atom with a U-O-C angle of 171.1 (2) °. It is to our knowledge the only complex reported with this coordination mode.

The η²(O,O) coordination mode is very common in the case of CO₂ adsorption on metal surfaces. In those cases, one oxygen originates from the surface and one from the CO₂ molecule, as could be observed for example on titanium^[35] and chromium^[36] surfaces.



Scheme 1.3. Coordination of CO₂ to a metal surface

CO₂ can also react with two or more metal centers which involves the coordination of the carbon to one metal and the bonding of one or two oxygen to a second (or third) metal center. Numerous examples are reported in the literature, and those complexes been reviewed several times.^[29b, 37]

The interaction of CO₂ with transition metal complexes has also been the subject of numerous theoretical studies.^[17b, 38]

A coordinated CO₂ to a metal center can further react in three possible ways:

- Via reactions with electrophiles: the oxygen of the η^2 - or η^1 -bonded coordinated CO₂ can undergo an electrophilic attack by protons or other similar reagents. For example, Fe(CO₂)(depe)₂ reacts with MeI and MeOTf to give Me₂O and the corresponding iron(II) carbonyl complexes FeX(CO)(depe)₂⁺X⁻ with X=I or OTf.^[22c]
- Via reactions with nucleophiles: only a couple of reaction of CO₂ complexes with nucleophiles have been reported.^[3]
- Via C=O bond cleavage and O transfer: the thermolysis of CO₂ containing complexes often lead to the cleavage of one C=O bond resulting in the loss of CO and the formation of an oxo compound.^[39]

1.4.2 Insertion of CO₂ into M-L bond

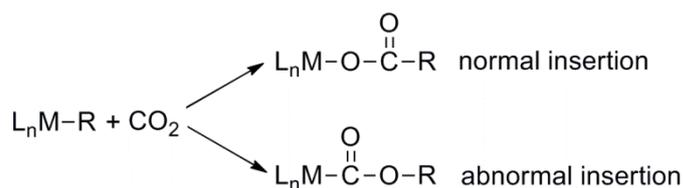
From a synthetic point of view, the formation of new bonds between CO₂ and a second group L is of high interest. In principle, these reactions can occur via one of the three following pathways:

- Attack of the reactant at the coordinated CO₂: $\text{LnM}(\text{CO}_2) + \text{L} \longrightarrow \text{LnM-O-C}(\text{O})\text{L}$
- Insertion of CO₂ into a M-L bond: $\text{LnM}(\text{L}) + \text{CO}_2 \longrightarrow \text{LnM-O-C}(\text{O})\text{L}$
- Simultaneous coordination of CO₂ and L at the metal:



Many stoichiometric and catalytic reaction proceeds through the reaction of free CO₂ with a metal complex leading to the insertion of CO₂ into M-L bonds and formation of new C-L bonds. These insertions have been extensively studied and numerous reviews have been published on this subject.^[9-10, 29, 40]

The insertion can proceed through two ways: either one of the oxygen coordinates to the metal (normal insertion) or the carbon coordinates to the metal (abnormal insertion).



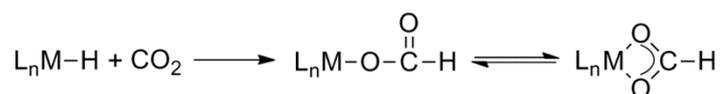
Scheme 1.4. Insertion of CO₂ into a M-R bond

The CO₂ insertion is mainly reported into M-C, M-H, M-O and M-N bonds. The insertion into other M-X bond remains quite exotic: only a few examples of insertion into M-P bonds have been reported.^[41]

The insertion into metal-carbon bond has been by far the most studied, as it leads to the formation of new C-C bonds and of important organic groups such as acids, esters, lactones and pyrones. The insertion proceeds almost only through the normal way (with the oxygen bonded to the metal). The first formal insertion of carbon dioxide into a

transition-metal carbon bond was reported in 1974 by Vol'pin et al. who treated $[(\text{Ph}_3\text{P})_3\text{RhPh}]$ with CO_2 to obtain the benzoate complex $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{OOCPh})]$.^[42] Since then, a very important number of papers have been published where this insertion has proceeded. The insertion is in general a quite straightforward reaction; however the cleavage of the transformation product and the regeneration of the catalyst is often problematic. An external compound has to be added to cleave the moiety, usually oxophilic compounds such as boronic esters^[43] or zinc halides.^[44]

The insertion into metal-hydride bond proceeds into highly polar M-H bonds^[45] and always leads to the formation of a formate complex.



Scheme 1.5. Formation of a formate complex by insertion of CO_2 into a M-H bond

This reaction usually proceeds relatively easily, and has been reported with a great variety of metals.^[46] The catalytic process leads to the formation of formic acid and derivatives, which are used as a silage agent, in the leather industry, and for the deicing of airplanes. Especially, the reaction between CO_2 and H_2 has been reviewed several times.^[47] The use of dipolar non-protic solvents and the presence of a base (amine, KOH , Na_2CO_3) are necessary to stabilize the hydrogenated product and to shift the equilibrium to the right. The best TONs were obtained with ruthenium^[48] and rhodium^[49] catalysts. Recently Nozaki et al. published an iridium-hydride catalyst bearing a PNP pincer ligand which exhibits the up to date highest reported TOF ($73\,000\text{ h}^{-1}$) and TON (3 500 000) values.^[50]

The insertion into metal-nitrogen bonds affords carbamic acid derivatives, especially carbamic acid esters (urethanes) $\text{N}_2\text{RCOOR}'$ in presence of crown ether^[51] or strong bases.^[52] Those carbamates compounds are important precursors in the pharmaceutical industry, as well as in the production of fungicides and pesticides.^[53] They are also precursors of isocyanate, which are important intermediates in the production of

plastics and polyurethanes. This insertion is mostly reported for early transition metals.^[54]

The insertion of carbon dioxide into metal-oxygen leads to the formation of linear or cyclic carbonates, and of polycarbonates, and is detailed in section 1.5.

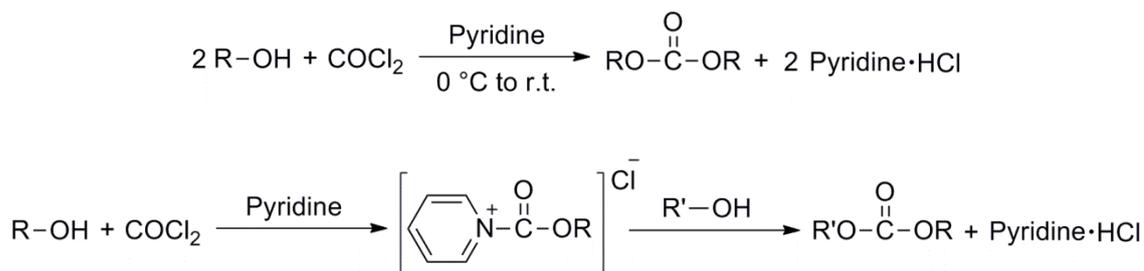
1.5 The formation of carbonates from CO₂

The market size of organic carbonate is relatively small (100,000 tons per year^[13]), however an important quantity do not reach the market as they are consumed as intermediates for the production of other chemicals, especially for the synthesis of polycarbonates. With polycarbonates, the four industrially most important organic carbonates are: dimethyl carbonate (DMC), diphenyl carbonate (DPC), ethylene carbonate (EC) and propylene carbonate (PC).

They have a wide range of applications:

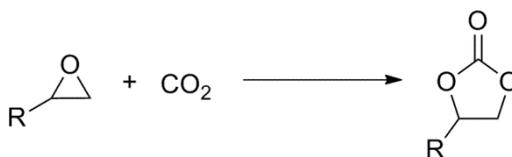
- For the production of engineering plastics: polycarbonates are highly impact-resistant and optically transparent. They are for examples used in CDs, DVDs, eyeglasses, aircraft windows, etc.^[12]
- Propylene carbonate is used as electrolyte solvents for lithium ion batteries principally due to its good solvent properties for lithium salts and its high dielectric constant.^[55]
- Five membered cyclic carbonates (ethylene carbonate and propylene carbonate) are highly polar solvents with a relatively low toxicity and suitable boiling point to be removed by vaporization. In many application, they offer a safer and cleaner alternative to more hazardous dipolar aprotic solvents.^[56]
- As fuel additives: the addition of dimethyl carbonate to gasoline results in an improved octane value. Its potential demand in this sector was estimated at 30 Mtons / year.^[57]
- As thickeners for cosmetic^[58]

Nearly all carbonates can be prepared by using phosgene, the symmetrical are obtained in one step, whereas unsymmetrical, alkyl aryl, or substituted alkyl aryl carbonates are obtained by a two steps reaction. This reaction proceeds through the reaction of alcohol with phosgene using pyridine as solvent and base.^[58]



Scheme 1.6. Synthesis of carbonates through phosgene route

This process leads to high yields and allows the preparation of functionalized carbonates. It has however several drawbacks, the main one being the toxicities of pyridine and phosgene. The excess of pyridine also has to be neutralized, and byproducts salts have to be completely removed and disposed.^[58] While the phosgene method is still widely use for the production of linear carbonates,^[13] the industrial synthesis of cyclic carbonates is performed through the coupling reaction between CO₂ and strained heterocycles. This reaction has the advantage of being 100 % atom economical.

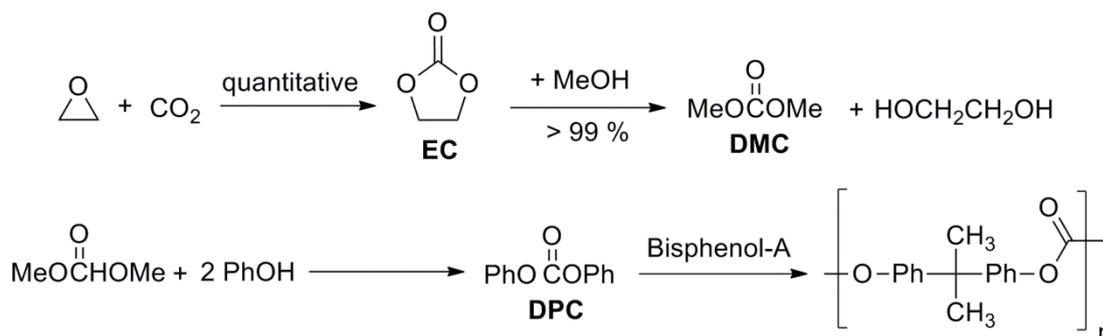


Scheme 1.7. Formation of carbonate from epoxides and carbon dioxide

The first publication on the formation of propylene carbonate from propylene oxide and carbon dioxide at a pilot plant scale dates from the 1950s.^[59] The reaction occurs easily due to the high energy level of the starting epoxides. It is usually carried out using Lewis

acid or base catalysts, which requires high temperature and pressures. These conditions are a limiting aspect of the process, both in terms of energy and economics.

The same route for the production of acyclic carbonates has started developing recently. A new process developed in 2002 is using waste CO₂ to produce ethylene carbonate, which is further reacted with alcohols to lead to dimethyl carbonate, diphenyl carbonate and finally polycarbonates.^[60]



Scheme 1.8. Asahi's process for the production of carbonates from carbon dioxide^[60]

This route is a promising way of producing all carbonate away from the phosgene route. This process is currently producing 50 000 tons per year of polycarbonate and can potentially use 450,000 tons of carbon dioxide per year if the worldwide polycarbonate production would be carried out with this process.^[40c]

Therefore, the synthesis of cyclic carbonates, especially ethylene carbonate, with inexpensive catalysts and under mild condition possesses a high industrial interest.

Several reviews have been published recently; summarizing the last advances on the synthesis of cyclic carbonates from epoxides and CO₂.^[12-13, 40c, 61] A very wide range of catalysts have been reported, from very simple systems such as metal halides or metal oxides to very complicated ones. Almost every transition metal has been reported to promote this synthesis, and recently even ionic liquids,^[62] simple bases such as TBAB^[63] and organocatalysts^[64] have been reported. The reaction has also been reported through electrolysis^[65] and in supercritical CO₂.^[66]

1.6 Objectives of this work

The incorporation of CO₂ into value-added chemicals has been widely studied in the literature. However, the stability of CO₂ renders it challenging to achieve catalytic reactions with this compound.

The formation of carbonates from epoxide and CO₂ is one of the well-known catalytic processes using CO₂ as the reaction has a low energy barrier to overcome. A wide range of catalysts have been discovered, however very few reports have been published with simple catalytic systems working under mild conditions. Moreover, only few kinetic and mechanistic studies have been published on this reaction. A screening of simple systems promoting the synthesis of propylene carbonate at room temperature and 1 bar of CO₂ is performed. The influence of different parameters such as the CO₂ pressure and the catalyst:co-catalyst ratio is investigated. A full mechanistic study with isolation of intermediates is also performed.

Palladium complexes are efficient catalysts for the synthesis of lactones from CO₂ and olefins, and for the telomerization of dienes with CO₂. However, very few reports on the insertion of CO₂ into palladium or platinum methyl or hydride bonds have been published. A range of palladium complexes bearing phosphine or carbene ligands is synthesized and their interaction with CO₂ is tested.

Introduction

2 Formation of propylene carbonate from propylene oxide and carbon dioxide with metal halides under mild conditions

This chapter is based on the publication: **Novel and highly efficient niobium-based catalysts for the synthesis of cyclic carbonates from epoxides and CO₂ under mild conditions**, Antoine Monassier, Valerio D'Elia*, Mirza Cokoja*, Jérémie Pelletier, Hailin Dong, Jean-Marie Basset and Fritz E. Kühn, *submitted to ChemCatChem*.

2.1 Introduction

Recently much interest has been devoted to achieve the synthesis of propylene carbonate at room temperature and atmospheric pressure. The first paper to report the synthesis of propylene carbonate from propylene oxide and CO₂ under those mild conditions dates from 1980.^[67] By use of simple metal halides systems (MoCl₅, WCl₆, FeCl₃, etc.) with triphenylphosphine as co-catalyst, low to moderate yields were obtained after 7 days of reaction. They later showed that nBu₄Ni was a better co-catalyst as triphenylphosphine and reached a TOF of 20 h⁻¹ using the system ZnCl₂/nBu₄Ni.^[68]

A great interest has been devoted on complexes with salen ligands^[69]. Different metals have proven to be active with those ligands, the best ones being Al, Co and Cr. North et al. developed an Aluminium(salen) catalyst capable of promoting the reaction with a maximal TOF of 9 h⁻¹.^[70] They further improved it, and designed a one-component catalyst in which the co-catalyst is linked to the ligand (Figure 2.1.).^[71] This system gave a TOF of 4 h⁻¹ for the synthesis of propylene carbonate and of 2 h⁻¹ for the synthesis of ethylene carbonate under 6 bar of CO₂.

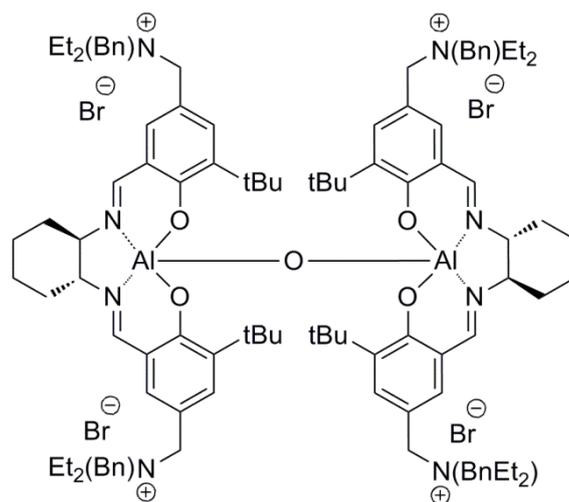


Figure 2.1. North's one-component catalyst^[71]

Lu, Sun et al. reported a TOF of 49 h^{-1} using a Chromium(salen) catalyst at very low catalyst concentration ($0.00002 \text{ mol } \%$) at $25 \text{ }^\circ\text{C}$ and 5 bar of CO_2 .^[72] The catalyst bears the nucleophilic center directly on the ligand, which allows an intra-molecular two-center cooperative catalysis. This intra-molecular reaction explains how the catalyst can still provide a high activity at this very high [epoxide]/[catalyst] ratio.

Lu et al. published a very efficient Cobalt(salen) complexes reaching a TOF of 245 h^{-1} at room temperature, however with 15 bar of CO_2 .^[73]

Zinc complexes were also reported as being particularly efficient under mild conditions. Kleij et al. published a Zn(II)(salphen) catalyst promoting the reaction of a wide range of epoxides.^[74] In particular propylene oxide could be obtained in $73 \text{ } \%$ yield in 18 h with a catalyst loading of $2.5 \text{ mol } \%$ ($\text{TOF} = 2 \text{ h}^{-1}$). Zinc clusters were recently reported as very efficient catalysts at r.t and 1 bar of CO_2 . A system with $n\text{Bu}_4\text{NI}$ as co-catalyst reached 99% conversion after only 6 h of reaction at $25 \text{ }^\circ\text{C}$ and under 1 atmosphere of CO_2 ($\text{TOF} = 8 \text{ h}^{-1}$).^[75]

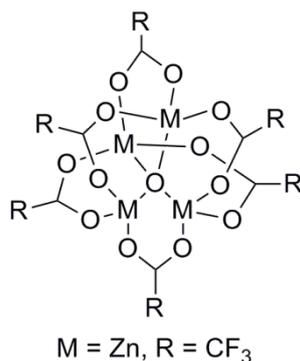


Figure 2.2. Zinc clusters^[75]

Bimetallic iron complexes are also active catalysts: Kleij et al. reported a TOF of 8 h⁻¹ at 25 °C and 2 bar of CO₂.^[76] Willams et al. reported the same TOF under 1 atmosphere of CO₂ and at 25 °C.^[77]

All those systems are relatively efficient under mild conditions; however their synthesis require several steps. A recent study showed that metal halide salts can also be efficient under mild conditions: InBr₃ with PPh₃ as co-catalyst allowed the formation of propylene carbonate with 72 % yield after 1 h at room temperature, under 1 atmosphere of CO₂ and in absence of solvent.^[78] However the catalyst loading needed to reach this yield was very high (5 mol % catalyst, 10 mol % co-catalyst).

An important step would be the development of very simple catalytic systems able to promote the reaction of propylene and ethylene oxide under mild conditions and with low catalyst loading.

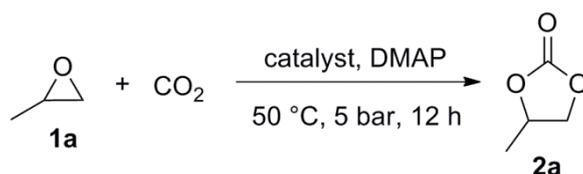
2.2 Screening of catalysts and co-catalysts

2.2.1 Screening of metals halides

A screening of some group IV- VI metal halides and oxychlorides using DMAP as co-catalyst was carried out at 50 °C and 5 bar of CO₂ for the synthesis of propylene carbonate from

Formation of propylene carbonate from propylene oxide and carbon dioxide

propylene oxide and carbon dioxide. All reactions brought to the formation of propylene carbonate as the only product.



Scheme 2.1. Formation of propylene carbonate from propylene oxide and carbon dioxide

Table 2.1. Screening of group IV-VI metal complexes for the synthesis of propylene oxide^a

| Entry | Catalyst | Conversion (%) ^b | TON ^c | TOF (h ⁻¹) |
|----------------|--------------------|-----------------------------|------------------|------------------------|
| 1 | TiCl ₄ | 61 | 244 | 20.3 |
| 2 | ZrCl ₄ | 68 | 272 | 22.5 |
| 3 | VCl ₃ | 68 | 272 | 22.5 |
| 4 | VCl ₄ | 10 | 40 | 3.3 |
| 5 | VOCl ₃ | 0 | - | - |
| 6 | NbCl ₅ | 96 ^d | 384 | 32.0 |
| 7 ^e | NbCl ₅ | 84 ^d | 336 | 67.2 |
| 8 | TaCl ₅ | 62 | 248 | 20.7 |
| 9 | CrCl ₃ | 0 | - | - |
| 10 | MoCl ₅ | 84 | 336 | 28.0 |
| 11 | MoOCl ₄ | 88 | 352 | 29.3 |
| 12 | WCl ₆ | 36 | 144 | 12.0 |

^a: Reaction condition: **1a** (100 mmol), catalyst (0.25 mmol), DMAP (0.5 mmol) at 50 °C, 5 bar for 12 h. ^b: Conversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^c: TON = mol_{PC}/mol_{cat}. ^d: Isolated yield. ^e: After 5 h

It was observed that the halides and the oxychlorides of 4d transition metals such as ZrCl₄, NbCl₅, MoCl₅ and MoOCl₄ were generally the most active. In particular, the NbCl₅/DMAP leads to almost quantitative conversion and can catalyse the synthesis of propylene carbonate with promising turnover frequency (entries 6 and 7). It is interesting to note that CrCl₃ is not an active catalyst under those conditions (entry 9). Although Cr(salen) complexes are active catalysts, it has already been observed that CrCl₃ is not promoting this reaction.^[67] The synthesis of propylene carbonate using Nb₂O₅ at 135 °C and 5 MPa of CO₂ has been reported previously.^[79]

2.2.2 Screening of nucleophiles

Under the same conditions used for the screening of metals, different nucleophiles were tested for the synthesis of propylene carbonate in presence of NbCl₅ as a Lewis acid. The results are summarized in Table 2.2.

Table 2.2. Screening of different nucleophiles in the presence of NbCl₅^a

| Entry | Nucleophile | Time (h) | Conversion (%) ^b | TON ^c | TOF (h ⁻¹) |
|-----------------|---------------------|----------|-----------------------------|------------------|------------------------|
| 1 | DMAP | 6 | 96 ^d | 192 | 32.0 |
| 2 ^e | DMAP | 5 | 84 ^d | 336 | 67.2 |
| 3 | PPh ₃ | 6 | 30 | 60 | 10.0 |
| 4 | TBD | 6 | 17 | 34 | 5.6 |
| 5 | DABCO | 6 | 34 | 68 | 11.3 |
| 6 | NBu ₄ Cl | 4 | 90 | 180 | 45.0 |
| 7 ^e | NBu ₄ Cl | 3 | 93 | 372 | 124.0 |
| 8 | NBu ₄ Br | 4 | 96 | 192 | 48.0 |
| 9 ^e | NBu ₄ Br | 2 | 65 | 260 | 130.0 |
| 10 ^f | NBu ₄ Br | 2 | 46 | 368 | 184.0 |

^a: Reaction condition: **1a** (100 mmol), NbCl₅ (0.5 mmol), nucleophile (0.5 mmol) at 50 °C, 5 bar. ^b: Conversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^c: TON = mol_{PC}/mol_{NbCl₅}. ^d: Isolated yield. ^e: NbCl₅ (0.25 mmol), nucleophile (0.5 mmol). ^f: NbCl₅ (0.125 mmol), nucleophile (0.25 mmol).

Four different N- and P-nucleophiles were tested, among them DMAP proved to be by far the most active. It reaches almost complete conversion after 6 h, while the second most active (DABCO) only reaches 34 % conversion under the same conditions. Triphenylphosphine is also not a particularly active co-catalyst for this reaction (30 % conversion). Quaternary ammonium salts are the most active co-catalysts, very high conversion can be reached in only 3 h, NBu₄Br being slightly more active than NBu₄Cl (entries 6-8). Experiences performed with low catalyst loading (0.25 and 0.125 mol %) led to high turn-over frequencies (entries 9 and 10).

Nevertheless, it has been observed that for the NbCl₅/DMAP system, easy purification from the catalyst can be achieved by simple exposure of the raw material to air for some hours which ensues the precipitation of white DMAP-Nb salts. No distillation of the product is

required after filtration of the solids and therefore the process is close to energy neutrality. Trace analysis reveals that the content of niobium into the propylene carbonate solution is below 1 ppm. GC and NMR analysis shows that the purity of the propylene carbonate obtained is $\geq 99.8\%$.

Thus, $\text{NbCl}_5/\text{NBu}_4\text{Br}$ and $\text{NbCl}_5/\text{DMAP}$ are the most promising catalytic systems for the formation of propylene carbonate from propylene oxide and CO_2 . The behavior of those systems at mild conditions (r.t. and atmospheric pressure of CO_2) and with different epoxides was further studied.

2.3 Behavior at mild conditions and with other epoxides

2.3.1 Behavior at low pressure and room temperature

The behavior of the $\text{NbCl}_5/\text{NBu}_4\text{Br}$ and $\text{NbCl}_5/\text{DMAP}$ systems at low CO_2 pressure (one atmosphere of carbon dioxide or less) and at room temperature has been investigated. Ideally, an efficient recycling of CO_2 involves the use of waste CO_2 directly from a power plant, and therefore, catalytic systems able to operate at nearly ambient temperature and under low CO_2 pressure/concentration.^[80] In a model study in a batch system, propylene carbonate has been synthesized under a CO_2 -argon atmosphere, with the partial pressure of CO_2 between 0.5 and 1 bar and the molar fraction of CO_2 in the gas mixture at 33 % and 50 % (Table 2.3.).

The molar fraction of CO_2 in the gas mixture is calculated following the formula:

$$x_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{P_{\text{CO}_2} + P_{\text{Ar}}}$$

with $P_{\text{Ar}} = 1$ bar, corresponding to the argon pressure in the reactor vessel.

Under such challenging reaction conditions, $\text{NbCl}_5/\text{NBu}_4\text{Br}$ emerges as a very active catalytic system capable to promote the synthesis of **2a** in moderate to high yields and relatively high TOFs. A TOF of 26.5 h^{-1} was obtained when 0.33 mol % of NbCl_5 and 0.66 mol % of NBu_4Br compared to propylene oxide were used at 30°C and 1 bar of CO_2 (Table 2.3.)

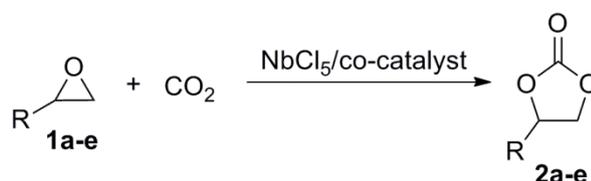
Table 2.3. Reaction at room temperature and low pressure^a

| Entry | Nucleophile | Time (h) | P _{CO2} (bar) | x _{CO2} (%) | Temp. (°C) | Conversion (%) ^b | TON ^c | TOF (h ⁻¹) |
|----------------|---------------------|----------|------------------------|----------------------|------------|-----------------------------|------------------|------------------------|
| 1 | DMAP | 12 | 1 | 50 | 30 | 90 ^d | 90 | 7.5 |
| 2 | DMAP | 18 | 0.5 | 33 | 25 | 52 ^d | 52 | 2.9 |
| 3 | NBu ₄ Br | 6 | 1 | 50 | 30 | 89 | 89 | 14.8 |
| 4 | NBu ₄ Br | 4 | 1 | 50 | 25 | 68 | 68 | 17.0 |
| 5 ^e | NBu ₄ Br | 6 | 1 | 50 | 30 | 60 | 120 | 20.0 |
| 6 ^e | NBu ₄ Br | 14 | 0.5 | 33 | 25 | 93 | 186 | 13.3 |
| 7 ^f | NBu ₄ Br | 8 | 1 | 50 | 30 | 70 | 212 | 26.5 |

^a: Reaction condition: **1a** (100 mmol), NbCl₅ (1 mmol), nucleophile (2 mmol). ^b: Conversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^c: TON = mol_{PC}/mol_{NbCl₅}. ^d: Isolated yield. ^e: **1a** (200 mmol), NbCl₅ (1 mmol), nucleophile (2 mmol). ^f: **1a** (300 mmol), NbCl₅ (1 mmol), nucleophile (2 mmol).

2.3.2 Reaction with other epoxides

The formation of carbonates from different epoxides using the catalytic systems NbCl₅/DMAP and NbCl₅/NBu₄Br was tested.



R = Me (**1a**), R = H (**1b**), R = Et (**1c**),
R = Ph (**1d**), R = CH₂Cl (**1e**)

Scheme 2.2. Formation of different carbonates

Both systems proved to be active for the five epoxides tested, with the system NbCl₅/NBu₄Br always more efficient than the system NbCl₅/DMAP (Tables 2.4. and 2.5.). Good activities are obtained for propylene oxide, butane oxide and epichloridryne oxide. The systems are less efficient for styrene oxide, especially the NbCl₅/DMAP system, probably due to viscosity issues and steric hindrance on the epoxide. Both systems show very high efficiency for ethylene oxide, reaching a TOF of 30.3 h⁻¹ for the NbCl₅/NBu₄Br system.

Table 2.4. Formation of different carbonates under mild conditions using NbCl₅/DMAP system^a

| Entry | Epoxide | PO:Cat:Nucl. | Time (h) | P _{CO₂} (bar) | CO ₂ conc. (%) ^b | Temp. (°C) | Conversion (%) ^c | TON ^d | TOF (h ⁻¹) |
|-------|---------|--------------|----------|--------------------------------------|---|---------------|--------------------------------|------------------|------------------------|
| 1 | 1a | 100:1:2 | 12 | 1 | 50 | 30 | 90 | 90 | 7.5 |
| 2 | 1b | 230:1:2 | 12 | 1.2 | 100 | 23 | 50 | 115 | 9.6 |
| 3 | 1b | 730:1:2 | 12 | 2 | 100 | 23 | 23 | 168 | 14.0 |
| 5 | 1c | 100:1:2 | 12 | 1 | 50 | 30 | 80 | 80 | 6.7 |
| 6 | 1d | 100:1:2 | 12 | 1 | 50 | 50 | 26 | 26 | 2.2 |
| 7 | 1d | 100:1:2 | 12 | 1 | 50 | 60 | 68 | 68 | 5.7 |

^aPartial pressure of CO₂ in the reaction vessel, total pressure is equal to P_{CO₂} + P_{Ar}. ^bMolar fraction of CO₂ in the reactor atmosphere (see SI). ^cConversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^dTON = (mol_{PC}/mol_{Nb}).

Table 2.5. Formation of different carbonates under mild conditions using NbCl₅/NBu₄Br system^a

| Entry | Epoxide | PO:Cat:Nucl. | Time (h) | P _{CO₂} (bar) | CO ₂ conc. (%) ^b | Temp. (°C) | Conversion (%) ^c | TON ^d | TOF (h ⁻¹) |
|-------|---------|--------------|----------|--------------------------------------|---|---------------|--------------------------------|------------------|------------------------|
| 1 | 1a | 100:1:2 | 4 | 1 | 50 | 25 | 68 | 68 | 17.0 |
| 2 | 1a | 200:1:2 | 6 | 1 | 50 | 30 | 60 | 120 | 20.0 |
| 3 | 1b | 570:1:2 | 12 | 1.2 | 100 | 23 | 64 | 365 | 30.3 |
| 5 | 1c | 100:1:2 | 8 | 1 | 50 | 35 | 99 | 99 | 12.4 |
| 6 | 1d | 200:1:2 | 12 | 1 | 50 | 45 | 91 | 182 | 15.2 |
| 7 | 1e | 100:1:2 | 8 | 1 | 50 | 40 | 95 | 95 | 11.9 |

^aPartial pressure of CO₂ in the reaction vessel, total pressure is equal to P_{CO₂} + P_{Ar}. ^bMolar fraction of CO₂ in the reactor atmosphere (see SI). ^cConversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^dTON = (mol_{PC}/mol_{Nb}).

To our knowledge, only North et al. reported a TOF of 2 h⁻¹ for the synthesis of ethylene carbonate under such condition.^[71b] Our NbCl₅/NBu₄Br system is by far more active.

2.4 Influence of different parameters on the formation of propylene carbonate

2.4.1 Influence of carbon dioxide pressure

The carbon dioxide pressure was varied from a range from 1 to 20 bar. For each reaction, 0.375 mol % of NbCl₅ and 0.5 mol % of DMAP in propylene oxide was used. Reactions were performed at 50 °C for several hours. The results are summarized in Figure 2.3. and Table 2.6.

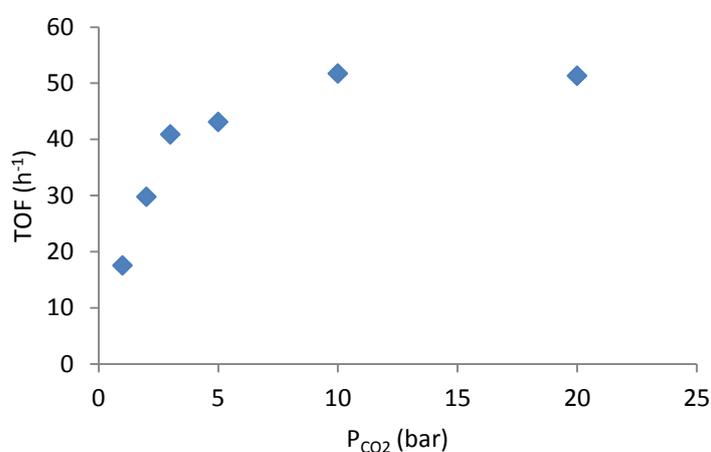


Figure 2.3. Influence of the carbon dioxide pressure over the TOFs

Table 2.6. Influence of the carbon dioxide pressure

| Entry | P _{CO2} | Time (h) | Conversion (%) ^b | TON ^c | TOF (h ⁻¹) |
|-------|------------------|----------|-----------------------------|------------------|------------------------|
| 1 | 1 | 12 | 79 | 211 | 17.6 |
| 2 | 2 | 6 | 67 | 179 | 29.8 |
| 3 | 3 | 6 | 92 | 245 | 40.9 |
| 4 | 5 | 6 | 97 | 259 | 43.1 |
| 5 | 10 | 5 | 97 | 259 | 51.7 |
| 6 | 20 | 4 | 77 | 205 | 51.3 |

^a: Reaction condition: **1a** (100 mmol), NbCl₅ (0.375 mmol), DMAP (0.5 mmol) at 50 °C ^b: Conversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^c: TON = mol_{PC}/mol_{cat}.

The influence of the pressure of carbon dioxide is limited above 3 bar. In those cases, CO₂ is in large excess and dissolves faster in solution than it is consumed. Below 3 bar, the TOFs are highly dependent on the CO₂ pressure. At 1 bar, the TOF is only half of the one at 3 bar. In this case, the CO₂ pressure is a limiting factor of the reaction. Therefore, a pressure of 3 bar seems to be the ideal pressure for the NbCl₅/DMAP system. Performing the reaction at higher CO₂ pressure is not necessary as the improvement in the TOFs is low as compared to the excess in energy spend to get CO₂ at high pressure.

2.4.2 Influence of the concentration of NbCl₅

The influence of the concentration of NbCl₅ was studied. The quantities of DMAP and propylene oxide are kept constant at respectively 0.5 mmol and 100 mmol, and the amount of NbCl₅ is varied from 0.167 mmol to 0.625 mmol. Thus, ratios of NbCl₅/DMAP between 0.334 and 1.5 were studied. Reactions were performed at 50 °C and 5 bar of carbon dioxide for 5 to 6 hours. The results are summarized in Figure 2.4. and Table 2.7.

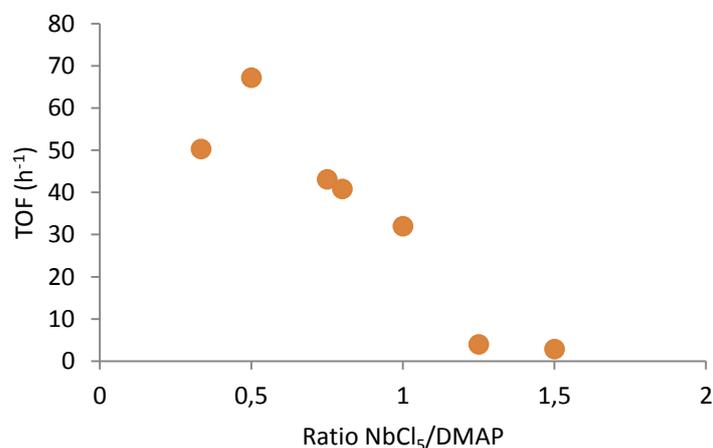


Figure 2.4. Influence of the concentration of NbCl₅ over the TOFs

Table 2.7. Influence of the concentration of NbCl₅

| Entry | n _{NbCl₅} (mmol) | Ratio NbCl ₅ /DMAP | Conversion (%) ^b | TON ^c | TOF (h ⁻¹) |
|----------------|--------------------------------------|----------------------------------|-----------------------------|------------------|------------------------|
| 1 ^d | 0.167 | 0.334 | 42 | 251 | 50.3 |
| 2 ^d | 0.25 | 0.5 | 84 | 336 | 67.2 |
| 3 | 0.375 | 0.75 | 97 | 259 | 43.1 |
| 4 | 0.4 | 0.8 | 98 | 245 | 40.8 |
| 5 | 0.5 | 1 | 96 | 192 | 32.0 |
| 6 | 0.625 | 1.25 | 15 | 24 | 4.0 |
| 7 | 0.75 | 1.5 | 12 | 17 | 2.9 |

^a: Reaction condition: **1a** (100 mmol), DMAP (0.5 mmol) at 50 °C, 5 bar for 6 h. ^b: Conversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^c: TON = mol_{PC}/mol_{cat}. ^d: After 5 h

The best result is obtained for a molecular ratio NbCl₅/DMAP of 0.5, which means there are two equivalents of DMAP for one equivalent of NbCl₅. At low ratios, the amount of catalyst is the limiting factor for the rate of the reaction. Until a 1:1 ratio, the efficiency of the system slowly decreases, probably because the amount of co-catalyst is not sufficient. Above a 1:1 ratio, a huge drop in the TOFs is observed, the system becomes totally inefficient: with a ratio NbCl₅/DMAP of 1.25, the TOF is only 4 h⁻¹. Thus, the system presents a very particular behavior at those ratios, which will be studied in more details in chapter 3.

2.4.3 Influence of the concentration of DMAP

The influence of the concentration of DMAP was studied. The quantities of NbCl₅ and propylene oxide are kept constant at respectively 0.375 mmol and 100 mmol, and the amount of DMAP is varied from 0.3 mmol to 1 mmol. Thus, ratios of DMAP/NbCl₅ between 0.8 and 2.667 were studied. Reactions were performed at 50 °C and 5 bar of carbon dioxide for 5 to 6 hours (except the one for a ratio of 1.33 which was performed at 20 bar). The results are summarized in Figure 2.5. and Table 2.8.

Formation of propylene carbonate from propylene oxide and carbon dioxide

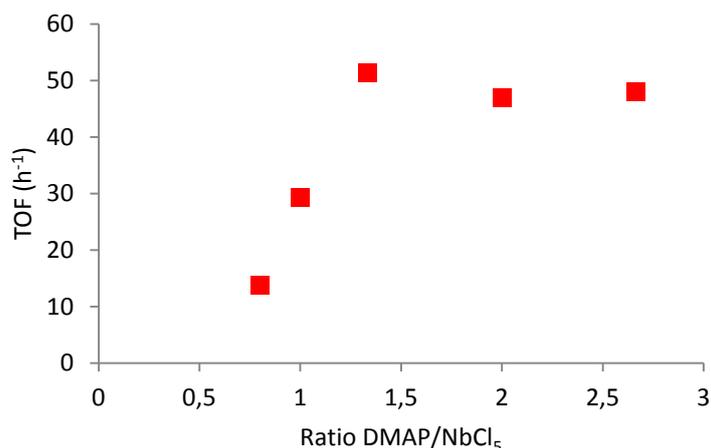


Figure 2.5. Influence of the concentration of DMAP over the TOFs

The curve can be divided in two parts:

- For a ratio DMAP/NbCl₅ over 1.33, the increase in the amount of DMAP does not bring any change to the TOFs. Adding more co-catalyst in solution does not bring to any improvement for the formation of propylene carbonate.
- For a ratio DMAP/NbCl₅ below 1.33, the amount of DMAP has a high influence over the TOFs. Less co-catalyst implies lower TOFs.

Table 2.8. Influence of the concentration of DMAP

| Entry | n_{DMAP} (mmol) | Ratio DMAP/NbCl ₅ | Conversion (%) ^b | TON ^c | TOF (h ⁻¹) |
|----------------|--------------------------|---------------------------------|-----------------------------|------------------|------------------------|
| 1 | 0.3 | 0.8 | 31 | 83 | 13.8 |
| 2 | 0.375 | 1 | 66 | 176 | 29.3 |
| 3 ^d | 0.5 | 1.33 | 77 | 205 | 51.3 |
| 4 ^e | 0.75 | 2 | 88 | 235 | 46.9 |
| 5 ^e | 1 | 2.67 | 90 | 240 | 48 |

^a: Reaction condition: **1a** (100 mmol), NbCl₅ (0.375 mmol) at 50 °C, 5 bar for 6 h. ^b: Conversion evaluated from the ¹H NMR spectrum by integration of epoxide vs. cyclic carbonate peaks. ^c: TON = mol_{PC}/mol_{cat.} ^d: Under 20 bar and after 4 h. ^e: After 5h.

From those studies, it could be concluded that there is an optimal NbCl₅/DMAP ratio, which seems to be at around 1 equivalent of NbCl₅ for 1.5 to 2 equivalent of DMAP. Higher

quantities of DMAP do not bring any improvement in the yield of the reaction, and an amount of NbCl₅ higher than the one of DMAP gives almost no reaction.

2.5 Conclusion

In this chapter, we studied the formation of carbonates from epoxides and carbon dioxide using very simple inexpensive and commercial metal halide catalysts. A screening of catalyst and nucleophilic co-catalyst showed that the system NbCl₅/nBu₄NBr is a particularly active system for this reaction. The system NbCl₅/DMAP presents the advantage of a very easy purification process, as the catalyst and co-catalyst precipitate and can be removed by a simple filtration. Both systems are active under very mild conditions (1 atmosphere and r.t.) and for a range of epoxides. Especially, the NbCl₅/nBu₄NBr is very efficient to catalyze the formation of ethylene carbonate from ethylene oxide and CO₂, reaching a TOF of 30 h⁻¹ at 23 °C and 1.2 bar of CO₂.

The influence of pressure and of the ratios catalyst:co-catalyst has also been studied. It was found that the pressure of carbon dioxide has a noticeable influence over the rate of the reaction below 3 bar, when it is performed at 50 °C. An optimal ratio of catalyst/co-catalyst exists for this formation of propylene carbonate, which is around 1.5 to 2 equivalents of co-catalyst for one of catalyst.

Formation of propylene carbonate from propylene oxide and carbon dioxide

3 Mechanistic study on the formation of propylene carbonate from propylene oxide and carbon dioxide using the catalytic system NbCl₅/DMAP

3.1 Introduction

Very few publications have been released with a detailed kinetic or mechanistic study of the formation of propylene carbonate from propylene oxide and carbon dioxide. A first kinetic study was published in 1990 with the catalytic system ZnCl₂/n-Bu₄Nl,^[81] and a second one in 2009 by North et al.,^[82] that they further completed in 2010.^[83]

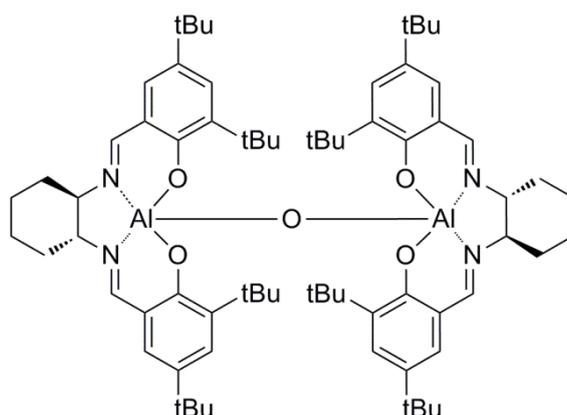


Figure 3.1. Catalyst used by North et al. for their kinetic study^[83]

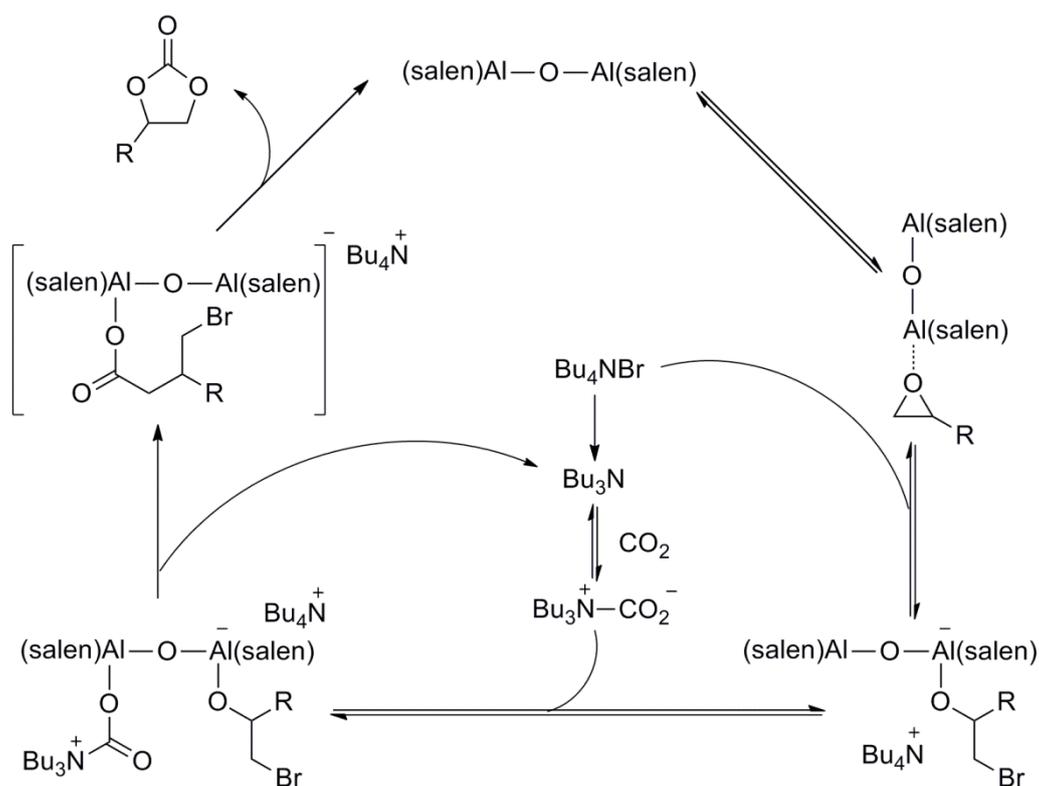
Through different kinetic experiments, they were able to determine that the reaction rate is first order in catalyst, epoxide and carbon dioxide; but surprisingly second order dependant in co-catalyst (tetrabutylammonium bromide: TBAB).

$$Rate = k[epoxide][CO_2][catalyst][Bu_4NBr]^2$$

The second order in TBAB implies that two molecules of TBAB are involved in the catalytic cycle. One role of nucleophiles such as DMAP or TBAB is known to be the opening of the epoxide ring to form an alkoxide.^[84] Through GC-MS, they were able to show that tributylamine was also present in solution. Therefore, they suggested that the second

equivalent of TBAB was transformed in tributylamine, and determined this proceeds through a S_N2 reaction (the reverse Menshutkin reaction). This reaction should lead to the formation of butyl bromide, that they were however unable to detect through GC-MS. They suspected butyl bromide to react with another component of the reaction giving a non-volatile by-product. They also argued that the concentration of tributylamine generated in-situ was extremely low.

Their kinetic data showed that the reaction had an induction period when the concentration of TBAB was low, which was not present anymore if they were adding tributylamine to the reaction. In presence of tributylamine, they detected that the reaction was not anymore second order in TBAB, but only with an order of 0.66. Therefore, they suggested the following catalytic cycle (Scheme 3.1.), in which the second equivalent of tetrabutylammonium bromide is used to form tributylamine, which then reacts reversibly with CO_2 to form a carbamate salt. This salt and the epoxide coordinate to the aluminium salen catalyst and react together. The bimetallic compound shows high activity as the epoxide and the CO_2 moiety are brought close to each other.



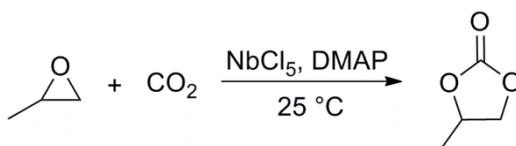
Scheme 3.1. Proposed catalytic cycle by North et al.^[83]

The interaction of CO₂ with tetrabutylammonium chloride (TBAC) was also suspected by Bu et al. through the observation of one absorbance peak at 1750 cm⁻¹ through IR spectroscopy, which could correspond to a carbamate adduct.^[85] On the contrary, when using a ZnCl₂/nBu₄NI system, Kisch et al. determined that their reaction was first order in catalyst, epoxide, CO₂ and also in co-catalyst. In this case, they suspected that TBAI only plays a role in the opening of the epoxide.^[81]

To our knowledge, no paper has been published where the proposed intermediates were observed in-situ and/or isolated. That is what we are aiming to in this chapter.

3.2 Description of the observations

A detailed mechanistic study of the formation of propylene carbonate from propylene oxide and CO₂ was performed.



Scheme 3.2. Formation of propylene carbonate from propylene oxide and carbon dioxide

In a typical experiment 0.5 mol % of NbCl₅ and 0.5 mol % of DMAP in propylene oxide were reacted with carbon dioxide. The formation of different intermediates was followed by in-situ IR spectroscopy by focusing in the range from 1600 to 1700 cm⁻¹. In this range comes the asymmetric ring stretching (ARS) band of the pyridine ring contained in DMAP (1603 cm⁻¹).^[86]

3.2.1 Observations with a 1:1 NbCl₅:DMAP ratio

At first DMAP (0.5 mmol), NbCl₅ (0.5 mmol) and propylene oxide (100 mmol) were added in the reactor, and reacted for several hours at room temperature.

No IR measurements were carried out for the first five minutes to allow for proper mixing of the reagents and in order to suppress artifacts arising from the presence of undissolved material on the autoclave window. After this time, two bands could be observed: one at 1601 cm^{-1} which corresponds to the ARS pyridine ring of DMAP in a propylene oxide solution, and the other one at 1621 cm^{-1} . After 10 minutes of reaction, a band grows at 1654 cm^{-1} , and the band at 1621 cm^{-1} decreases. Figure 3.2. is a typical spectrum after 15 minutes of reaction.

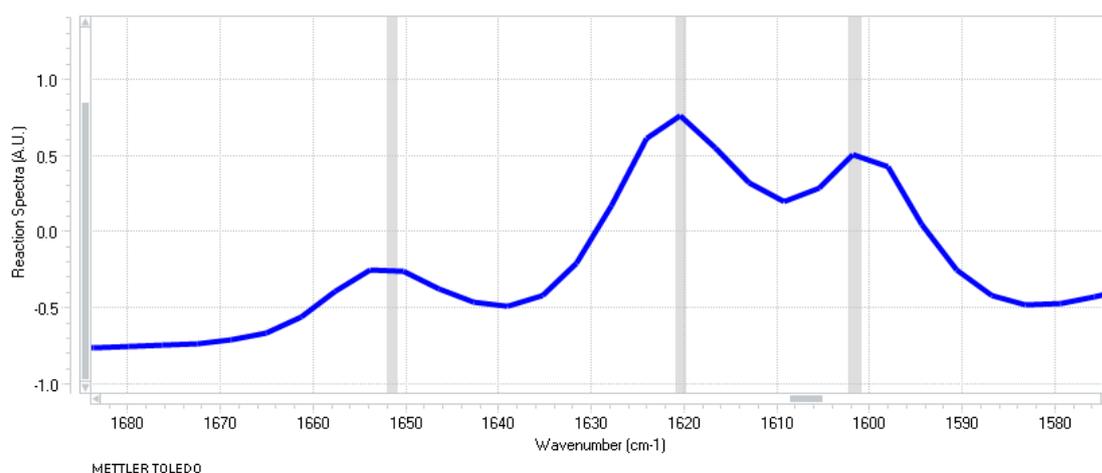


Figure 3.2. IR spectrum after 15 minutes of reaction between NbCl_5 , DMAP and PO

After around 90 minutes of reaction, the band at 1621 cm^{-1} has completely disappeared and only two bands are present: at 1601 cm^{-1} and at 1654 cm^{-1} (Figure 3.3.).

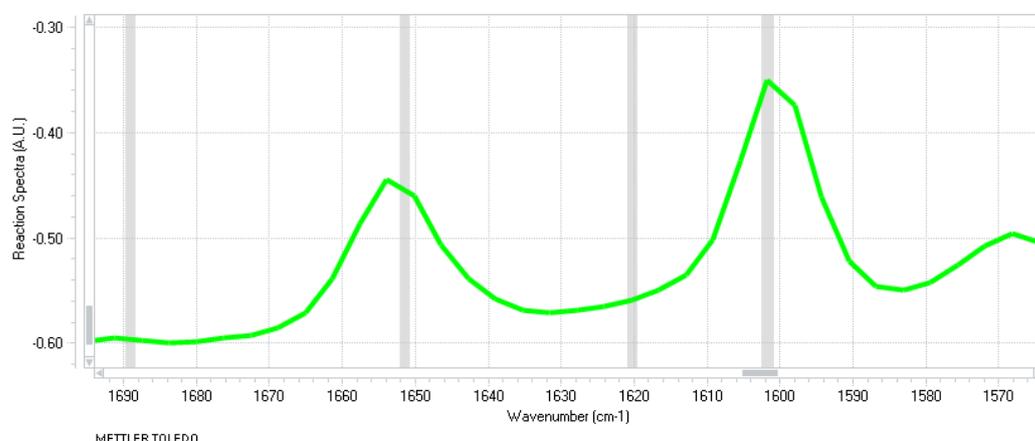


Figure 3.3. IR spectrum after 90 minutes of reaction of NbCl_5 , DMAP and PO

No other change is observed in the IR-spectra when the reaction was allowed to run for 3 h.

When CO₂ is pressed, a band at 1686 cm⁻¹ immediately appears and the formation of the propylene carbonate (PC) begins as can be observed by the growing of the band at 1810 cm⁻¹. The intensity of the band of free DMAP at 1601 cm⁻¹ decreases slightly. Apart from the growing of the band of PC at 1810 cm⁻¹, no other change is observed in the IR spectra even if the reaction was let proceed for several hours.

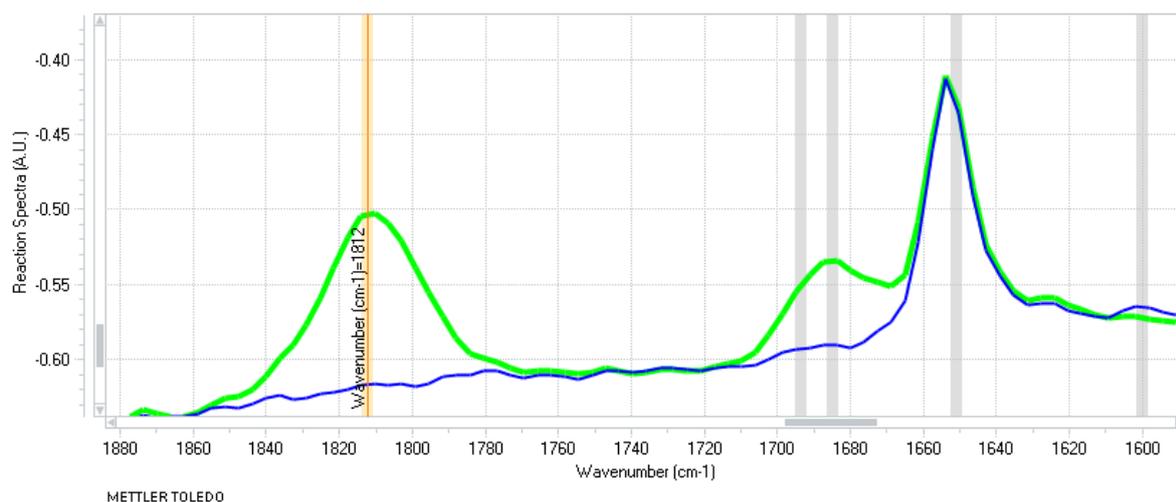


Figure 3.4. IR spectra before CO₂ is added (blue curve) and 10 minutes after CO₂ is pressurized (green curve) on a mixture of NbCl₅, DMAP and PO which has previously reacted for 90 minutes

3.2.2 Observations with a 1.5:1 NbCl₅:DMAP ratio

It was observed in chapter 2 that when the quantity of NbCl₅ exceeds the quantity of DMAP, the reaction speed for the formation of propylene carbonate was very slow. In order to explain this phenomenon, the same detailed IR-study was performed with an excess of NbCl₅: 0.75 mol % of NbCl₅ and 0.5 mol % of DMAP compared to propylene oxide.

The same trend that with 1:1 NbCl₅:DMAP was observed with first the formation of a peak at 1621 cm⁻¹ and then its decreases while the peak at 1654 cm⁻¹ grows. The difference is the absence of free DMAP in solution as the peak at 1601 cm⁻¹ could not be observed. When CO₂ is pressed, the peak at 1686 cm⁻¹ appears, but the speed of formation of propylene carbonate is very low.

To summarize, four different characteristic bands corresponding to four different species could be detected:

Table 3.1. Summary of the bands observed by IR spectroscopy

| ν (cm^{-1}) | Observations |
|----------------------------|--|
| 1601 | Band characteristic of free DMAP. Only observed for a 1:1 NbCl_5 :DMAP ratio. |
| 1621 | Specie forms immediately in presence of DMAP, NbCl_5 and PO. Its concentration slowly decreases until being null after 90 minutes of reaction. |
| 1654 | Specie starts forming almost immediately in presence of DMAP, NbCl_5 and PO. Its concentration rises until the species at 1621 cm^{-1} has disappeared. |
| 1682 | Specie appears immediately when CO_2 is pressurized over the DMAP, NbCl_5 , PO mixture after it had reacted for 90 minutes. |

In the case of an excess of NbCl_5 as compared to DMAP, only three species are detected: no free DMAP is observed. Apart from this element, the general trend is exactly the same regardless of the ratio between DMAP and NbCl_5 .

A detailed study was performed to characterize the three unknown species.

3.3 Study of the formation of the specie with a characteristic band at 1621 cm^{-1}

3.3.1 Control experiment

On this first part of this mechanistic study, NbCl_5 , DMAP and propylene oxide are in contact under argon, in absence of CO_2 . The fastest reaction expected is the acid/base reaction between DMAP and NbCl_5 . This reaction should occur independently of the solvent used, therefore it was first studied in an organic solvent.

Under a protective atmosphere, DMAP was dissolved in dry dichloromethane. After five minutes NbCl_5 was added to the solution. The development of the IR intensities of the signals belonging to the ARS region was monitored (Figure 3.5.). The peak at 1601 cm^{-1} relative to free DMAP disappears immediately following the addition of NbCl_5 to yield a new peak at 1625 cm^{-1} which can be attributed to the formation of a DMAP- NbCl_5 adduct. This is in good agreement with the IR frequencies reported in the literature for other DMAP-transition metals complexes such as $\text{Cd}(\text{NCO})_2(4\text{-dmap})_2$ (ARS at 1622 cm^{-1} , KBr pellet) or $\text{Hg}_{1.5}(\text{SCN})_3(4\text{-dmap})_2$ (ARS at 1625 cm^{-1} , KBr pellet).^[86]

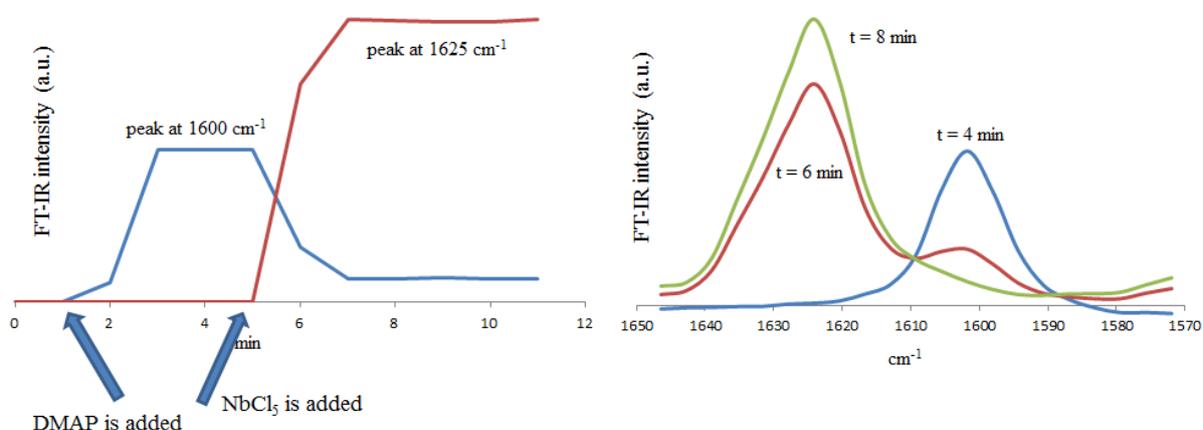


Figure 3.5. (Left) Time development of IR intensities relative to the ARS for DMAP (1601 cm^{-1}) and for the DMAP- NbCl_5 complex (1625 cm^{-1}). (right) The IR spectrum of the ARS region at different times; $t = 4\text{ min}$ (blue), $t = 6\text{ min}$ (red), $t = 8\text{ min}$ (green).

3.3.2 Synthesis of the DMAP- NbCl_5 species

This DMAP- NbCl_5 complex was synthesized and isolated. When DMAP and NbCl_5 were mixed together under argon in dry dichloromethane, a violet suspension was immediately obtained from which complex **3** could be isolated as a dark purple solid. It was characterized as being a complex between one molecule of NbCl_5 and one molecule of DMAP (Figure 3.6.). **3** is highly air and moisture sensitive and in its solid form exhibits the ARS IR band from the pyridine moiety at 1616 cm^{-1} in accordance with the band observed at 1621 cm^{-1} in a propylene oxide solution.

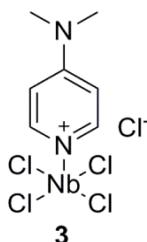
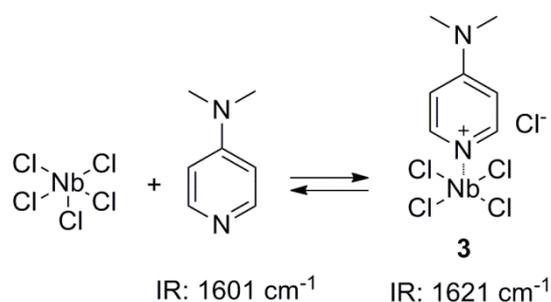


Figure 3.6. Complex **3**

Therefore, the first reaction occurring is an acid/base reaction:



Scheme 3.3. Formation of complex **3**

3.4 Study of the formation of the specie with a characteristic band at 1654 cm⁻¹

3.4.1 Isolation of the species

After 90 minutes of reaction of NbCl₅, DMAP and propylene oxide, **3** has totally disappeared and the band at 1654 cm⁻¹ has reached his maximum. Our attempts to stop the reaction at this time and to recover a compound remained unsuccessful. Indeed, after evaporation of the solvent, a sticky oily air sensitive solid was obtained, whose recrystallization remained unsuccessful.

By replacing NbCl₅ by MgCl₂, no reaction could be observed when performed at room temperature. However, when the reactor was warmed to 60 °C, a band at 1654 cm⁻¹ grew. When the band reaches its maximum, the reactor was cooled down, and a yellow solution was recovered, from which compound **4** could be precipitated as a white solid upon addition of acetone.

3.4.2 Characterization of complex 4

Complex 4 contains one molecule of propylene oxide bonded to the pyridine-ring of DMAP. It could be fully characterized through NMR (1D and 2D) and mass spectroscopy.

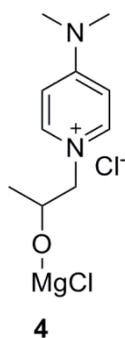


Figure 3.7. Complex 4

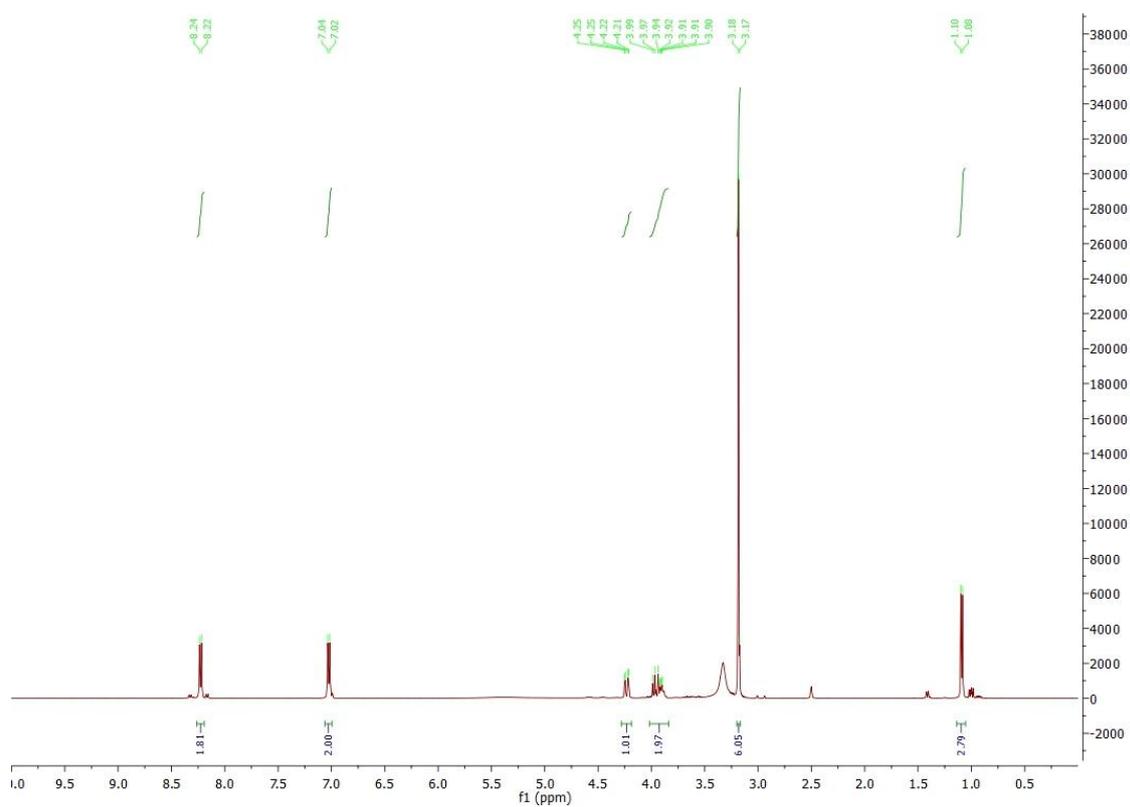


Figure 3.8. ^1H NMR of complex 4

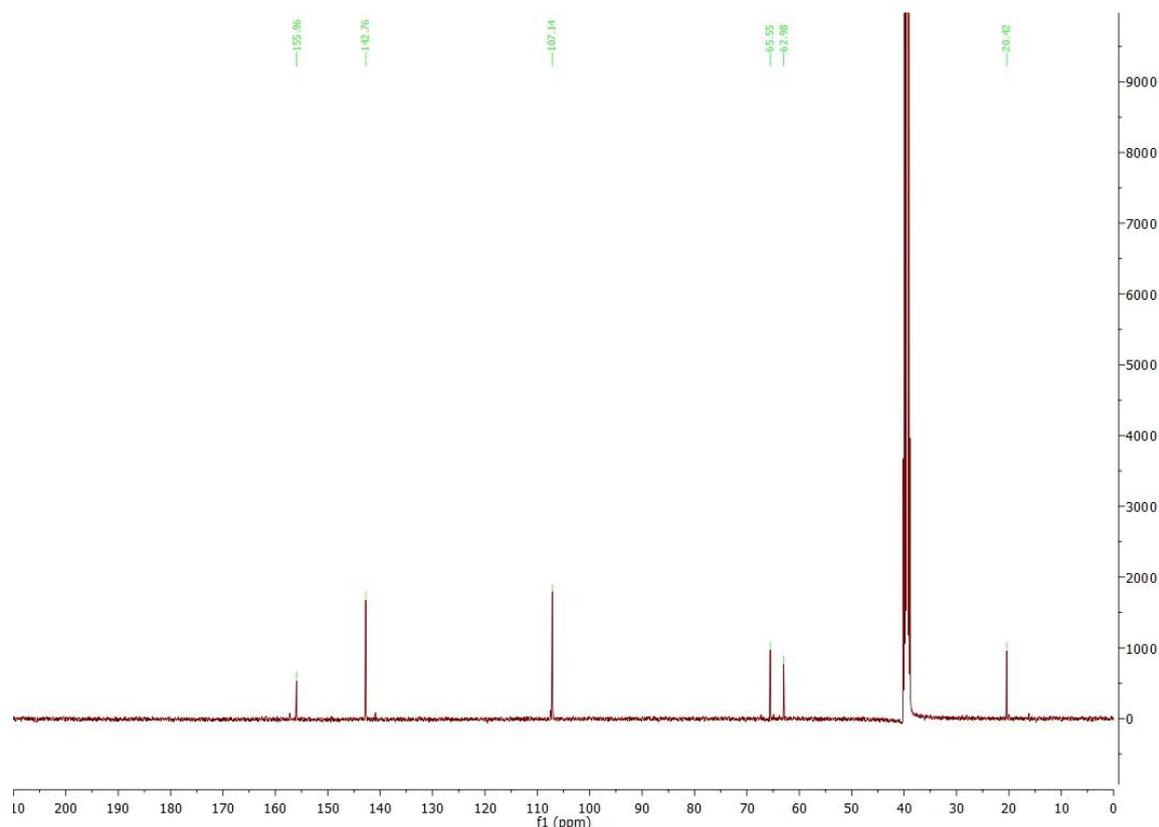


Figure 3.9. ^{13}C NMR of complex **4**

^1H and ^{13}C NMR (Figure 3.8. and Figure 3.9.) show the presence of protons and carbons belonging to DMAP molecule and to the epoxide.

The protons of the aryl ring of DMAP are shifted, as compared to a sample of pure DMAP measured in d_6 -DMSO. They are encountered at respectively 8.23 and 7.03 ppm, whereas the protons in a DMAP molecule exhibits peaks at 8.09 and 6.57 ppm. The protons of the methyl rest are shifted from 2.93 to 3.18 ppm. The influence is more marked on the epoxide protons and carbons. The loss of the aromaticity and the influence of the basic molecule of DMAP explains the large changes in the shifts. The CH protons are shifted from a range of 2.5 to 3.0 ppm at a range in between 3.8 and 4.3 ppm, and the carbons from 47.9 and 48.1 ppm to 63.0 and 63.5 ppm. The HMBC NMR spectrum demonstrates the bonding of the epoxide to the aryl ring through the sterically less encumbered carbon of the epoxide.

Complex **4** exhibits a strong IR-band at 1646 cm^{-1} in its solid form, in accordance with the band at 1654 cm^{-1} observed in propylene oxide solution. It is in the range of other 1-alkyl-4-dimethylaminopyridinium salts reported in literature.^[87] The mass spectroscopy gives the highest m/z at 181 g/mol, which fits with complex **4** without the Mg moiety.

A proof of the connectivity between the oxygen and the magnesium atoms could not be observed by the different analytic method used to characterize the complex. Nevertheless, by hydrolyzing complex **4** with water, a complex is obtained which exhibits an extra-hydrogen at 5.20 ppm. It was characterized by 1D and 2D NMR as complex **5**.

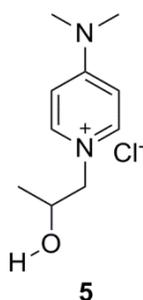
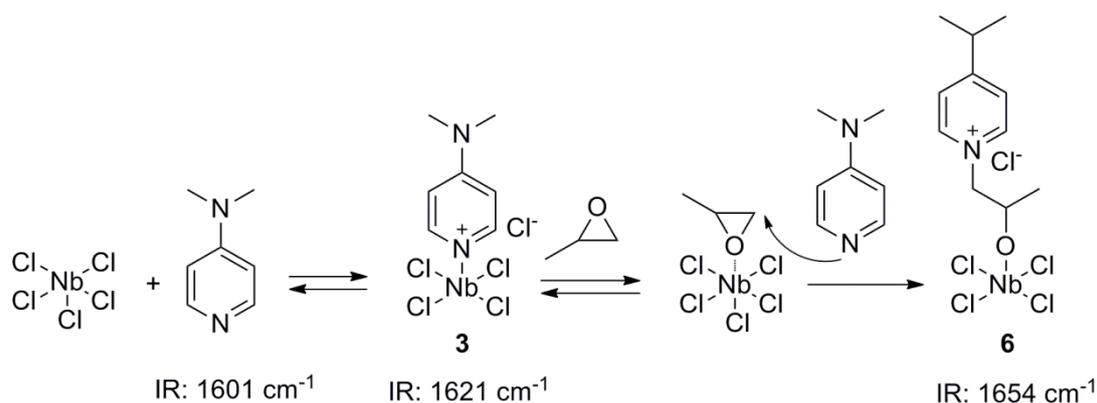


Figure 3.10. Complex **5**

From this it can be concluded that complex **6** is the complex which exhibits a band at 1654 cm^{-1} . It is, to our knowledge, the first time that such an intermediate was isolated and characterized.

The behavior of NbCl_5 , DMAP and propylene oxide in solution could be summarized by the following Scheme 3.4.:



Scheme 3.4. Equilibrium between unbounded DMAP, **3** and **6**

NbCl_5 and DMAP react immediately in an acid-base reaction forming complex **1**, which is in equilibrium with the complex formed by NbCl_5 and the epoxide. Unbounded DMAP attacks the activated epoxide in an irreversible reaction to form complex **6**.^[84a, 84d, 88]

3.5 NMR study of the equilibrium between unbounded DMAP, **3** and **6**

An NMR study of the observed equilibrium between free DMAP, **3** and **6** was performed. 0.4 mL from a solution of 0.5 mol % of NbCl₅ and 0.5 mol % of DMAP in propylene oxide were added to 0.1 mL of dry CDCl₃, and NMRs were recorded every 5 minutes during 90 minutes.

The NMR spectra exhibit huge peaks corresponding to propylene oxide at 0.79 (d, J = 5.3 Hz, 3H, CH₃), 1.87 (m, 1H, OCH₂), 2.18 (m, 1H, OCH₂) and 2.44 (m, 1H, OCHCH₃) ppm. However, by focusing in the range from 5 to 9 ppm, two groups of three peaks could be observed.

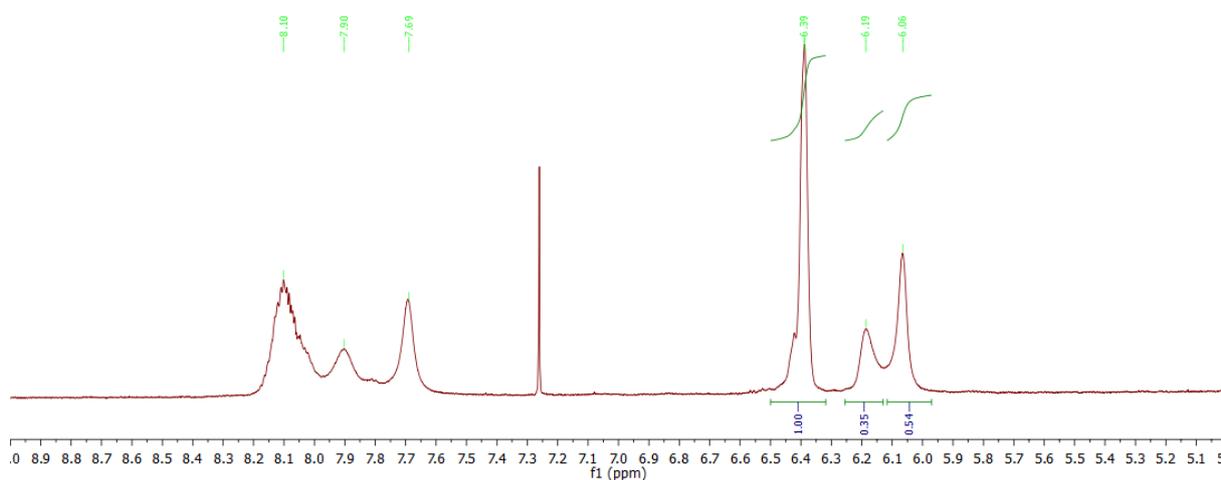


Figure 3.11. NMR spectra of a sample with a 1:1 ratio of NbCl₅:DMAP after 20 minutes of reaction in propylene oxide

By comparison to a blank sample of DMAP in propylene oxide, free DMAP could be assigned to the peaks at 7.69 ppm and 6.06 ppm. Throughout the kinetic study, it was observed that the intensities of the peaks at 8.10 and 6.39 ppm are decreasing while the intensities of the ones at 7.90 and 6.19 ppm are increasing. Based on our precedent IR observations, it can be concluded that the peaks decreasing in intensity belong to complex **3** (8.10 and 6.40 ppm) and the one increasing to complex **6** (7.98 and 6.18 ppm). With the relative intensity of the

peaks at 6.40, 6.18 and 6.05 ppm, the percentage of each species in solution could be estimated. The results are presented in Figure 3.12.

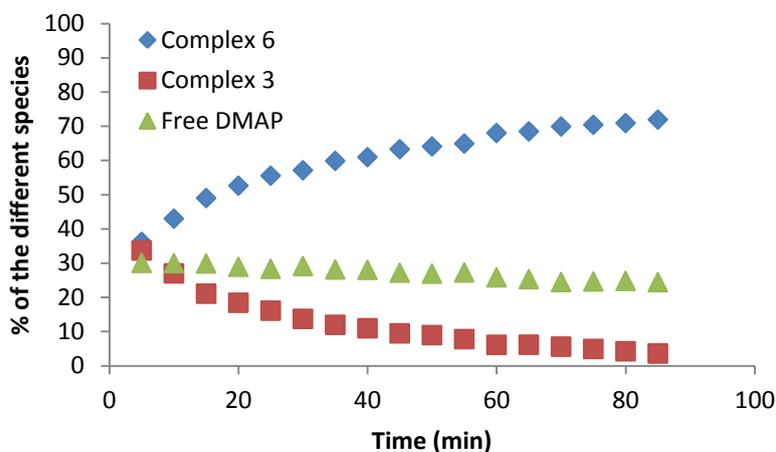


Figure 3.12. Relative % of complexes **3**, **6** and free DMAP in a PO solution with a 1:1 NbCl₅:DMAP ratio

The percentage of free DMAP is staying relatively constant over 90 minutes. The concentration of **4** decreases very quickly in the first twenty minutes, and then more slowly. After 90 minutes its concentration is below 5 % and almost not detectable anymore by ¹H NMR. Another measurement was performed after 240 minutes, the solution now contains 21 % of free DMAP and 79 % of **6**; **4** was not be observed any more.

Another experiment was conducted with a 1:5:1 ratio of NbCl₅:DMAP, using 0.75 mol % of NbCl₅ and 0.5 mol % of DMAP as compared to PO. NMR spectra were recorded every 2 minutes from 5 to 90 minutes after the start of the reaction. The results are presented in Figure 3.13.

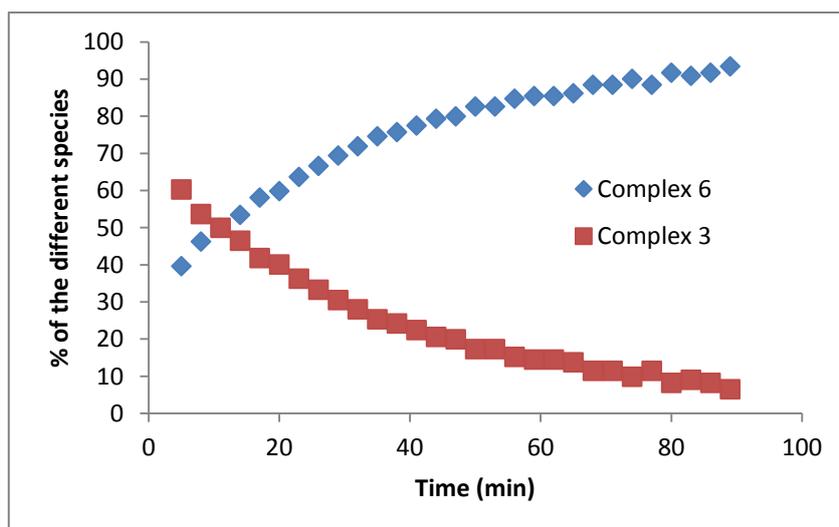


Figure 3.13. Relative % of complexes **3**, **6** and unbounded DMAP in a PO solution with a 1:1 NbCl₅:DMAP ratio

In this case, only complexes **3** and **6** were observed. The presence of free DMAP in solution was never detected. The concentration of **3** decreases slowly and it was almost not detectable after 90 minutes, being entirely transformed into complex **6**.

3.6 Compound **6** as an intermediate in the formation of propylene carbonate from propylene oxide and CO₂

The role of **6** as an intermediate of the reaction was investigated.

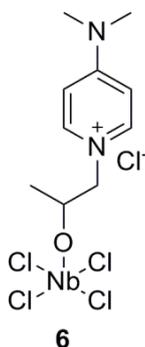


Figure 3.14. Complex **6**

A reaction is performed at room temperature with 1 mol % NbCl₅ and 1 mol % of DMAP in propylene oxide where 10 bars CO₂ are pressured after 10 minutes. By observing the

characteristic band of propylene carbonate at 1810 cm^{-1} , it was observed that an induction time of around 90 minutes was needed before the formation of propylene carbonate reaches its constant rate.

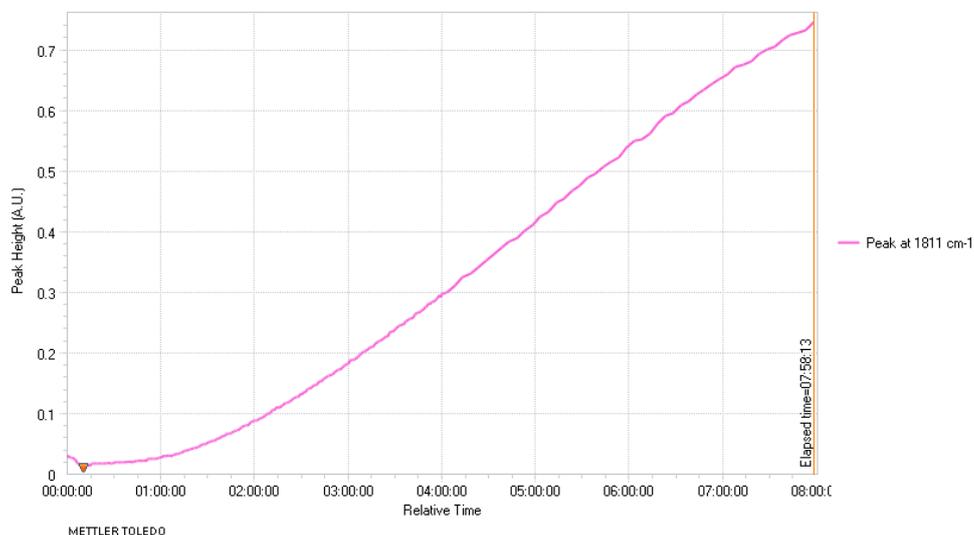


Figure 3.15. Evolution of the formation of propylene carbonate when CO_2 is added after 5 minutes with the $\text{NbCl}_5/\text{DMAP}$ system at room temperature

This experiment was repeated with 10 bars of CO_2 pressed after different reaction times. The formation of propylene carbonate was followed during the first 20 minutes after which CO_2 was pressed, and the starting rate of its formation was recorded. A linear fitting was performed, and the results are shown in Table 3.2.

Table 3.2. Slope of the starting rate of formation of propylene carbonate related to the time after which CO_2 is added

| Time (min) | Slope (a. u.) |
|------------|---------------|
| 10 | 0.0001 |
| 45 | 0.0003 |
| 90 | 0.0014 |
| 180 | 0.0016 |
| 240 | 0.0014 |

If CO_2 is pressed during the first 50 minutes, an induction period was observed. The reaction starts at constant rate after around 90 minutes. On the contrary, if CO_2 is pressed after 90

min, when almost all the intermediate **3** has converted to complex **6**, propylene carbonate starts forming immediately. The starting rate remains unchanged even for longer reaction times. Therefore, these experiments suggest that **6** is an intermediate in the formation of propylene carbonate from propylene oxide and CO₂.

3.7 Formation of a new intermediate with CO₂

3.7.1 Formation of a new intermediate with CO₂

The following experiment was conducted: 0.5 mol % of NbCl₅ and 0.5 mol % of DMAP compared to propylene oxide were reacted for 90 min under argon, before CO₂ was added. When CO₂ is pressurized, a new band immediately appears at 1690 cm⁻¹, and the band at 1654 cm⁻¹ decreases (Figure 3.16.). The apparition of such a band assigned to a carbonyl group was already observed at 1680 cm⁻¹ for the complex (tetraphenylporphinato)Aluminium Alkoxide upon introduction of CO₂.^[89] After the initial drop/increase, an equilibrium is reached where the quantities of **6** and of this new compound stay stable. Propylene carbonate starts to form immediately at a constant rate.

In order to be sure that this compound is CO₂-dependant, an experiment was performed where the pressure of CO₂ was varied. Starting from 0 bar of CO₂ (and 1 atmosphere of argon), 2 bar of CO₂ were pressurized and the pressure was kept constant for 7 minutes. Then, 2 more bar were pressed, and the pressure was again held for 7 minutes. This step was repeated until the pressure inside the reactor reached 9 bar (corresponding to 8 bar of CO₂). Then the pressure was released following the same trend (Figure 3.17.). As can be observed, the band at 1690 cm⁻¹ grows immediately when CO₂ was pressed, and stabilizes after a couple of minutes. When more CO₂ is pressed, the intensity of the band increases again. Over 4 bar, the growth becomes limited, more CO₂ pressure does not contribute to much increase in the intensity of the band. Exactly the same trend is observed when the pressure of CO₂ is decreased, proving that the reaction is reversible.

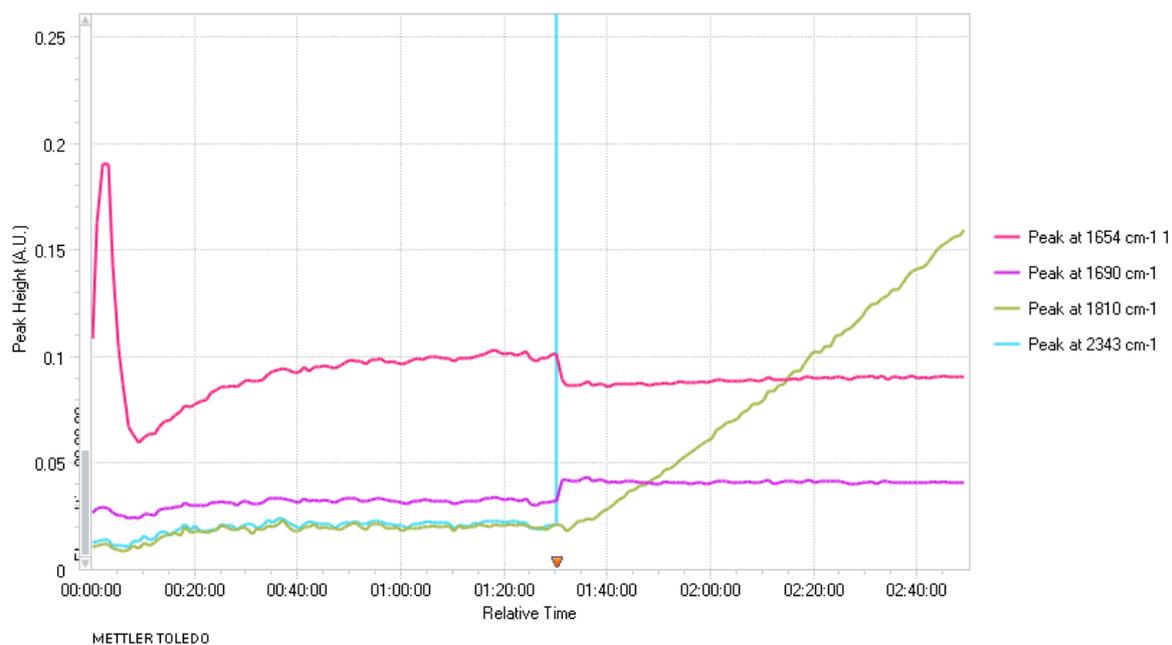


Figure 3.16. Evolution of specie 6 (pink curve), propylene carbonate (brown curve) and of a new specie with a characteristic band at 1690 cm^{-1} (purple curve) upon addition of CO_2 (blue curve) with the $\text{NbCl}_5/\text{DMAP}$ system at room temperature

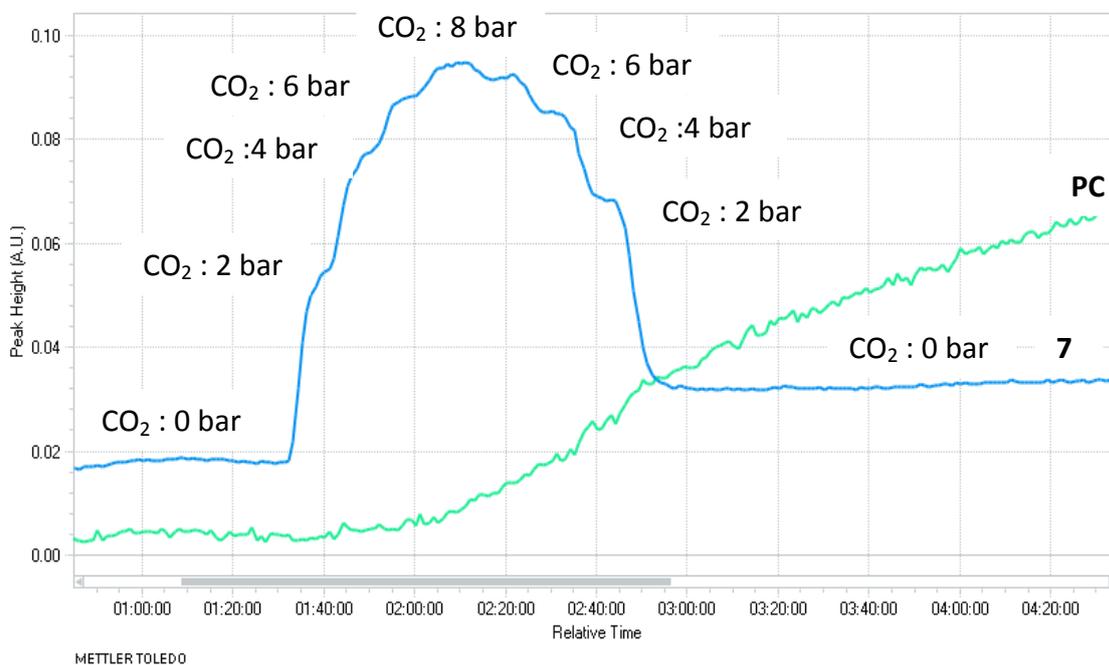


Figure 3.17. Evolution of formation of the band at 1690 cm^{-1} (blue curve) and of the formation of propylene carbonate (green curve)

Therefore, this CO₂-containing compound is probably the compound resulting from the CO₂ insertion into the O-Nb bond of complex **6** (Figure 3.18).^[89]

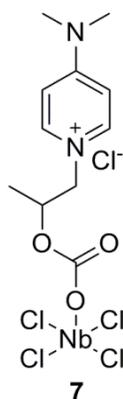
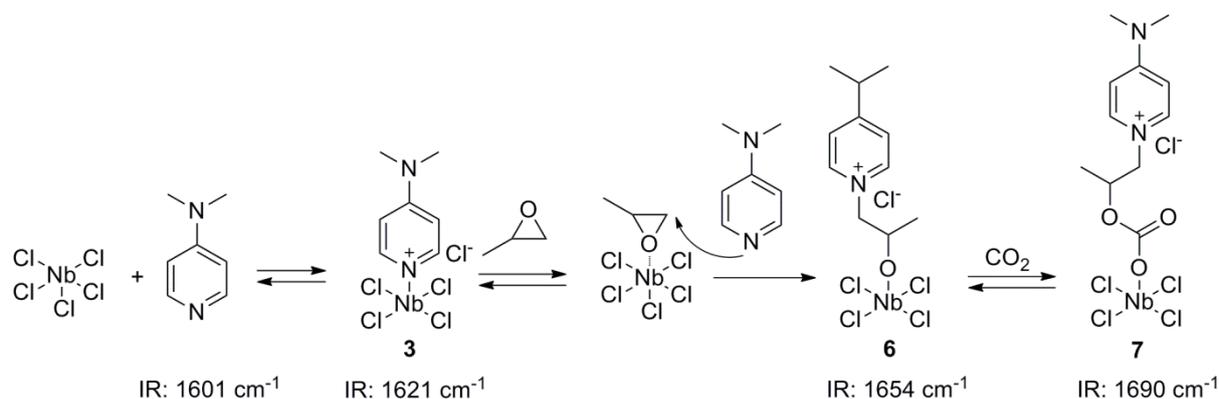


Figure 3.18. Complex **7**

This insertion step proceeds almost immediately as can be seen from Figure 3.17. Under those conditions of temperature and pressure, this step is not the rate determining step of the reaction. It is observed that the rate of formation of propylene carbonate is not influenced by the variations of CO₂ pressure. Therefore, the next step of the reaction (the liberation of the organic moiety and the ring closure) is slower than the insertion of CO₂ needed to form complex **7**.



Scheme 3.5. Formation of complexes **3**, **6** and **7**

3.7.2 NMR experiment with ¹³CO₂

NMR experiments were performed in order to observe the formation of complex **7**. DMAP, NbCl₅ and PO were mixed in an NMR tube and around 5 bar of CO₂ was pressed after

240 minutes. A 1:1.5 DMAP:NbCl₅ ratio was chosen in order to prevent the fast formation of propylene carbonate.

In the range from 5 to 9 ppm, the ¹H NMR spectra without and with CO₂ are almost identical. The only slightly change appears on the peak of DMAP at 8.01 ppm where a little shoulder is present (Figure 3.19.)

The ¹³C NMR spectrum before CO₂ is pressed show high peaks at 17 and 46 ppm corresponding to propylene oxide which is in large excess. The peaks of DMAP are observed at 38, 105, 143 and 155 ppm (Figure 3.20.). Once CO₂ is pressed, a huge peak appears at 124 ppm corresponding to free CO₂ dissolved in propylene oxide. The peaks of propylene carbonate could be detected at 17, 69, 72 and 154 ppm, the last peak being very intense due to the use of ¹³CO₂ for the reaction. The peaks of DMAP have decreased in intensity and have almost disappeared (except for the peak at 38 ppm). A new peak has appeared at 120 ppm, as well as a very broad peak at 158 ppm. The peak at 120 ppm has also been observed in absence of catalyst (see section 3.8. for a more complete discussion). The broad peak at 158 ppm might correspond to complex **7**.

The proofs from this NMR experiment are however not sufficient enough to establish any definitive conclusion.

Mechanistic study on the formation of propylene carbonate

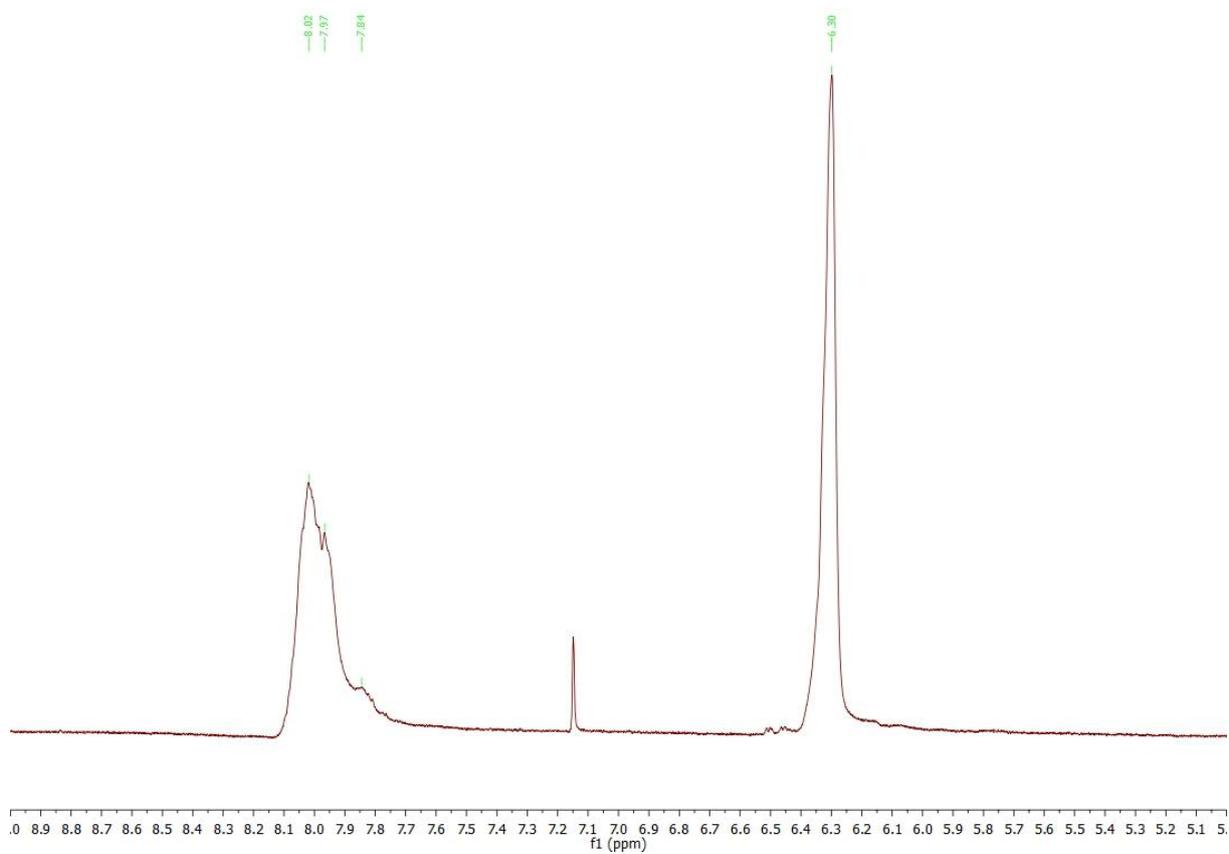
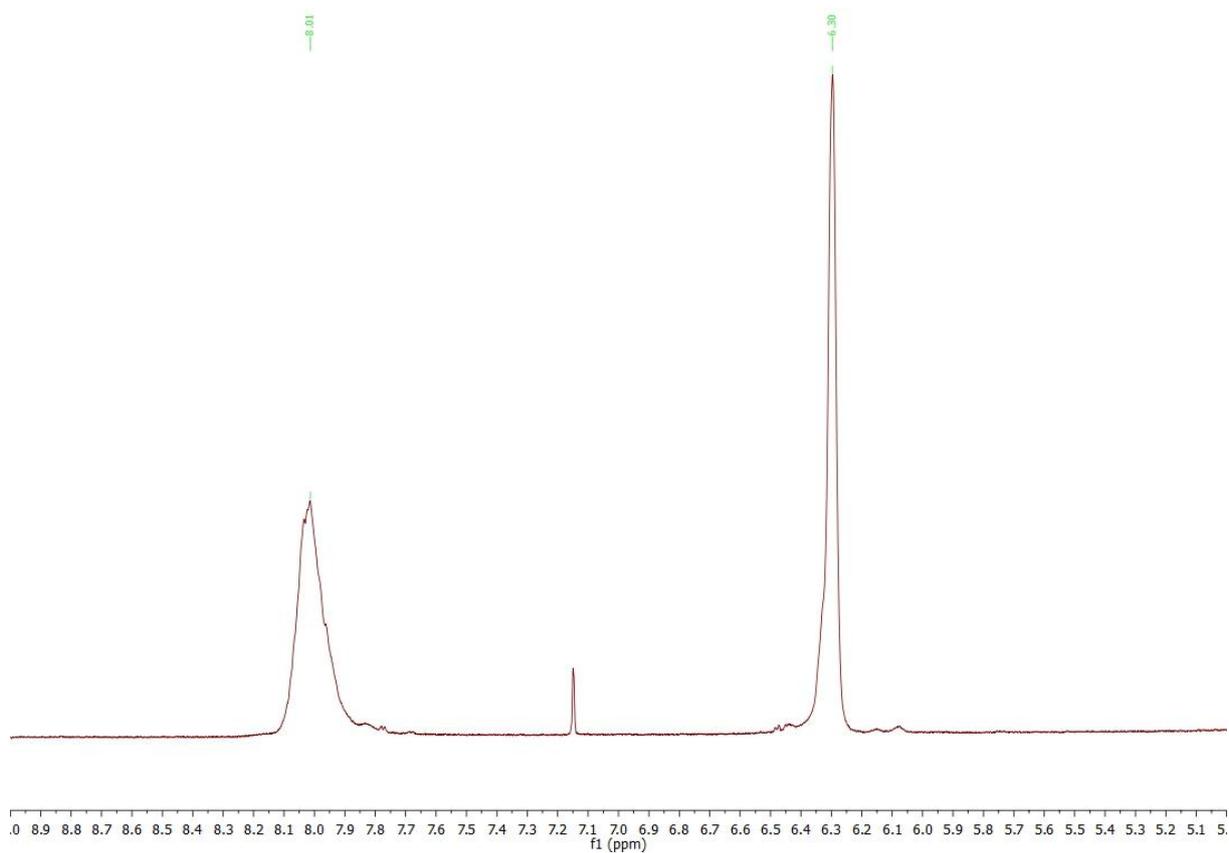


Figure 3.19. ¹H spectra before (top) and after (bottom) ¹³CO₂ is pressed

Chapter 3

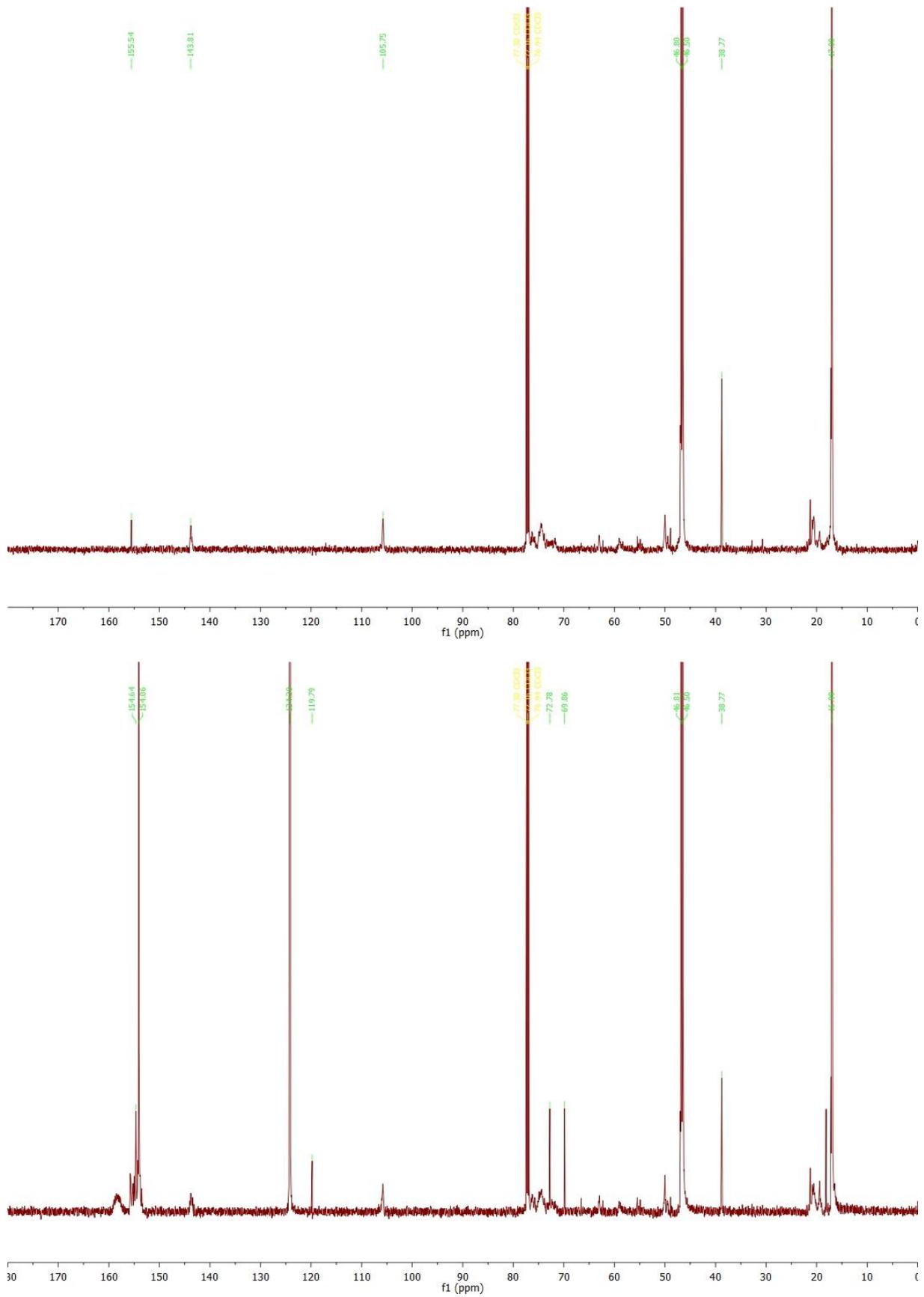


Figure 3.20. ^{13}C spectra before (top) and after (bottom) $^{13}\text{CO}_2$ is pressed

3.7.3 Control experiment with species 3

A control experiment was performed to see if complex **3** was able to insert CO₂.

DMAP and NbCl₅ were dissolved in dichloromethane, as previously observed (see section 3.2) complex **3** forms immediately. 20 bars of CO₂ were pressurized and no change in the IR spectra could be observed even after 40 hours of reaction. When the solution was recovered, it was dark violet in color and through NMR analysis it was determined it contained only free DMAP and complex **3**. Thus, complex **3** does not react with carbon dioxide, thus does not play any role in the catalytic cycle.

3.8 The role of free DMAP

As observed previously in chapter 2 and section 3.3., if more than 1.5 equivalent of NbCl₅ is used compared to DMAP, no free DMAP is present in solution and the formation of propylene carbonate proceeds slowly. Given these facts, it is expected that free DMAP has a role in the reaction. As previously described, no difference is seen between the 1:1 ratio and the 1.5:1 ratio for the formation speed of complexes **3**, **6** and **7**. The only step remaining for the formation of propylene carbonate is the liberation of the organic moiety and its ring closure. Therefore we expect free DMAP to play a role in this step.

In the literature, one can often find that one role of the nucleophile could be the activation of the CO₂ molecule, allowing its insertion into the M-O bond to be easier.^[71b, 79a, 82-83, 88a, 90] Tertiary amines do not lead to the formation of stable carbamates adduct with CO₂, as it lacks the N-H bond required to form the carbamate ion. However, Franco et al. succeeded in isolating and characterizing a DBU-CO₂ adduct.^[91] Based on this observation, the presence of a CO₂-activated DMAP specie has been suggested.^[88b, 92] Darensbourg et al. noticed the presence of a band at 1650 cm⁻¹ in presence of CO₂, DMAP and their catalyst in toluene. They suggested the formation of a zwitterionic-DMAP species which would be stabilized by the catalyst, enhancing its stability enough to make it detectable through IR spectroscopy.^[93]

Two experiments were conducted by IR: in the first one free DMAP and PO were put in the reactor and 20 bar of CO₂ were pressed; in the second one free DMAP and dry

dichloromethane were put in the reactor and 20 bar of CO₂ were pressed. In both cases, no change could be observed by in-situ IR neither to the bands of DMAP nor to the bands of CO₂.

The first experiment was also conducted by ¹³C NMR using ¹³CO₂. Upon a ¹³CO₂ pressure of around 5 bar, new peaks could be detected both in ¹H (at 6.30 and 7.89 ppm) and ¹³C NMR (at 120 ppm), however with very low intensity (see Figures 3.21. and 3.22.) The new peaks in ¹H NMR seem to come from a DMAP-containing specie as they possess the same multiplicity as the peaks of DMAP at 5.89 and 7.52 ppm (doublets). A 2D NMR experiment (HMBC) was performed, and no correlation was detected between these peaks and the peak at 120 ppm in ¹³C NMR. However, the intensities of the peaks were so low that it is possible that the NMR was unable to detect any correlation even if they existed. Those new peaks might come from a CO₂-DMAP zwitterionic adduct, however there are not enough elements to assure this assumption. It might also come from interactions between the epoxide and DMAP, or between the epoxide, DMAP and CO₂.

Our precedent observations showed that complex **7** forms immediately when CO₂ is pressed, in presence or in absence of free DMAP. Therefore, our thought is that free DMAP does not interact directly with CO₂, but rather with complex **7**.

Mechanistic study on the formation of propylene carbonate

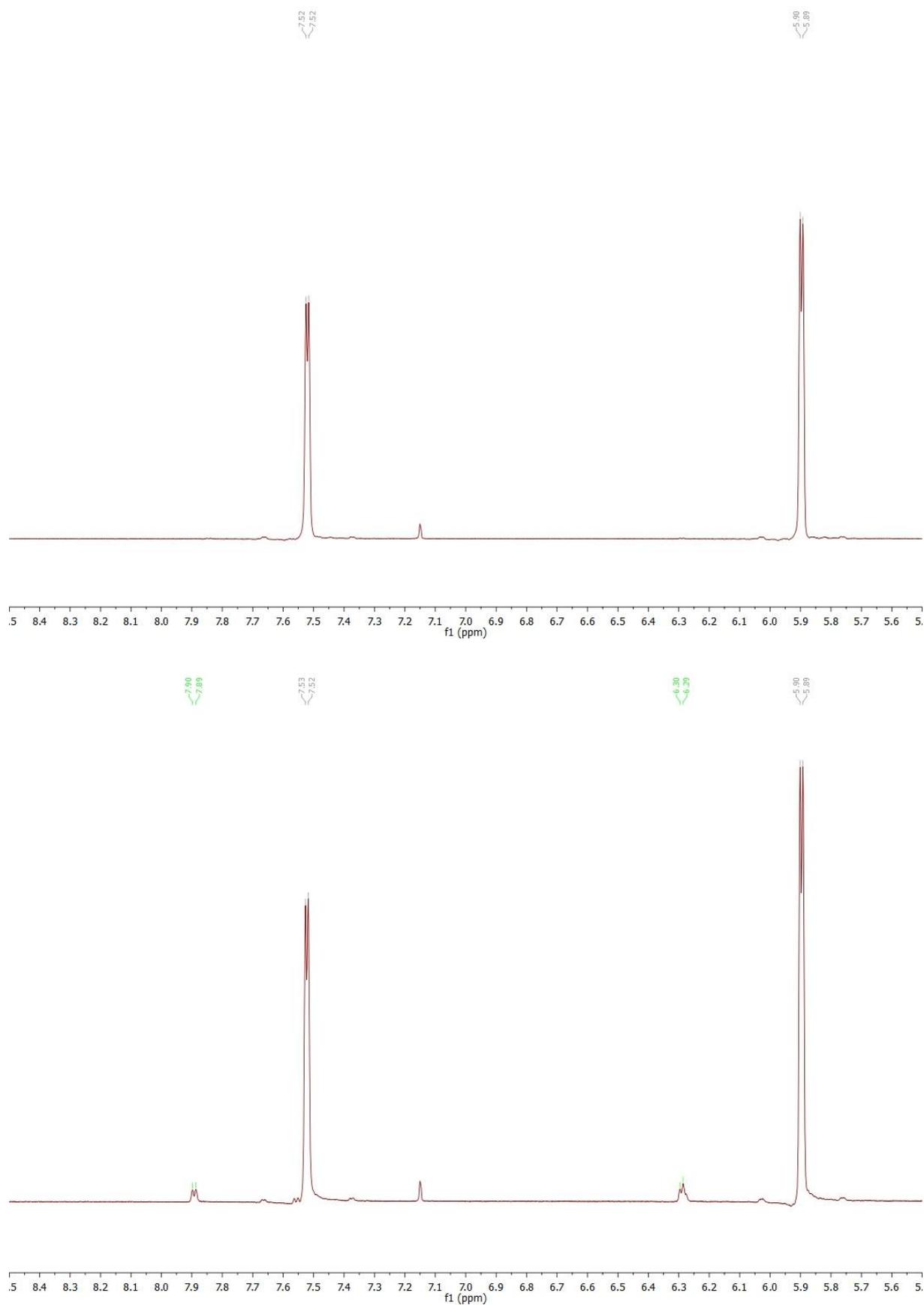


Figure 3.21. ^1H spectra before (top) and after (bottom) $^{13}\text{CO}_2$ is pressed

Chapter 3

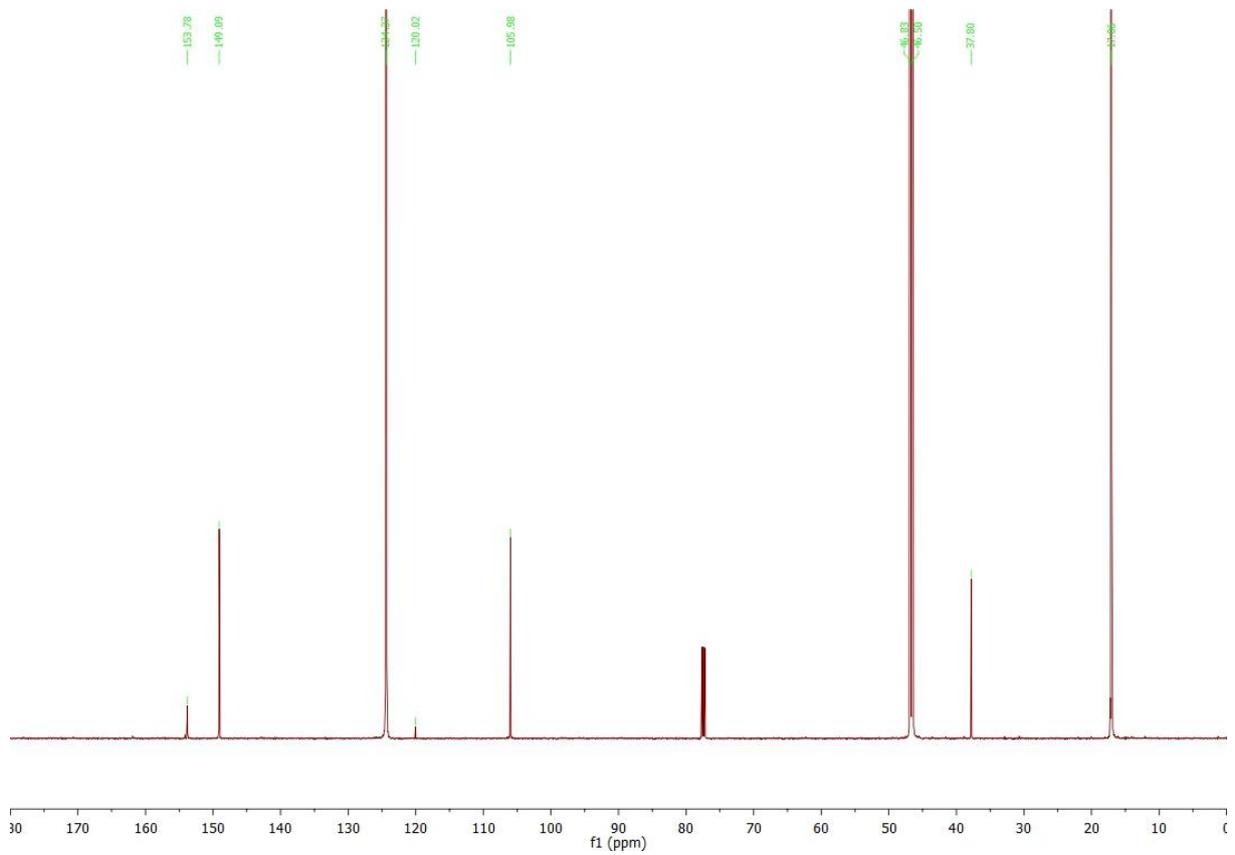
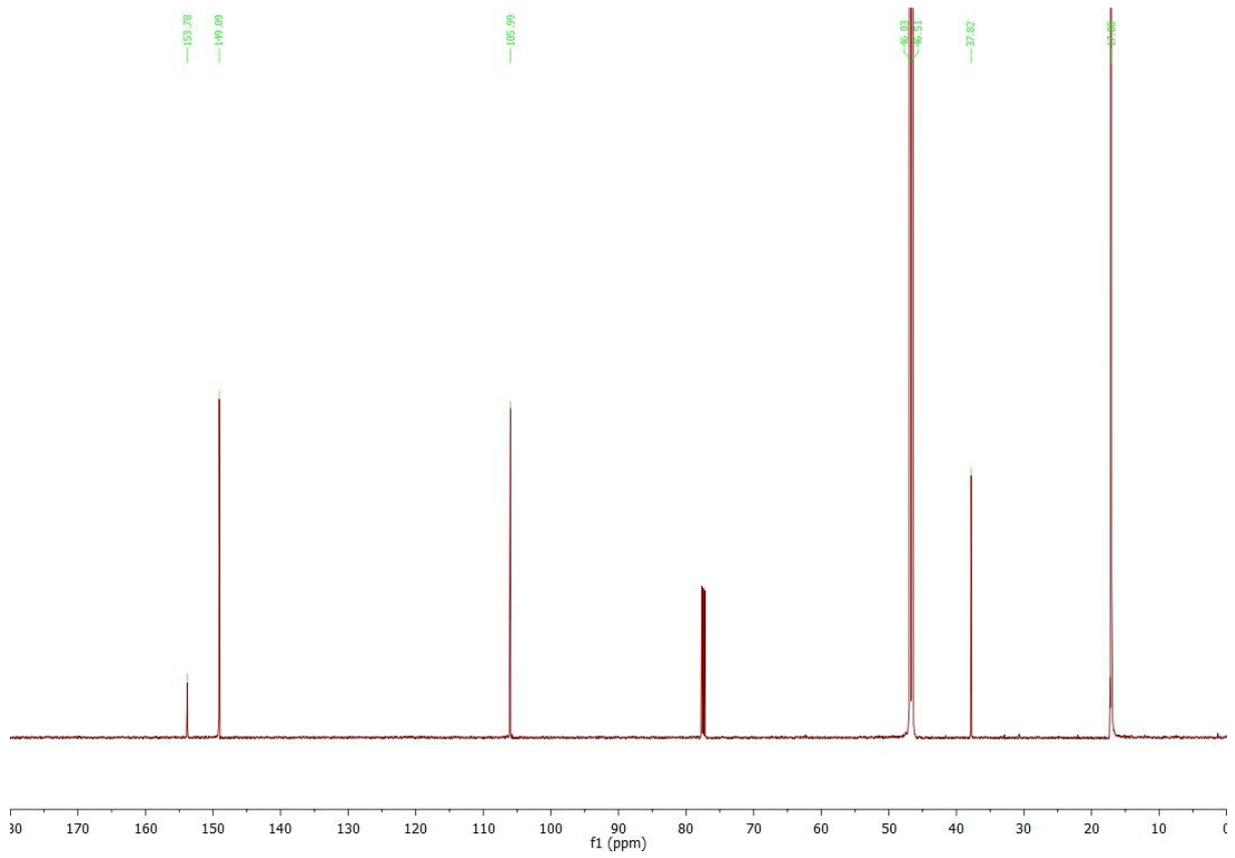
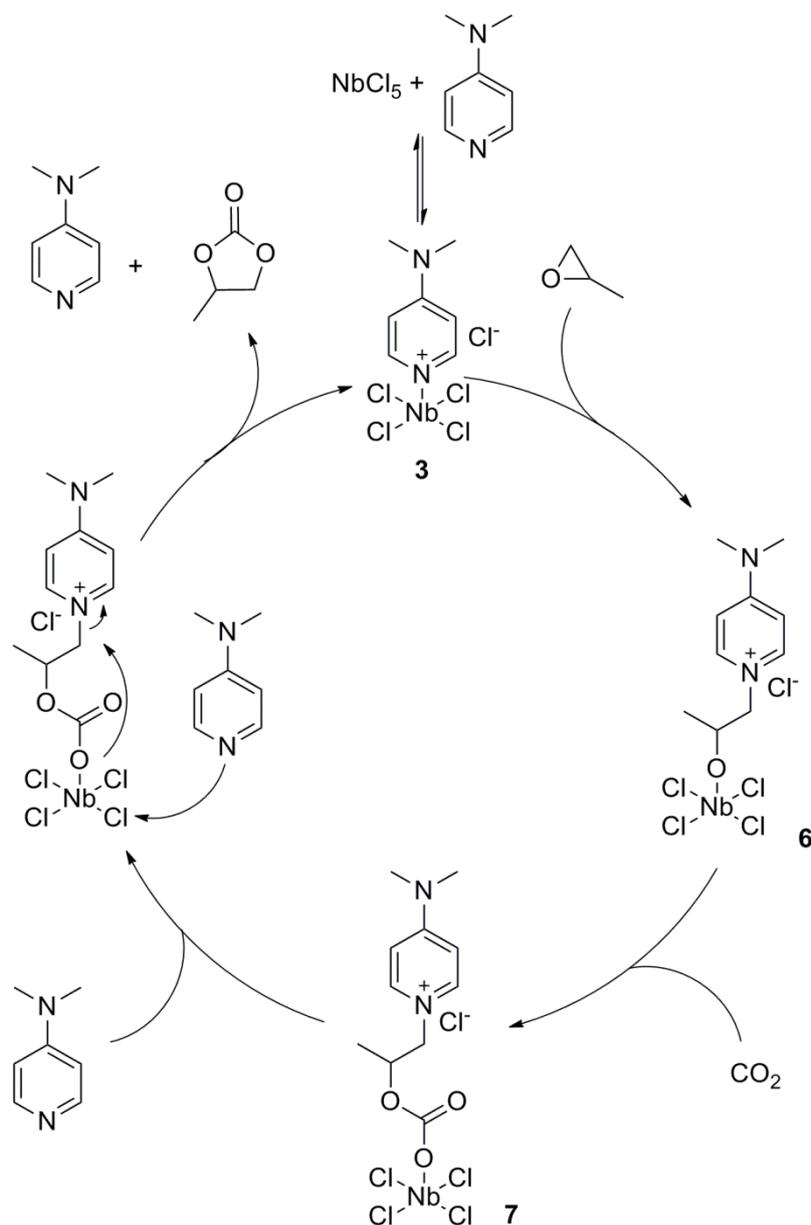


Figure 3.22. ^{13}C spectra before (top) and after (bottom) $^{13}\text{CO}_2$ is pressed

3.9 Proposed catalytic cycle

Based on all the elements observed above, the following catalytic cycle is proposed:



Scheme 3.6. Proposed catalytic cycle for the formation of propylene carbonate from propylene oxide and CO₂ using NbCl₅/DMAP as catalyst

In a first step, specie **6** is forming. It results in an equilibrium between the unbounded molecule of DMAP, **3** and **6**. Then, CO₂ inserts into the Nb-O bond of complex **6** to form complex **7**. Free DMAP is then necessary to release the cyclic carbonate. We believe that DMAP interacts with the metal, promoting the release. The ring closure is then immediate as the molecule is thermodynamically more stable in its cyclic form than in its open form.

3.10 Influence of different parameters over the starting rate of formation of propylene carbonate

3.10.1 Influence of carbon dioxide pressure

0.5 mol % of NbCl₅, 0.5 mol % of DMAP compared to propylene oxide were stirred under 1 atmosphere of argon during 180 minutes. After this time, different pressures of CO₂ were pressurized in the reactor, and the formation of propylene carbonate was followed during 20 minutes through the band at 1810 cm⁻¹. The slope of the starting rate of formation propylene carbonate are measured and compiled in Table 3.3.

Table 3.3. Influence of carbon dioxide pressure over the starting rate of formation of propylene carbonate

| CO ₂ pressure (bar) | Slope (a. u.) |
|--------------------------------|---------------|
| 2 | 0.0015 |
| 5 | 0.0016 |
| 10 | 0.0018 |

As can be observed from Table 3.3., the pressure of CO₂ has practically no influence over the formation rate of cyclic carbonate. This confirms the observation made during the catalysis experiment at 50 °C (see section 2.5) in which the influence of the CO₂ pressure could only be noticed for pressures below 3 bar.

3.10.2 Influence of the propylene oxide concentration

For each experiment 135 mg (0.5 mmol) of NbCl_5 and 61 mg (0.5 mmol) of DMAP were reacted in a propylene oxide/dichloromethane mixture. Those quantities correspond to 0.5 mol % compared to propylene oxide if the solvent is pure propylene oxide. Tetrahydrofuran would have been a more suitable solvent as it is chemically closer to propylene carbonate than dichloromethane is; however NbCl_5 was reported to promote the polymerization of THF.^[94]

The quantities of propylene oxide were varied from 2 to 6 mL, and dichloromethane was added to reach a total volume of solvent of 7 mL. When less than 4 mL of propylene oxide was used, the band at 1810 cm^{-1} was not detectable until an important quantity of propylene carbonate had formed. Therefore, it was impossible to determine the starting slope of its formation for those volumes. The results are presented in Table 3.4.

Table 3.4. Influence of propylene oxide concentration over the starting rate of formation of propylene carbonate

| V_{PO} (mL) | PO concentration (M) | k_{obs} (a. u.) |
|----------------------|----------------------|--------------------------|
| 4 | 8.1 | 0.0012 |
| 5 | 10.2 | 0.0016 |
| 6 | 12.2 | 0.0019 |

The plot of k_{obs} against $[\text{PO}]$ gives a linear correlation passing through the origin (Figure 3.23.). Thus, the formation of propylene carbonate is first order in propylene oxide.

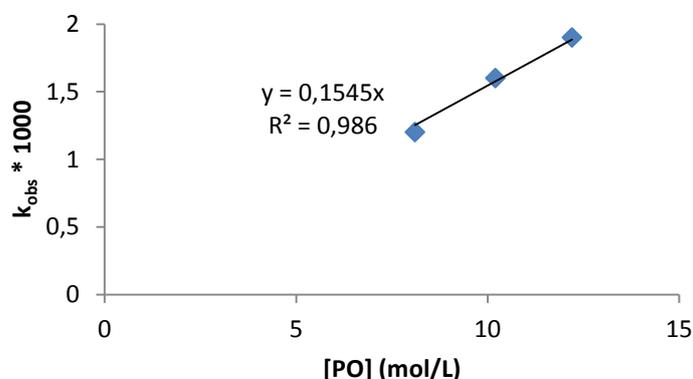


Figure 3.23. Plot of k_{obs} against $[\text{PO}]$

3.11 Conclusion

A full mechanistic study has been performed for the synthesis of propylene carbonate from propylene oxide and carbon dioxide using the catalytic system NbCl₅/DMAP. The study of the formation of the different intermediates was possible by following the asymmetric ring stretching of the pyridine ring from the DMAP moiety.

It was demonstrated that the catalytic cycle proceeds through the formation of a complex incorporating the opened form of the epoxide in between the metal catalyst and the nucleophilic co-catalyst (complex **6**). The next step is the CO₂ insertion into the metal-oxygen bond, this step proceeds immediately when CO₂ is pressurized over complex **6**. No coordination between CO₂ and the nucleophilic co-catalyst could be observed and this hypothesis could even be excluded as the CO₂ insertion proceeds the same way in presence or in absence of free DMAP in solution. The nucleophilic molecule still has a second role in helping to release the organic moiety from the metal, which then immediately cyclizes to lead to propylene carbonate.

The good activity of NbCl₅ seems to come from its ability to activate the epoxide and to immediately insert CO₂ between the metal atom and the oxygen of the epoxide.

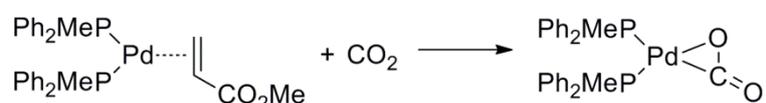
Mechanistic study on the formation of propylene carbonate

4 Palladium (0) complexes bearing phosphine or NHC ligands as precursors for reactions involving carbon dioxide

4.1 Introduction

4.1.1 Interaction of palladium (0) complexes with CO₂

The activation of CO₂ by metal (0) compounds has been performed with different transition metals, especially with Ni^[17, 19], Fe^[22]- or Nb^[18, 21a]-complexes (see section 1.3.1. for a detailed study of such complexes). However to our knowledge, only one palladium (0) complex able to activate CO₂ has been discovered up to date. Yamamoto et al. succeeded in isolating and characterizing the complex Pd(η^2 -CO₂)(PMePh₂)₂ by reacting the methyl acrylate complex Pd(PMePh₂)₂(CH₂CH₂CO₂Me) with 20 bar of CO₂ for 12 h at room temperature.^[25]



Scheme 4.1. Yamamoto's first synthesis of a coordinated CO₂ to a palladium complex^[25]

The complex, in which CO₂ is bonded through a η^2 -C,O coordination mode, is only stable in a CO₂ atmosphere. Heating it over 100 °C leads to its fast thermolysis resulting in the liberation of CO₂ and formation of a black precipitate.

The synthesis of [Ni(PCy₃)₂]₂(η -CO₂) from a nickel (0) compound and gaseous CO₂ was the first report of a CO₂ molecule bounded to a metal center.^[17a] Ibers et al. reproduced this synthesis starting from [Ni(PCy₃)₂]₂(μ -N₂) in dry liquid CO₂. Under the exact same conditions, they reported that both Pd(PCy₃)₂ and Pt(PCy₃)₂ did not react with CO₂. The platinum compound eventually reacted in wet CO₂ to form the carboxylate PtH(PCy₃)₂(O₂COH),

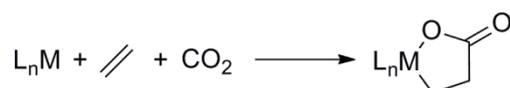
contrary to the palladium complex which remained unreactive towards CO₂.^[95] Previous reports have stated that both Pd(PPh₃)₄ and Pt(PPh₃)₃ did not react with CO₂.^[96]

Seyler et al. performed a theoretical mechanistic study of the coordination of CO₂ in palladium complexes bearing different phosphino-ligands. They found that independently of the basicity and bulkiness of the ligand, the preferential mode of bonding in (PR₃)₂Pd(CO₂) complexes would always be the η²-C,O side-on coordination mode.^[97]

4.1.2 Formation of metallalactones from ethylene and CO₂

The first reactions between olefins and CO₂ at transition metal center were performed by Hoberg et al. during the 1980s.^[98] Reacting nickel(0) complexes with different olefins and CO₂ led each time to the formation of stable cyclic intermediates including the metal center: metallalactones. Such reactions have been afterwards reported for other nickel complexes,^[99] as well as for a wide range of transition metals such as Fe^[100], Ti^[101], Zr^[102], V^[103] and Rh^[104].

The simplest of those metallalactones is formed by the reaction of ethylene and CO₂ leading to five-membered rings.

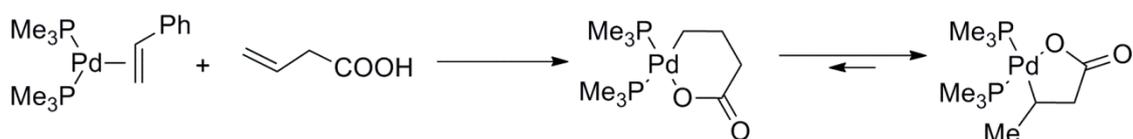


Scheme 4.2. Formation of a metallalactone from CO₂ and ethylene

The formation of lactones with nickel precursors has been extensively studied. Hober et al. reacted Ni(cdt) with a biphosphine ligand (dcpe) under stoichiometric amount of CO₂ and five equivalents of ethylene in toluene at room temperature for 7 days to obtain the nickelalactone bearing biphosphine ligand with 50 % yield.^[98b] A higher yield (85 %) could be reached with bipyridine ligand. The nickelalactones were isolated and further reacted with different alkene systems leading to carboxylic acids after hydrolysis.^[105] The catalytic formation of acrylates directly from ethylene and CO₂ would be of industrial relevance.

However, even if the opening of the lactone has proven to be feasible by DFT calculations^[106] and has been performed recently^[107], no catalytic process has been achieved yet.

To the best of our knowledge, the formation of palladalactones from ethylene and CO₂ has never been achieved. Five-membered ring palladacycles including a CO₂ moiety have been isolated through rearrangement of a six-membered ring formed by the reaction of a palladium(0) complex with 3-butenoic acid.^[108]



Scheme 4.3. Formation of a palladalactone^[108]

Aresta et al. recently succeeded in synthesizing stoichiometrically methyl acrylate from ethylene and CO₂ using a palladium complex as catalyst. Their proposed mechanism proceeds through the formation of a palladalactone intermediate that they did not succeed to isolate.^[109]

The synthesis of γ -lactones (five-membered rings) using palladium catalysts was published first by Inoue et al. from the reaction of methlenecyclopropane with carbon dioxide.^[110] A mechanism was proposed later on, going through the formation of a six-membered ring palladalactone.^[111] Palladium complexes are also efficient catalysts for the telomerization of 1,3-butadiene with CO₂ affording 6-membered ring lactones (δ -lactones).^[112]

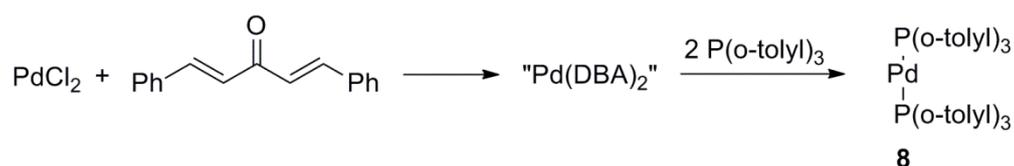
4.2 Synthesis of palladium(0) precursors

Different palladium (0) complexes bearing phosphine or carbene ligands were synthesized to be tested in the activation of CO₂ and employed as precursors for the synthesis of palladium (II) complexes bearing Pd-H or Pd-Me bonds.

4.2.1 Synthesis of Pd(IMes)₂ and of Pd(Idipp)₂

The synthesis of palladium (0) complexes bearing two carbene ligands proceeded via two steps. First, the complex Pd[P(o-tolyl)₃]₂ was synthesized and then a ligand exchange was performed between the phosphine ligands and free carbenes.

The first experiments performed to synthesize Pd[P(o-tolyl)₃]₂ were through the formation of "Pd(DBA)₂", which is defined by Hartock et al. as an equimolar mixture of Pd₂(DBA)₃ and Pd(DBA)₃^[113] (Scheme 4.4.).



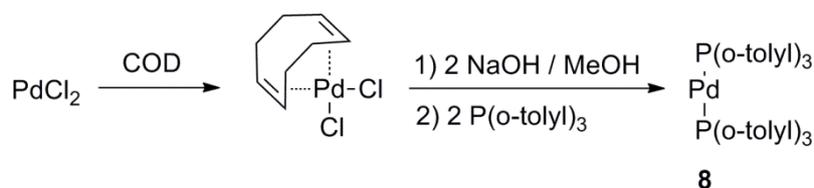
Scheme 4.4. Synthesis of Pd[P(o-tolyl)₃]₂ through the formation of "Pd(DBA)₂"

However this reaction raised several problems:

- The purity of "Pd(DBA)₂" was hard to certify, as it was impossible to differentiate the free DBA ligand to the one bound to palladium by NMR or IR spectroscopy. The only way to analyze this complex was through elemental analysis, which is not such a convenient technique as compared to NMR or IR.
- The synthesis of Pd[P(o-tolyl)₃]₂ required the use of a large excess of phosphine, as well as high quantity of solvents for the reaction and recrystallization of the product.

Moreover, the overall yields obtained were low (from 15 to 20 %).

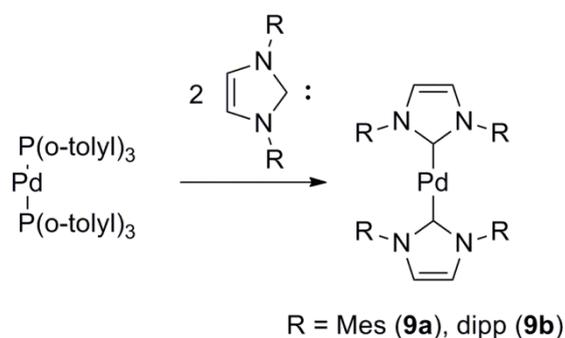
Another route was used, based on the publication and patent of Calacot et al.^[114]



Scheme 4.5. Synthesis of Pd[P(o-tolyl)₃]₂ through the formation of Pd(COD)Cl₂

The first step consisted in the synthesis of Pd(COD)Cl₂ from PdCl₂ and 1,5-cyclooctadiene. This reaction proceeded easily at room temperature in 48 h and led to excellent yields. In the second step, this compound was reacted with NaOH in methanol leading to the nucleophilic attack of a MeO⁻ anion at one of the double bonds of COD. Adding of the phosphine led to the formation of Pd[P(o-tolyl)₃]₂(H)(Cl) which reacted with the base affording complex **8**. The procedure described by Calacot et al. had to be adapted as PdCl₂ was used as starting material and not PdBr₂ as reported. The NaCl salt which formed was insoluble in toluene contrary to NaBr, therefore a filtration step had to be added. This route, which required only two equivalents of the phosphino-ligand, was straightforward and led to good yields. A particular attention was paid to the washings, as the phosphine ligands easily dissociated in solution. This explains why the ³¹P NMR spectrum displayed a peak corresponding to free phosphine. The quality of the product was determined by ¹H, ¹³C, ³¹P NMR and Elemental Analysis. The product was stored in the glove box.

The exchange from a phosphine to a carbene ligand was performed following the procedure of Herrmann and al^[115]. It consists in the reaction of Pd[P(o-tolyl)₃]₂ with free carbenes.

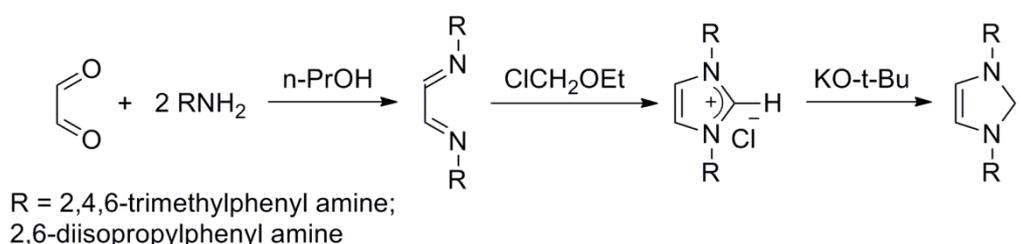


Scheme 4.6. Synthesis of Pd(Imes)₂ and Pd(Idipp)₂

The reaction proceeded in 40 min at room temperature with 2.1 equiv. of the free carbene. The separations of the desired products from the free phosphines were highly problematic because both compounds were soluble in similar solvents. Several washings with only few mL of hexane at – 78 °C were necessary to get rid of the free phosphines. The moderate yields (50 to 60 %) were attributed to these purification steps. The purity of the complexes

was confirmed by ^1H , ^{13}C and ^{31}P NMR. The products were stored in the glove box at room temperature.

The free carbenes were synthesized from the respecting imidazolium salts upon reaction with a strong base (potassium tert-butoxide) following the procedure of Arduengo et al.^[116] The imidazolium salts were synthesized in several steps from glyoxal and respectively 2,4,6-trimethylphenylamine and 2,6-diisopropylphenylamine.

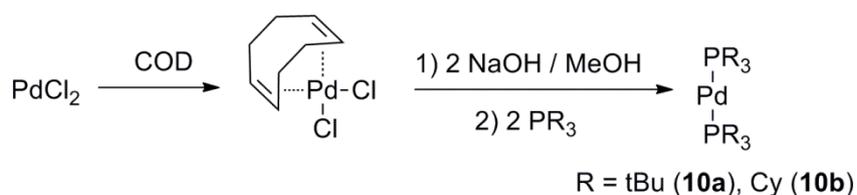


Scheme 4.7. Synthesis of free carbenes

The reactions were relatively straightforward, as all the intermediates were air stable. Only the formation of the free carbene required air and moisture free conditions.

4.2.2 Synthesis of $\text{Pd}(\text{PtBu}_3)_2$ and of $\text{Pd}(\text{PCy}_3)_2$

Two different palladium (0) complexes bearing phosphino-ligands were synthesized. The procedure for their synthesis was based on the one reported by Colacot et al.^[114]



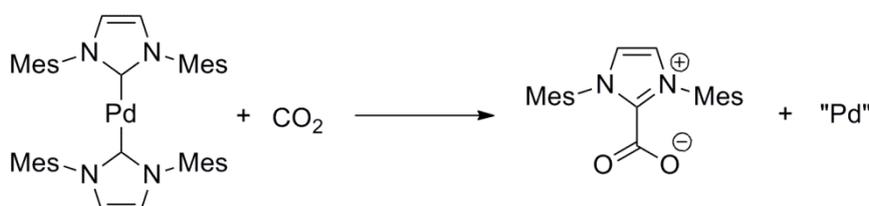
Scheme 4.8. Synthesis of $\text{Pd}(\text{PtBu}_3)_2$ and $\text{Pd}(\text{PCy}_3)_2$

Changes had to be made to their procedure since it led to degradation of the complexes and formation of a black precipitate, probably palladium metal. In order to prevent the decomposition of the product, reaction times had to be shortened and temperature lowered. Those problems might have come from the quality of the solvents: the reactions were performed in the King Abdullah University of Science and Technology (KAUST) where no Karl-Fischer apparatus was available for the determination of the water content of the solvents. It is possible that the solvents were not perfectly dried, especially methanol which was distilled from CaH_2 . The yields obtained were lower than the one reported in literature, probably due to the changes in the reaction conditions. The purity of the complexes was verified by ^1H and ^{13}C NMR. The products were stored in the glove box at $-35\text{ }^\circ\text{C}$ and in the exclusion of light.

4.3 Reaction of palladium (0) complexes **9a** and **9b** with CO_2

$\text{Pd}(\text{IMes})_2$ was first reacted in an NMR tube under 3 bar of CO_2 . Before adding CO_2 , the solution of $\text{Pd}(\text{IMes})_2$ in C_6D_6 was orange and slightly fluorescent. The fluorescence was lost as soon as CO_2 was added. After 15 minutes to 1 h, a solid started to precipitate. The same phenomenon was observed with $\text{Pd}(\text{Idipp})_2$. The reaction was performed in higher scale in a pressure glass reactor, which allowed starting with hundreds of mg of educt. A white solid was collected after 4 days of reaction under 4 bar of CO_2 .

The solid collected from the reactions of **9a** and **9b** with CO_2 were analyzed by ^1H , ^{13}C , IR and elemental analysis. Comparison to literature values showed that they correspond to the carboxylate adduct of the imidazolium salts.^[117]



Scheme 4.9. Formation of a carboxylate adduct

A high absorption band of the carboxylate group was particularly visible in IR spectroscopy at 1673 cm^{-1} for the I_{mes}-CO₂ adduct and at 1680 cm^{-1} for the Idipp-CO₂ adduct.

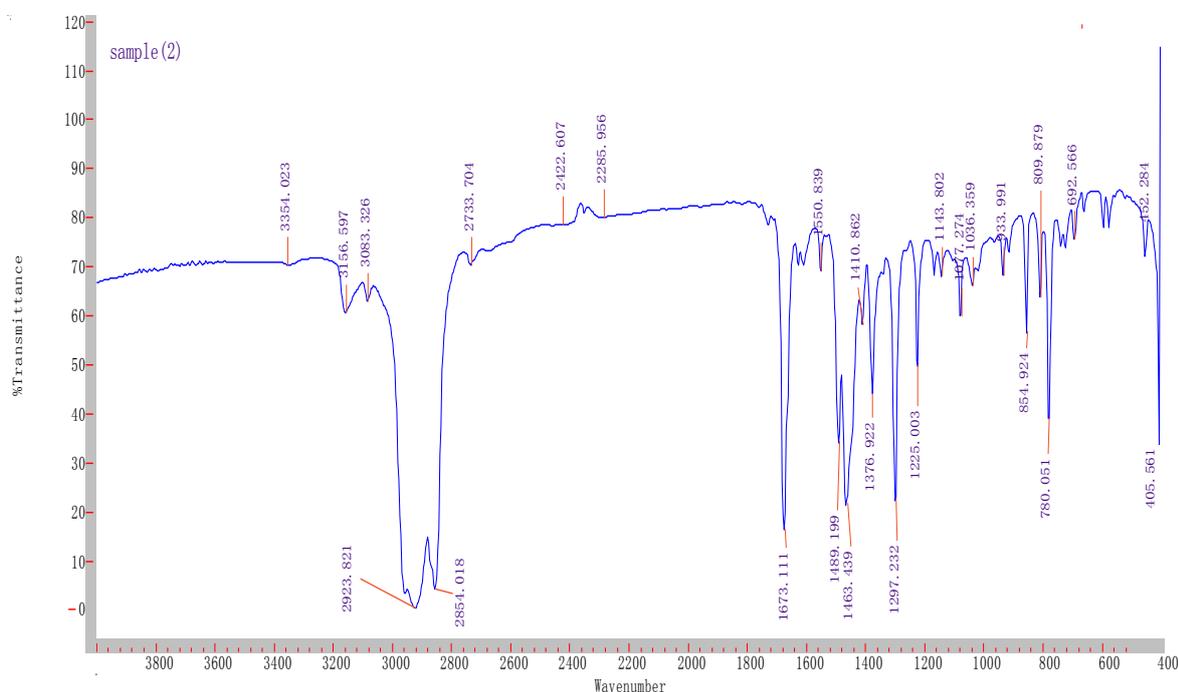


Figure 4.1. IR of the product of the reaction between **9a** and CO₂

A FAB mass spectroscopy analysis was performed with the I_{mes} adduct. The highest *m/z* peak is observed at 348, corresponding to the carboxylate product. The highest peak in intensity is observed at 305, corresponding to the imidazolium ligand. Crystallization was performed from the compound with diisopropylphenyl ligands from a THF/hexane mixture. Crystals were obtained after 2 days, however they were too small for crystal analysis. Unfortunately, even after growing for 2 months, their size was unchanged. This phenomena of formation of the carboxylate adduct from a metal (0) compound bearing two NHC ligands was already observed by Langer et al. with nickel (0) complexes.^[118]

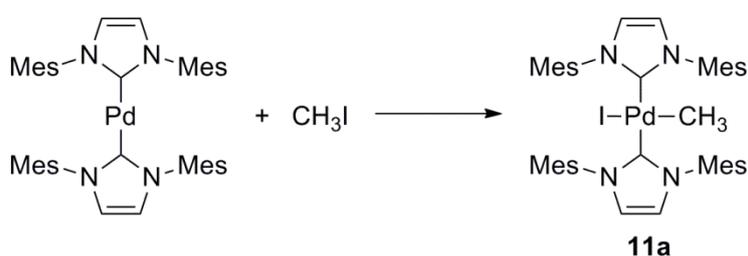
The liquid phase was analyzed by NMR and showed a mixture of several products, probably products of decomposition of the palladium (0) compound. No clean product could be isolated from it.

Those reactions show no evidence of any bonding of CO₂ to the palladium (0) compounds. It seems that CO₂ is able to break the Pd-carbene bond in order to form a carboxylate adduct with the carbene ligand.

4.4 Formation of palladium (II) complexes by reaction of palladium (0) compounds with CH₃I and their reaction with CO₂

4.4.1 Reaction of Pd(IMes)₂ and Pd(PCy₃)₂ with CH₃I

Pd(IMes)₂ was reacted at NMR scale in C₆D₆ with one equivalent of CH₃I showing quantitative conversion to Pd(IMes)₂(CH₃)(I).



Scheme 4.10. Synthesis of Pd(IMes)₂(CH₃)(I)

The reaction was performed at higher scale and Pd(IMes)₂(CH₃)(I) was isolated as a yellow solid with high yield (89 %). The loss of symmetry of the molecule is seen by NMR spectroscopy. The peaks from the ortho- and meta- position of the aryl ring are now separated, both in ¹H and ¹³C NMR. As depicted in Figure 4.2., the peak from the ortho-position of the aryl ring which was previously a singlet at 2.04 ppm integrating for 24 protons is now splitted in two peaks at 2.12 and 1.78 ppm both integrating for 12 protons. The meta- position changed from one peak at 6.82 ppm (8 protons) to two peaks at 6.93 and 6.88 ppm (4 protons each).

The peak of the methyl group linked to the metal appear at -0.34 and -5.4 ppm respectively in ¹H and ¹³C NMR. The proton is moved upfield as compared to other palladium-methyl compounds^[119] (see chapter 6 for a more complete discussion about this point), showing a relatively weak palladium-methyl bond, letting hope for a CO₂ insertion reaction. To the contrary, the peak in ¹³C NMR is downfield as compared to other complexes.^[119a-c]

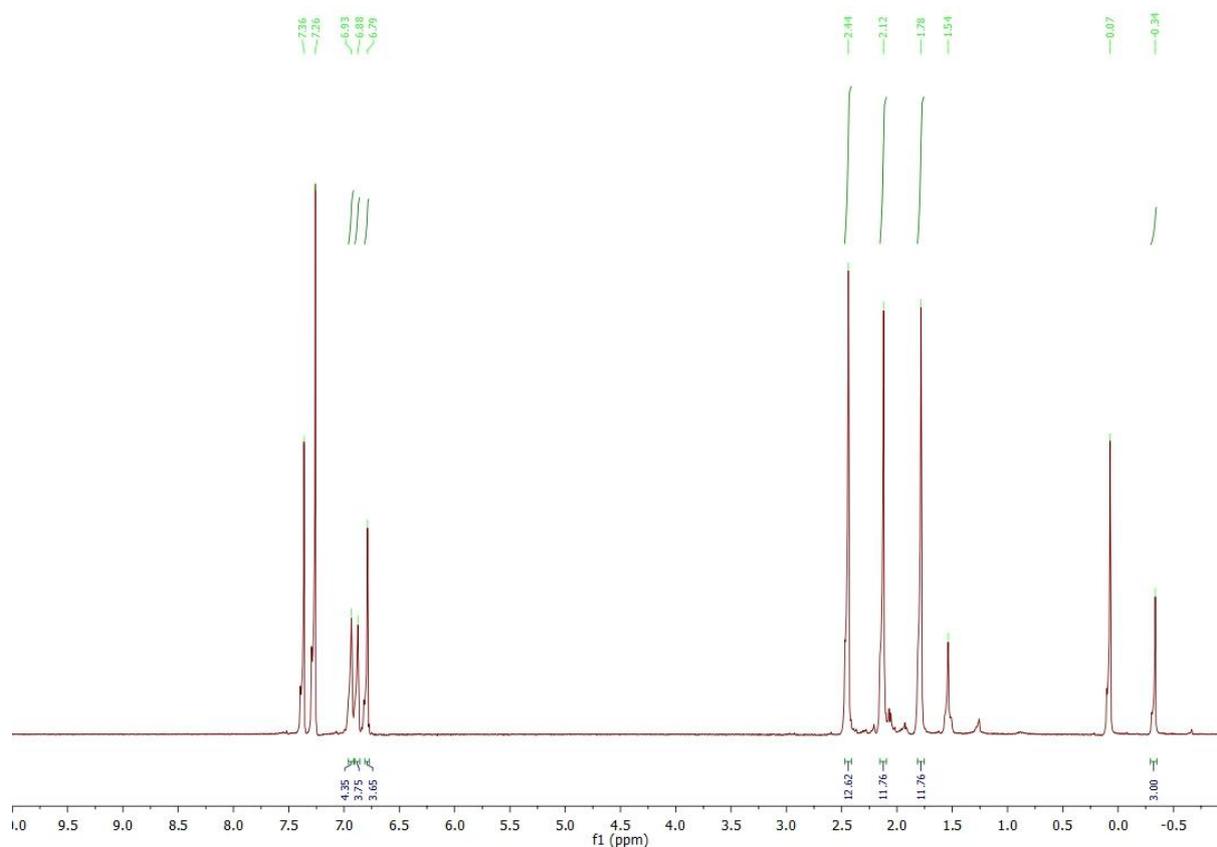


Figure 4.2. ¹H NMR spectra of **11a**

This new compound was characterized by ¹H and ¹³C NMR, elemental analysis (calculated C 60.11, H 6.22, N 6.52%, found C 60.52, H 5.97, N 6.72%) and mass spectroscopy. FAB mass spectroscopy displays the maximum signal at $m/z = 730$, corresponding to $[\text{Pd}(\text{IMes})_2(\text{CH}_3)]^+$. The peak with the highest intensity is observed at 319 corresponding probably to the molecule $[(\text{Imes})_2\text{-Me}]^+$ being a rearrangement of complex **11a**. The second main peak is found at 305 corresponding to the carbene ligand. A crystal structure has not yet been obtained.

Complex **11a** is stable under air and in a benzene solution for several days. It is nevertheless stored in the glove box to prevent any risk of decomposition.

The same reaction was performed with $\text{Pd}(\text{PCy}_3)_2$, leading to $\text{Pd}(\text{PCy}_3)_2(\text{CH}_3)(\text{I})$ (**11b**) which was characterized by ¹H, ¹³C and ³¹P NMR.

Its ^1H and ^{13}C NMR show the peaks of the methyl group at 0.8 ppm and -1.8 ppm respectively. Both peaks are downfield as compared to complex **11a** and to literature reports.^[119a-c] Interestingly, the peak of the methyl group is a triplet in ^1H NMR, and not a singlet as other palladium-methyl compounds. It is believed that the methyl group is in interaction with two equivalent protons from the cyclohexyl rings, and therefore appears as a triplet. This interaction between the ring and the methyl group strengthens the palladium-methyl bond, which explains why the peaks of the methyl groups appear downfield. The interaction between the cyclohexyl ring and the methyl group is also probably the origin of the presence at 2.44 ppm of 6 protons from the aryl ring in the ^1H NMR.

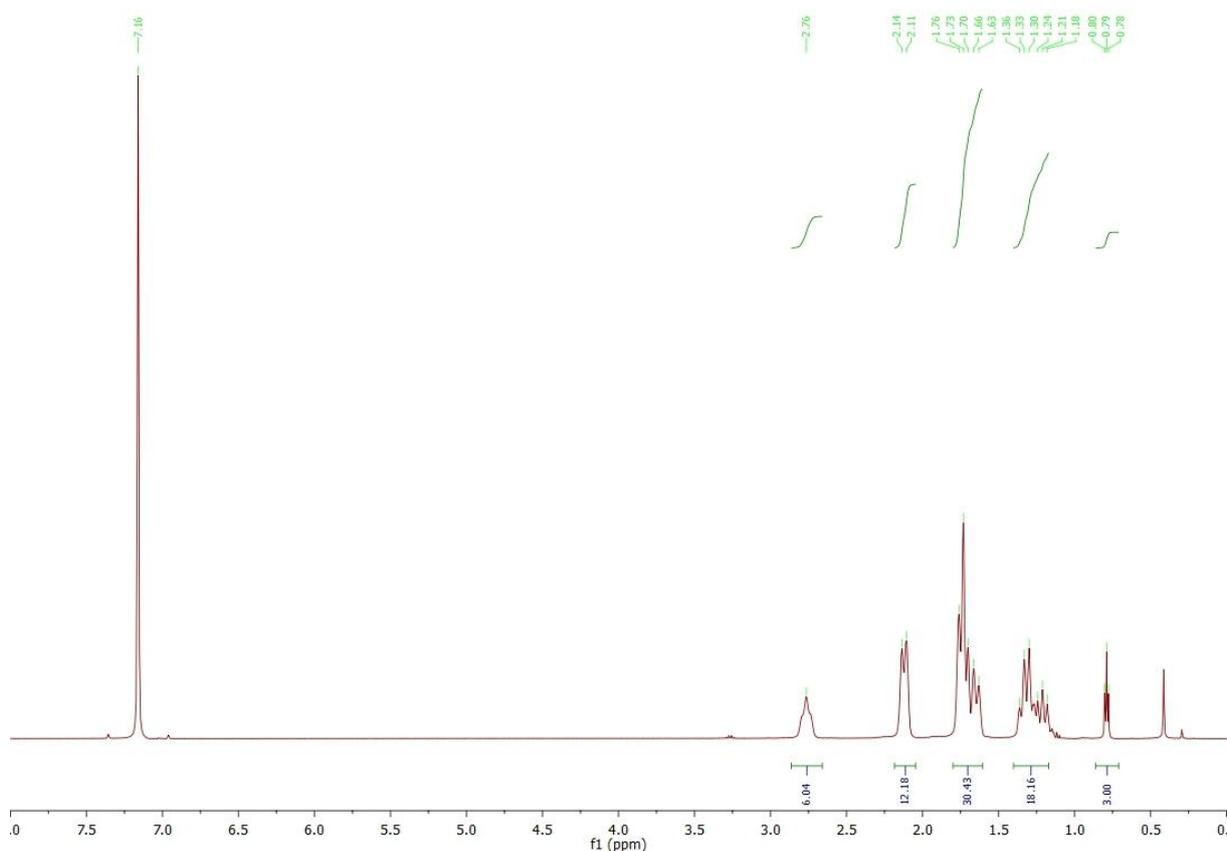


Figure 4.3. ^1H NMR spectrum of **11b**

4.4.2 Reaction of Pd(IMes)₂(CH₃)(I) and Pd(PCy₃)₂(CH₃)(I) with CO₂

In an NMR tube, 4 bar of CO₂ were pressed over a C₆D₆ solution of Pd(IMes)₂(CH₃)(I). After 15 minutes of reaction, no change was observed in the NMR spectra. The tube was heated at 70 °C for 3 days, however no sign of reaction could be detected. When the reaction was performed at higher scale in a sealed tube, only the starting material was recovered after 3 days of reaction at 60 °C.

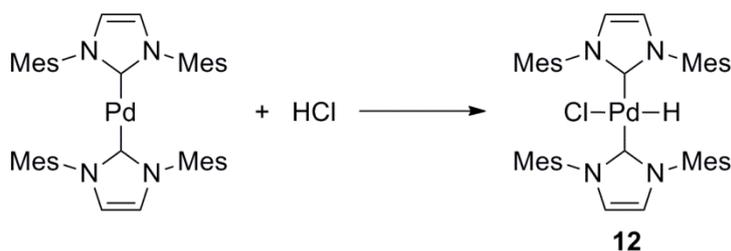
In a sealed autoclave, 26.5 bar of CO₂ were pressurized over a solution of Pd(PCy₃)₂(CH₃)(I) in toluene for one day at 50 °C. However, only the starting material was recovered and no sign of CO₂ insertion into the palladium-methyl bond could be detected.

Therefore, it can be concluded that both Pd(IMes)₂(CH₃)(I) and Pd(PCy₃)₂(CH₃)(I) are unreactive towards CO₂.

4.5 Reaction of Pd(IMes)₂ with HCl and its reaction with CO₂

4.5.1 Reaction of Pd(IMes)₂ with HCl

Pd(IMes)₂ was reacted with one equivalent of hydrochloric acid to give quantitatively Pd(IMes)₂(H)(Cl). It is important to use exactly one equivalent of HCl, otherwise the complex Pd(IMes)₂Cl₂ will form.



Scheme 4.11. Synthesis of Pd(IMes)₂(H)(Cl)

The ¹H NMR spectra of **12** shows the presence of the hydride peak at -14.8 ppm, in the range of other palladium hydrides.^[120]

The elemental analysis (calculated C 66.10, H 6.57, N 7.45%, found C 66.76, H 6.52, N 7.14%) is in accordance with complex **12**. By FAB mass spectroscopy, the maximal m/z is found at 715, corresponding to $[\text{Pd}(\text{IMes})_2\text{H}]^+$. The peak with the maximal intensity is found at 305 corresponding to the IMes carbene ligand. Contrary to the mass spectrum of complex **11a**, no peak is present at 318 ppm proving that the one observed for complex $\text{Pd}(\text{IMes})_2(\text{CH}_3)(\text{I})$ comes from a rearrangement of the carbene with the methyl group.

Complex **12** is air sensitive, and is stable for about one day in benzene. It decomposes by forming the complex $\text{Pd}(\text{IMes})_2(\text{Cl})_2$, as seen by the disappearance of the hydride peak in ^1H NMR and by elemental analysis (calculated C 64.16, H 6.15, N 7.13%, found C 64.20, H 6.32, N 6.86%).

4.5.2 Reaction of $\text{Pd}(\text{IMes})_2(\text{H})(\text{Cl})$ with CO_2

In an NMR tube, 4 bar of CO_2 were pressed over a C_6D_6 solution of 30 mg of $\text{Pd}(\text{IMes})_2(\text{Cl})(\text{H})$ at room temperature. No reaction can be observed after 1 day at room temperature. The tube was heated for a day at 50 °C, but the NMR spectra still show no evolution.

Under those conditions, there is no insertion of CO_2 into the palladium-H bond of $\text{Pd}(\text{IMes})_2(\text{Cl})(\text{H})$.

4.6 Reaction of $\text{Pd}(\text{IMes})_2$ with HCOOH

$\text{Pd}(\text{IMes})_2$ was reacted at r.t. for 30 min with one equivalent of formic acid, the yellow/orange solution turned immediately to pale yellow. A yellow solid was collected after removing of the solvent, whose ^1H NMR shows two hydride peaks (a singlet at -14.86 ppm, and a doublet at -17.98 ppm) with an approximate ratio of 2:1 (see Figure 4.4.).

Palladium (0) complexes as precursors for reactions involving carbon dioxide

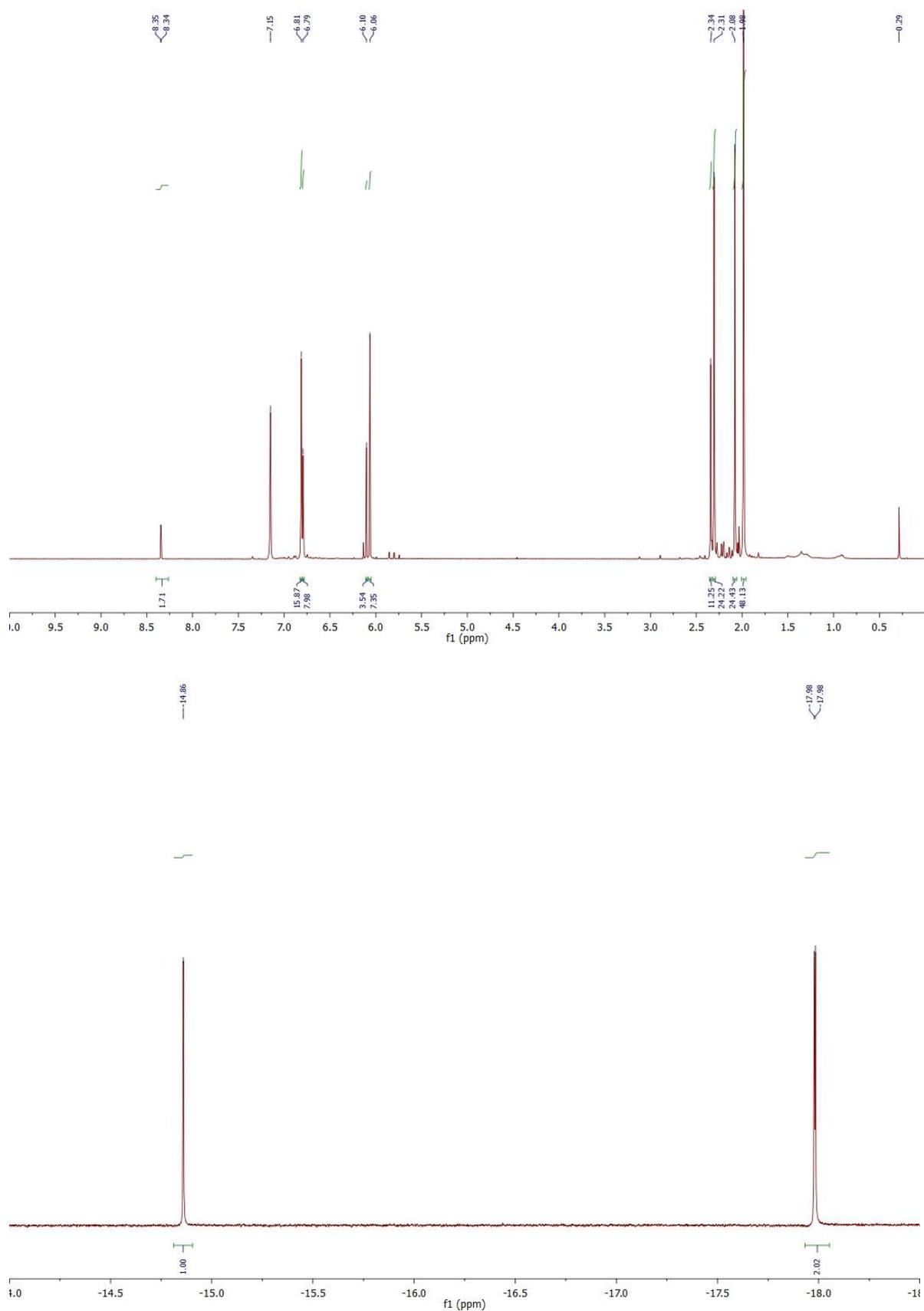


Figure 4.4. ^1H NMR spectra of the mixture with zoom over the 10-0 ppm range (top) and over the range -14 to -19 ppm (bottom)

The following peaks can be attributed to species **13** and **14**.

Table 4.1. ^1H NMR displacement of the protons of species **13** and **14** and their assignment

| Species 13 | Species 14 | Assignment |
|-------------------|-------------------|-------------------|
| 8.35 ppm (d, 1H) | - | COOH |
| 6.81 ppm (s, 8H) | 6.79 ppm (s, 8H) | m-H |
| 6.06 ppm (s, 4H) | 6.10 ppm (s, 4H) | NCH |
| 2.31 ppm (s, 12H) | 2.34 ppm (s, 12H) | p-CH ₃ |
| 1.98 ppm (s, 24H) | 2.08 ppm (s, 24H) | o-CH ₃ |
| -17.98 (d, 1H) | -14.86 (s, 1H) | Pd-H |

Previous report on palladium(IMes)(H)(OAr) species have shown their hydride peaks display a singlet at -17.8 ppm.^[121] Interestingly the signal of the hydride in species **13** is a doublet, which tends to prove that **13** is a dimeric specie. The peak belonging to the carboxylic group is also a doublet at 8.35 ppm.

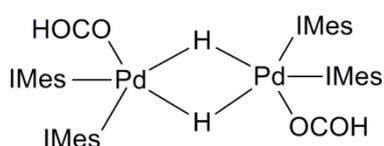


Figure 4.5. Postulated structure of complex **13**

Species **14** displays a singlet hydride peak at -14.86 ppm, however no peak of the carboxylate group could be associated to this species. More analysis are required to define its structure.

The product was kept for two days in the NMR tube, and a ^1H NMR was measured again (Figure 4.5.). By comparing this spectrum to the previous one, it could be observed that species **14** is stable in solution as the intensity of its peak remained constant. To the contrary, the peaks attributed to species **13** have decreased, the new ratio between the two species being 1:1.25. New peaks have appeared whose displacements (6.81, 6.14, 2.33 and 2.03 ppm) correspond exactly to the one of the starting material Pd(IMes)₂. Therefore, it is thought that product **13** is slowly reforming the starting material in solution.

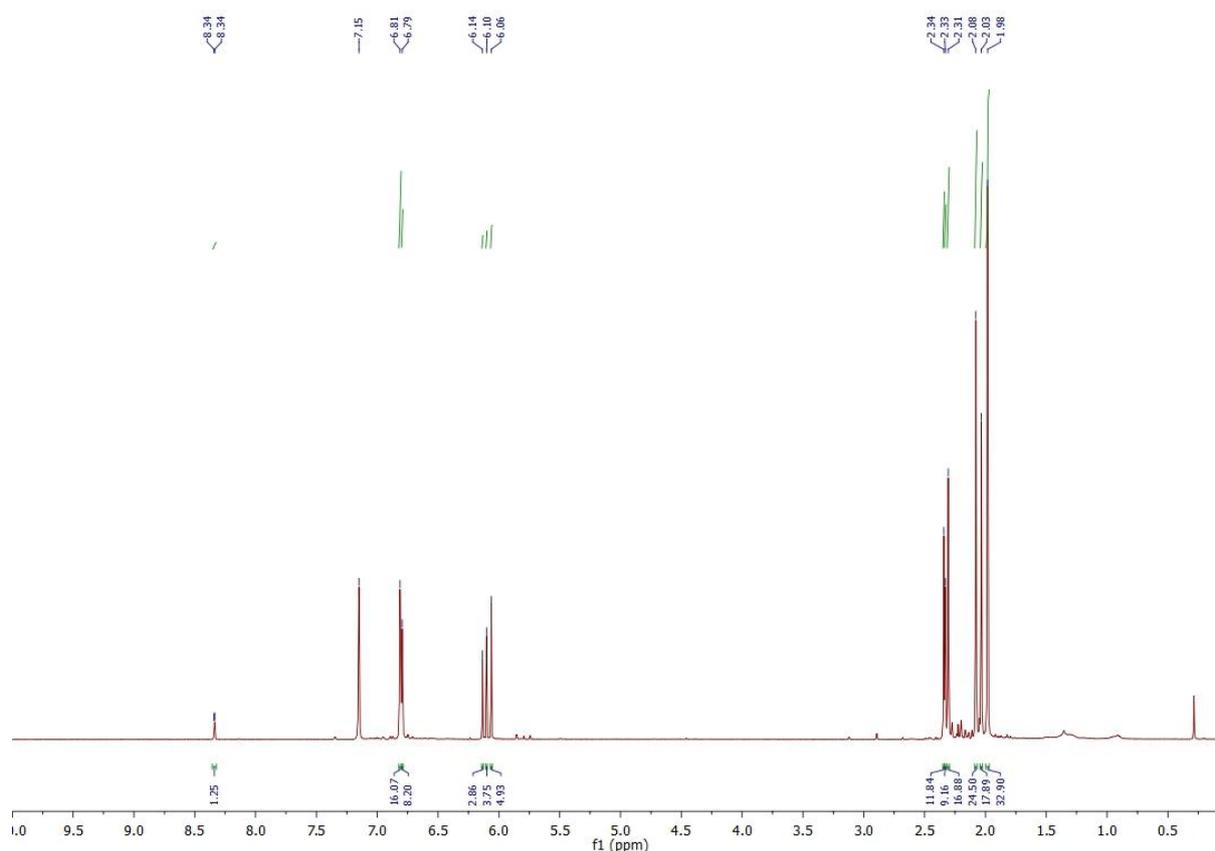


Figure 4.6. ^1H NMR spectra of the mixture with zoom over the 10-0 ppm range

No further studies have been performed on this subject. However, it would be of high interest to determine precisely the exact structure of those species and to test their behaviour towards agents such as bases, alkenes, CO_2 , etc.

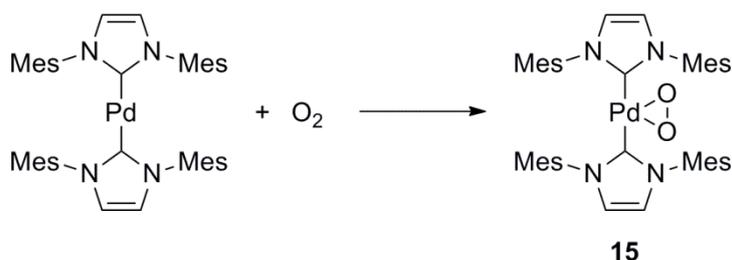
4.7 Reaction of 9a and 9b with gases: H_2 and O_2

4.7.1 Reaction of $\text{Pd}(\text{Idipp})_2$ with H_2

$\text{Pd}(\text{IPr})_2$ was reacted with 3 bar of H_2 in C_6D_6 at NMR scale, however no reaction was observed even after 3 days at 70°C . Nolan et al. reported that the choice of the ligand is crucial in the success of H-H bond activation reaction employing palladium (0) complexes. They observed no reaction when they reacted $\text{Pd}(\text{IPr})_2$ and $\text{Pd}(\text{PCy}_3)_2$ with 1 bar of hydrogen at room temperature, but observed the formation of the trans dihydride complex when they reacted the mixed complex $\text{Pd}(\text{IPr})(\text{PCy}_3)$ with hydrogen.^[122]

4.7.2 Reaction of Pd(IMes)₂ with O₂ and epoxidation of cyclooctene

In an NMR tube, Pd(IMes)₂ was reacted in C₆D₆ with 3 bar of O₂. In 5 minutes it converted quantitatively to Pd(IMes)₂(O₂) as seen by ¹H NMR.^[121a] Exposure of **9a** to air did not lead immediately to the formation of this product as described by Stahl et al.^[123], the presence of oxygen pressure was required for the reaction to proceed.



Scheme 4.12. Synthesis of Pd(IMes)₂O₂

Peroxo-compounds such as **15** are known intermediates for the epoxidation of olefins^[124]. An NMR experiment was performed with cis-cyclooctene, which has proven to be easily prone to epoxidation.^[125]

15 min after the addition of cyclooctadiene to the solution of Pd(IMes)₂O₂ in a 1:1 ratio, a NMR was recorded (Figure 4.7.). The peaks of Pd(IMes)₂O₂ are observed at 6.67, 6.03, 2.28 and 2.05 ppm, the ones of cyclooctadiene at 5.55 (m, 2H, -CH=CH-), 2.08 (m, 4H, -CH₂-CH-) and 1.43 (m, 8H, -CH₂-CH₂-). The formation of cyclooctene oxide would be noticed by the disappearance of the peak at 5.55 ppm, and the growing of a new multiplet in the range of 1.5 to 1.6 ppm. Thus, it is clear that the reaction did not proceed under such conditions.

The NMR tube was warmed for 16 h at 40 °C, however no formation of cyclooctene oxide could be detected. Therefore, it can be concluded that Pd(IMes)₂O₂ is unable to react with cyclooctene; no further effort was conducted on the epoxidation of other compounds.

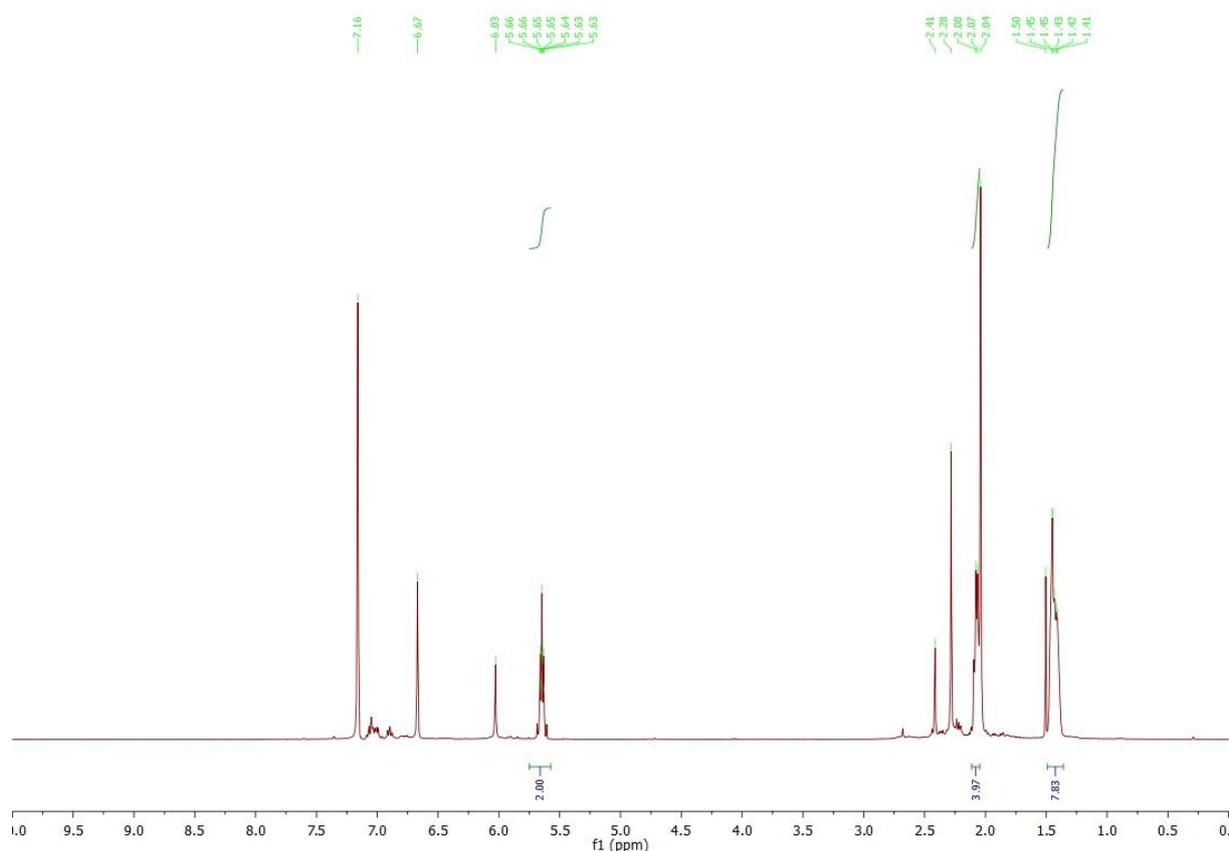


Figure 4.7. ^1H NMR of $\text{Pd}(\text{IMes})_2\text{O}_2$ in presence of cyclooctene

4.8 Reaction of $\text{Pd}(\text{PtBu}_3)_2$, $\text{Pd}(\text{PCy}_3)_2$ and $\text{Pd}(\text{PPh}_3)_4$ with ethylene and CO_2

In a typical experiment, $\text{Pd}(\text{PPh}_3)_4$ (**16**) or $\text{Pd}(\text{PCy}_3)_2$ (**10b**) was dissolved in toluene and reacted in a sealed autoclave with 15 bar of ethylene for 30 minutes and then 20 bar of CO_2 for several hours, the reaction being followed in real-time by IR-spectroscopy. $\text{Pd}(\text{PPh}_3)_4$ is known to dissociate to $\text{Pd}(\text{PPh}_3)_2$ and two equivalents of the free phosphine PPh_3 in solution.

No change was observed in the IR spectrum after ethylene was pressurized over **10b** or **16**. However, as soon as CO_2 was pressurized, a band at 1666 cm^{-1} was observed growing, which stabilized after 15 to 20 minutes. This band is in the range of the C=O stretching of carboxylate units and of nickelalactones complexes.^[107a, 107c]

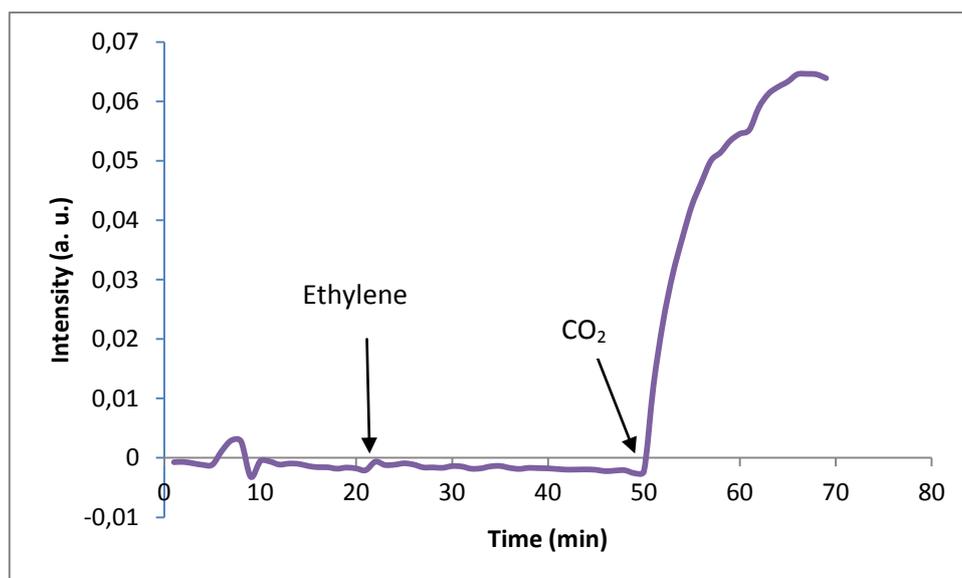


Figure 4.8. Evolution of the intensity of the band at 1666 cm^{-1}

If only one of the two gases was pressurized, this band was not observed. More surprisingly, if CO_2 was pressurized immediately after ethylene, or if CO_2 was pressed before ethylene, it required several hours before this band reached its maximal intensity. Thus, it is expected that the first step of the reaction is the bounding of ethylene to the palladium atom,^[99b] followed by an attack of CO_2 over this complex.

After removing of the gases, a suspension was recovered from which a yellow solid could be precipitated by adding of hexane, or simply by cooling the suspension at $-30\text{ }^\circ\text{C}$ overnight. IR spectroscopy of the liquid and of the solid phase reveals the presence of a band at 1640 cm^{-1} only for the solid compound. However, this compound was insoluble in any apolar solvent and decomposed readily in chlorinated solvents or DMSO. NMR measurements were performed; however the product might already have decomposed before the spectrum was acquired. The compound seemed to be air stable, as an IR spectrum measured after storing the product two weeks under air was perfectly identical to the one measured immediately after its isolation. To the contrary, drying the compound *in vacuo* for several hours resulted in its change of color from yellow to grey, and the disappearance of the band at 1640 cm^{-1} in IR spectroscopy. This point stresses out the presence of a CO_2 moiety in this compound, which dissociates under vacuum leading to the decomposition of the product.

A sample made from Pd(PCy₃)₂ was brought back from King Abdullah University of Science and Technology to the Technische Universität München for a mass spectroscopy analysis. The highest set of peak is found at m/z = 682, 17 units over the peak at 665 which can be attributed to Pd(PCy₃)₂. The peak with the highest intensity is at 281 corresponding to PCy₃, and the second highest one is at 297, probably being the oxide PCy₃=O. Therefore, no sign of the formation of a palladalactone could be detected by mass spectroscopy; however oxygen must be present at some point in the molecule.

No reaction was observed when Pd(tBu₃)₂ was used as starting material. Probably, the tert-butyl ligands are too bulky to allow the formation of the complex. An experiment was conducted with Pd(acac)₂ and two equivalents of PCy₃ hoping to form the complex from an in-situ reaction, however no change could be detected in the IR spectrum when ethylene and CO₂ were pressurized.

From all those elements, it can be concluded that a reaction has occurred between the palladium (0) complexes, ethylene and CO₂. However, no proof of the formation of a lactone could be detected up to now. Two major problems are still to overcome:

- The stability of the solid in solution is very poor, which complicates its purification and its analysis by NMR spectroscopy and prevents its recrystallization.
- Up to now, a maximum yield of 15 % (based on the formation of a palladalactone) could be obtained. Raising the temperature of the reactor or the gas pressures did not lead to any improvement in the yields.

As nickelalactones have recently been reported with saturated and unsaturated N-heterocyclic carbene ligands,^[118] the reaction of ethylene and CO₂ can be tried with Pd(IMes)₂ or Pd(dipp)₂.

4.9 Conclusion

In this chapter, the synthesis of various palladium (0) complexes bearing two phosphines or two NHC ligands was detailed. These complexes were reacted with carbon dioxide or

hydrogen, however they showed no interaction with those gases. Pd(IMes)₂ reacted quickly with oxygen to form Pd(IMes)₂O₂, unfortunately this complex was unactive in the epoxidation of cyclooctadiene.

The complexes Pd(PCy₃)₂ and Pd(PPh₃)₄ reacted with a mixture of ethylene and CO₂, forming complexes which exhibit a band at 1666 cm⁻¹ in IR spectroscopy. This band probably comes to a C=O stretching, which would correspond to a CO₂ moiety linked to the metal. Further research is ongoing to determine the precise structure of those complexes.

The palladium (0) complexes bearing NHC ligands were reacted with CH₃I and HCl to lead to the synthesis of palladium (II) - methyl or palladium (II) - hydride compounds. Unfortunately those compounds remained unreactive towards CO₂.

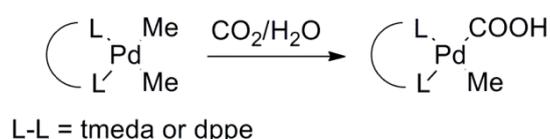
Palladium (0) complexes as precursors for reactions involving carbon dioxide

5 Synthesis of platinum (II)- and palladium (II)-methyl complexes bearing bisphosphine or bis-NHC ligands and their reaction with carbon dioxide

5.1 Introduction

Only few examples of reactions of carbon dioxide with palladium or platinum complexes bearing bidentate phosphines or N-heterocyclic carbenes are reported.

Wendt et al. dedicated their efforts on the reaction of CO₂ with the palladium complexes (tmeda)PdMe₂ and (dppe)PdMe₂.^[126] Those complexes showed no reaction with dry CO₂, however when little amount of water was added the formation of the carbonate complex was observed as well as release of methane.

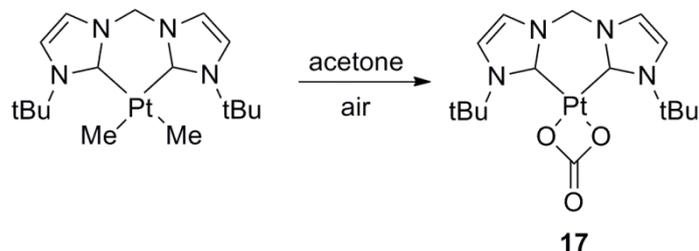


Scheme 5.1. Formation of a carbonate complex

Very recently, Rosenthal et al. synthesized a Pd(bis-NHC)Me₂ complex and studied its reactivity with CO₂.^[127] Carbene ligands are stronger σ -donors than phosphine ligands^[128], therefore the methyl groups undergo a stronger trans-influence, which can be seen by the lengthening of the palladium-methyl bonds: 2.077 Å compared to 2.028 Å for (tmeda)Pd(Me)₂. However, this complex did not react with dry CO₂, but rather with a CO₂/H₂O mixture to form the carbonate complex. Detailed mechanistic study through IR and NMR spectroscopy suggested that the reaction proceeds via direct protonolysis of the complex by carbonic acid formed upon reaction of carbon dioxide with water.^[127]

Jamali et al. exposed an acetone solution of platinum(dimethyl)(bis-NHC) complex to air for 24 h and observed the formation of the platinum carbonate complex [Pt(CO₃)(bis-NHC)] in

65 % yield (Scheme 5.2.). They suggested that the carbonate ligand originated from hydration of atmospheric CO₂ to give H₂CO₃, which underwent deprotonation to afford **17**.^[129]



Scheme 5.2. Synthesis of **17**

Contrary to palladium and platinum compounds, the insertion of CO₂ into metal-methyl bonds of iron and ruthenium complexes bearing bisphosphine ligands proceeds under mild conditions. Field et al. reported the insertion of CO₂ into one of the methyl bond of Fe(dmpe)₂(Me)₂ and Fe(depe)Me₂ at 300 K and 1 bar. Under 330 K and 6 bar of CO₂, the bis-acetate complex Fe(dmpe)₂(OCOCH₃)₂ was obtained.^[130] The same behavior was observed with the complexes *cis*- and *trans*-Ru(dmpe)₂Me₂.^[131]

5.2 Synthesis of Pt(bis-phosphine)Me₂ complexes and their reaction with CO₂

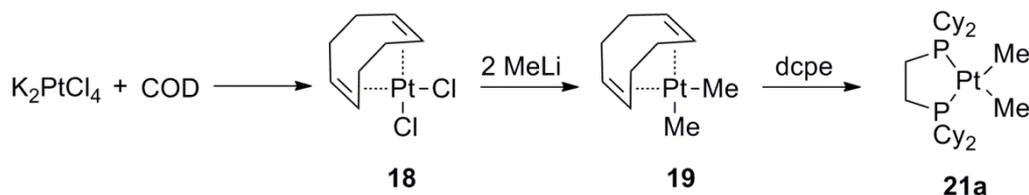
5.2.1 Synthesis of Pt(dcpe)Me₂ and Pt(dtbpe)Me₂

Two different complexes of platinum with bis-phosphinoligands were synthesized, one bearing a dicyclohexylphosphinoethane (dcpe) ligand and the other one a ditertbutylphosphinoethane (dtbpe).

The complex Pt(dcpe)Me₂ (**21a**) was synthesized from two different routes:

- By reduction of Pt(dcpe)Cl₂ with MeLi
- From Pt(COD)Me₂ by displacement of the COD ligand with the phosphino ligand

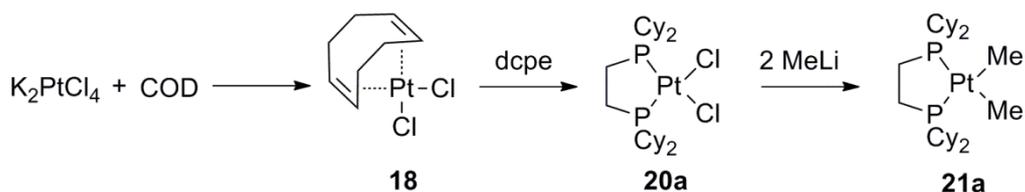
Pt(COD)Cl₂ (**18**) was synthesized from the reaction of K₂PtCl₄ with COD for three days at room temperature. This synthesis proceeded under air with very high yields. **18** was stored under argon to prevent the dissociation of the cyclooctadiene ligand.



Scheme 5.3. Synthesis of Pt(dcpe)Me₂ through the reduction of Pt(COD)Cl₂

In the first route, **18** was reduced with two equivalents of MeLi leading to Pt(COD)Me₂ (**19**). MeLi ignites spontaneously in air, thus has to be handled with care. **19** is air stable for short time; it was stored under argon and in the exclusion of light to prevent its decomposition. The ligand exchange from COD to the phosphine was easily performed at room temperature in 45 minutes. The purity of all intermediates and products was verified by ¹H, ¹³C and ³¹P NMR.

In the second route, the ligand exchange was performed first, before the reduction of the chloride ligands to methyl groups.

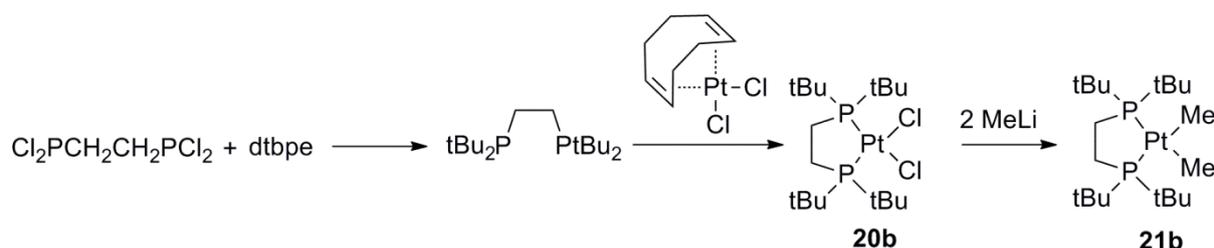


Scheme 5.4. Synthesis of Pt(dcpe)Me₂ through the reduction of Pt(dcpe)Cl₂

Mixing **18** with the phosphine for 5 hours at room temperature afforded the complex Pt(dcpe)Cl₂ (**20a**) with high yields. The reduction of **20a** was performed with two equivalents of methyllithium.

Both ways of syntheses afforded the desired product with moderate to high yields. The second way offers the advantage that Pt(dcpe)Cl₂ can be stored for long time under argon without decomposition, contrary to Pt(COD)Me₂ which slowly loses the COD ligand. Pt(dcpe)Cl₂ is also an intermediate used for the synthesis of Pt(dcpe)H₂ (see section 5.3.).

A second complex with a different bisphosphine ligand was synthesized: Pt(dtbpe)Me₂ (**21b**). Contrary to dcpe, dtbpe is not commercially available and had to be synthesized from 1,2-bis(dichlorophosphino)ethane (Cl₂PCH₂CH₂PCl₂) and four equivalents of tert-butyl lithium (tBuLi). tBuLi is a pyrophoric substance which reacts vigorously with oxygen and air moisture. Thus it has to be handled with the greatest care. The synthesis of dtbpe followed the experimental procedure from Schick et al. in which a yield of 40 % was reported.^[132] A yield of 25 % was achieved by us, purity of the product being determined by ¹H and ³¹P NMR. The product was stored in the glovebox.



Scheme 5.5. Synthesis of Pt(dtbpe)Me₂

Following the same procedures as for the synthesis of **21a**, **18** was reacted with dtbpe to lead to Pt(dtbpe)Cl₂, which was further reduced with MeLi to form Pt(dtbpe)Me₂ (**21b**). The purity of the intermediates and products was determined by ¹H, ¹³C and ³¹P NMR. All products were stored in the glovebox.

5.2.2 Reactivity of Pt(dcpe)Me₂ and Pt(dtbpe)Me₂ with CO₂

In a first experiment, **21b** was dissolved in d-THF and 3 bar of CO₂ were pressurized. ¹H, ³¹P and ¹³C NMRs were regularly recorded over 5 days, however no change in the spectra could

be observed. The sample was heated at 70 °C for 12 h but still no sign of reaction could be observed. Two other reactions were conducted: one in d-toluene at room temperature for 16 h and then at 100 °C for 5 h, the second one in C₆D₆ at room temperature for 16 h and then at 70 °C for 5 h; however no sign of interaction between **21b** and CO₂ was detected.

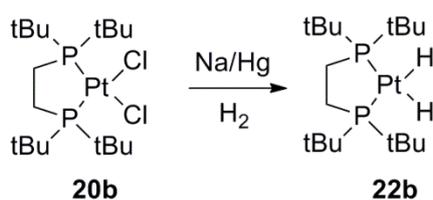
The same experiment was performed with **21a** in C₆D₆ under 3 bar of CO₂ for 16 h at room temperature. As no sign of insertion of CO₂ into the palladium-methyl bond could be detected, the sample was heated at 70 °C for 5 h, however no change was observed in the NMR spectra.

It can thus be concluded that Pt(dcpe)Me₂ and Pt(dtbpe)Me₂ are unreactive towards CO₂.

5.3 Synthesis of Pt(bis-phosphine)H₂ complexes and their reaction with CO₂

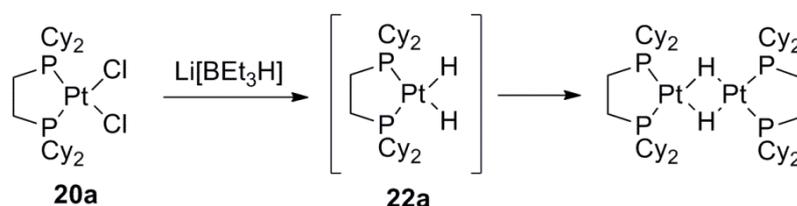
5.3.1 Synthesis of Pt(bis-phosphine)H₂ complexes

It was observed that platinum dihydride compounds with a *cis* geometry are prone to hydrogen elimination and formation of dimer complexes.^[133] However, the use of ligands with bulky substituents such as tert-butyl groups help to stabilize these complexes and prevent their decomposition.^[134] The reduction of Pt(dtbpe)Cl₂ to Pt(dtbpe)H₂ (**22b**) was performed following the synthesis from Otsuka et al.^[134] Pt(dtbpe)Cl₂ was reacted for 16 h at room temperature with 2.5 bar of H₂ over mercury amalgam. Mercury amalgam was formed in situ by the reaction of 19 g of mercury with 190 mg of sodium powder (11:1 ratio). It is a strong reducing agent safer to handle than sodium powder. **22b** was obtained with moderate yield. It is stable outside an atmosphere of H₂, it is however highly air sensitive and must be stored under argon. Its purity was determined by ¹H, ³¹P and ¹³C NMR.



Scheme 5.6. Synthesis of Pt(dtbpe)H₂

As reported in the literature^[134-135], Pt(dcpe)H₂ (**22a**) is only stable for a couple of hours in solution. The synthesis reported by Manners et al.^[135] was reproduced in an NMR tube: Pt(dcpe)Cl₂ was suspended in C₆D₆, and 1 equivalent of “super-hydride” Li[BEt₃H] was added. Immediately the solid dissolved and a NMR recorded after 1 h of reaction showed the formation of complex **22a**: the ³¹P NMR displays a triplet with the main peak at 76.9 ppm (literature: 77.2 ppm) with satellites peak of ¹⁹⁵Pt at 1904 Hz (reported: 1875 Hz).



Scheme 5.7. Synthesis of Pt(dcpe)H₂ and formation of a dimer complex

The reaction was performed again in a Schlenk flask: a sample taken after 1.5 h displayed the same triplet by ³¹P NMR. After evaporation of a part of the solvent and overnight recrystallisation, a white solid was obtained whose NMR is in accordance with the dimer [Pt(dcpe)H₂]₂.^[133a] Its ³¹P NMR displays a triplet of triplet at 84.1 ppm, and the hydride peaks displays a quintuplet of quintuplet at -2.66 ppm. This compound is formed by rearrangement of complex **22a**. All those elements prove the in-situ formation of Pt(dcpe)H₂ which is stable for at least 1.5 hours in a benzene solution.

5.3.2 The reactions of Pt(bis-phosphino)H₂ complexes with CO₂

The complex Pt(dcpe)H₂ was formed in situ by the reaction of Pt(dcpe)Cl₂ with Li[BEt₃H] on which 3 bar of CO₂ were pressurized. Immediately a change in the color of the solution was observed. An NMR measured after 1 hour showed the presence of new peaks between 1 and 2 ppm, however in low concentration as compared to the main compound present in solution: the dimer [Pt(dcpe)H₂]₂. After 20 h, the same NMR spectrum is observed with the presence of new peaks coming probably from decomposition of the catalyst. A reaction has

occurred, however the yield is low. Heating the sample did not improve the yield, but rather led to decomposition of the compound in numerous byproducts.

The complex $\text{Pt}(\text{dtbpe})\text{H}_2$ was reacted with 3 bars of CO_2 in an NMR tube. In opposition to $(\text{dcpe})\text{PtH}_2$, this compound is stable in solution^[133a]. Upon addition of CO_2 , the peaks of the starting material, especially the peaks of the hydride are decreasing. After 40 hours of reaction, the peak of the hydride was not present anymore, however a wide range of new compounds have formed as was observed from the numerous peaks in ^1H and ^{31}P NMR.

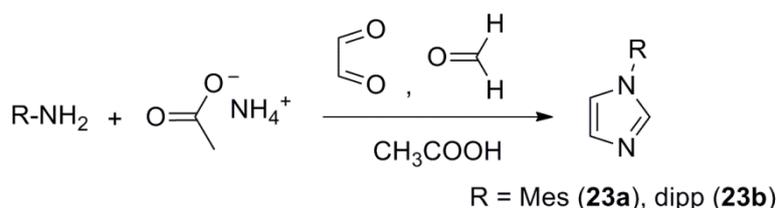
Higher scale reactions were performed, however no single pure compound containing a CO_2 moiety could be isolated.

5.4 Synthesis of $\text{Pd}(\text{bis-NHC})\text{Br}_2$ complexes

In order to stabilize the complexes, bis-NHC ligands were employed rather than bisphosphine ligands. Carbene ligands have proven to be more strongly bounded to the metal than the phosphine ones.^[128]

5.4.1 Synthesis of bis-imidazolium salts

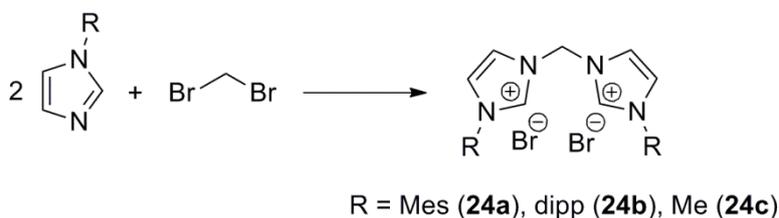
2,4,6-trimethylphenyl imidazole (**23a**) and 2,6-diisopropylphenyl imidazole (**23b**) were synthesized from glacial acetic acid and aqueous glyoxal and 2,4,6-trimethylaniline.^[136]



Scheme 5.8. Synthesis of **23a** and **23b**

High yields were obtained with the mesityl ligands. The higher steric hindrance from the dipp groups renders the formation of the imidazole ring more challenging. The purification method reported in the literature (recrystallization from a mixture of ethyl acetate and hexane) was unefficient for 2,6-diisopropylphenyl imidazole, leading to the formation of a brown solid being of mixture of several compounds. As a result, column chromatography (ethyl acetate:hexane = 1:1) was chosen to be a suitable purification technique. The purity of the products was verified by ^1H and ^{13}C NMR.

The biscarbene salts were synthesized according to the procedure published by Herrmann et al.^[137]

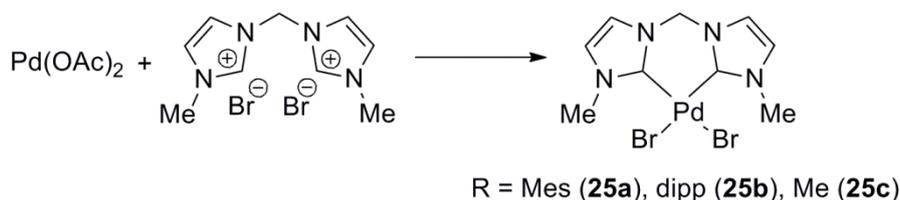


Scheme 5.9. Synthesis of bis-imidazolium salts

This synthesis proceeded in an ACE pressure tube where high pressure reactions can be performed. The high stability of the biscarbene salts to high temperature and pressure made it possible to perform the reaction in THF at 130 °C for 72 h. The conversion of the imidazole precursor bearing mesityl substituents was almost quantitative. The yield of the imidazole with methyl and diisopropylphenyl groups was slightly lower. Important washings with THF had to be performed to remove the dark brown solid which has formed as byproduct of the reaction. The purity of the products was determined by ^1H and ^{13}C NMR. A mass spectroscopy measurement was also performed for complex **24a**. The peak with the highest intensity appears at m/z 385 attributed to the biscarbene cation. A peak with high intensity is also found at m/z 465.0 corresponding to the biscarbene cation with one bromide anion. This was attributed to an incomplete decomposition caused by the high speed at which the sample passed through the ion channel.

5.4.2 Synthesis of Pd(bis-NHC)Br₂ complexes

The synthesis proceeded from the reaction of the bis-imidazolium salt in presence of Pd(OAc)₂ and does not require the presence of a base.



Scheme 5.10. Synthesis of Pd(bis-NHC) complexes

The target products were synthesized according to the publication of Albrecht et al.^[138] by a gradual temperature rise over a period of several hours, which significantly elevated the yield and avoided various byproducts formation in comparison to a sharp temperature rise method. The compounds were purified by crystallization from a DMSO/dichloromethane/diethyl ether solution. DMSO is used as solvent for the synthesis, as it is the only organic solvent in which the complexes are soluble. Their drying was problematic due to the high boiling point of this solvent. In consequence, the NMRs always display a peak coming from DMSO even after overnight drying *in vacuo*.

5.5 Synthesis of Pd(bis-NHC)Me₂ complexes

5.5.1 Synthesis from the reaction of Pd(bis-carbene)Br₂ with MeLi

As previously reported for Pt(bisphosphine) complexes, methyllithium is a very good methylating agent, able to reduce the chlorine ligand to methyl groups. The synthesis was performed under the same conditions (with 2 equivalents of MeLi in ether at -40 °C), using Pd(IMes)₂Br₂ as starting material. However, a rapid decomposition of the complex occurred when the temperature was risen over 15 °C: the solution turned to black color, and no palladium containing complexes could be isolated. Experiences conducted at lower temperature led to a mixture of products; however no formation of a palladium-methyl bond could be detected by ¹H or ¹³C NMR. A ¹H NMR study of this reaction was performed at -78 °C in C₆D₆. After around 15 minutes of reaction, it was observed that signals of the

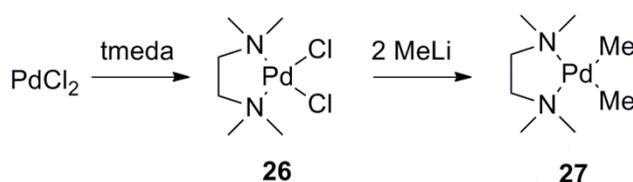
protons of the methyl bridge (at 6.52 ppm) started to be modified. Therefore, it seems that methyl lithium, which is a strong base, attacks preferentially the acid protons of the methyl bridge rather than performing the reduction of the chlorides to methyls.

Rosenthal et al. also tried the same reactions, and report that they could not generate any analytically pure material through this way of synthesis.^[127]

5.5.2 Synthesis from the formation of the free carbene

As the methyllithium route did not give satisfaction, another way was followed going through the formation of the free carbene, either in situ or after its isolation. The synthesis of Pd(IMes)₂Me₂ was already reported by Slaughter et al.^[139] with an in-situ formation of the free carbene at -78 °C which was then reacted with Pd(tmeda)Me₂ in THF, leading to 59 % yield.

PdCl₂ and tmeda were reacted together to afford Pd(tmeda)Cl₂ which was reduced to Pd(tmeda)Me₂ by reaction with two equivalents of MeLi.



Scheme 5.11. Synthesis of Pd(tmeda)Me₂

The products were characterized by ¹H and ¹³C NMR, and compared with literature data. Pd(tmeda)Me₂ was stored under argon at the exclusion of light.

Following the procedure of Slaughter et al.^[139], different experiments were performed with the formation of the free carbene in-situ by deprotonation of the imidazolium salt in presence of Pd(tmeda)Me₂. However those experiments never led to the formation of the desired product. Therefore, the preparation of the free carbene was intended following the procedure of Green et al. for the isolation of the free bis-NHC bearing tert-butyl ligands.^[140]

Complex **24a** was reacted with potassium tert-butoxide for 12 hours at 25 °C in THF, and the

solution was put to recrystallize from benzene at -78°C . However, despite all our efforts, the free carbene was never obtained.

Rosenthal et al. succeeded in synthesizing $\text{Pd}(\text{IMes})_2\text{Me}_2$ in 2012 by bringing major changes to the procedure reported by Slaughter et al.^[127] Especially, they performed the deprotonation of the carbene for 10 h at room temperature. Therefore, the conditions we used were surely too harsh to allow the free carbene to form, which would explain why it could never be isolated as well as why the in-situ reaction did not lead to the formation of any product.

5.6 Synthesis of Pd(bis-NHC) hydride complexes

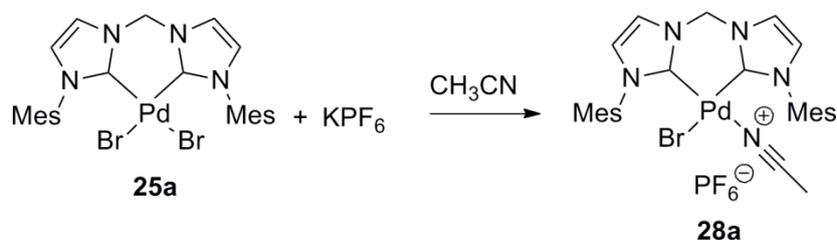
5.6.1 Synthesis of Pd(bis-NHC)H₂ complexes

The reduction of $\text{Pd}(\text{IMes})\text{Br}_2$ and $\text{Pd}(\text{dipp})\text{Br}_2$ to the corresponding palladium dihydride complexes was intended with different reducing agents: mercury amalgam under 3 bar of H_2 , NaBH_4 and NaH . Reactions were tried in different solvents (THF, ethanol, toluene) and from temperature varying between -78°C and r.t. After each reaction, a ^1H NMR of the obtained solution was performed before proceeding to the purification steps. In each case, numerous peaks were observed showing the formation of several byproducts, and no peak of hydride was ever observed. This might be due to the high instability of dihydride complexes.

5.6.2 Synthesis of Pd(bis-NHC) hydride complexes

As palladium-monohydrides are expected to be more stable than their dihydrides equivalents, one bromide ligand was replaced by an acetonitrile ligand, with PF_6^- as a counteranion. The experimental procedure described by Herrmann et al.^[141] using 18 equivalents of KPF_6 was followed.

Synthesis of platinum and palladium methyl complexes and their reaction with carbon dioxide



Scheme 5.12. Synthesis of **28a**

However, the product isolated was the complex bearing two acetonitrile ligands, as was observed by ¹H, ¹⁹F, ¹³C NMR and Elemental Analysis. A crystal structure of this compound was obtained (Figure 5.1.). Thus the procedure was slightly modified: only one equivalent of KPF₆ was used under the same reaction conditions, which leads to the formation of the desired complex in high yields. It was characterized by ¹H, ¹⁹F, ¹³C NMR and Elemental Analysis. Its crystal structure was obtained (Figure 5.2.).

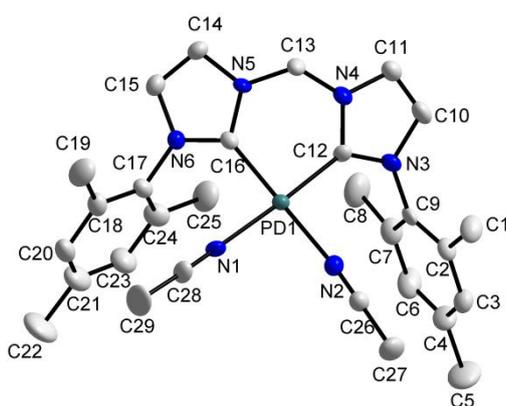


Figure 5.1. ORTEP diagram of **29a**; H and PF₆⁻ have been omitted for clarity

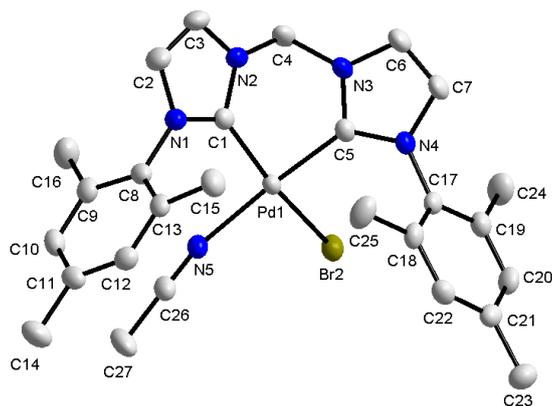


Figure 5.2. ORTEP diagram of **28a**; H and PF_6^- have been omitted for clarity

The reduction of **28a** to the hydride was intended with NaBH_4 and $\text{Li}[\text{B}(\text{Et}_3)\text{H}]$ as reducing agents. Reactions were performed at NMR scale in in d-THF and in CD_3CN at -78°C and -35°C .

In each case, a new peak at -15 ppm attributed to a palladium-hydride bond was observed in ^1H NMR. However, the product decomposed above -20°C as could be seen when the rise of temperature was monitored by ^1H NMR. At this temperature, the hydride peak disappears in a few minutes, and numerous new peaks coming from decomposition of the complex are observed. A sample kept in a Schlenk tube turns from light pink to black when the temperature reaches -10°C . As the product formed is very instable, it was decided not to pursue in this direction.

5.7 Conclusion

The synthesis of platinum and palladium methyl or hydride complexes bearing bisphosphine or bis-NHC ligands was performed, and their reactions with CO_2 were studied.

The complexes $\text{Pt}(\text{dcpe})\text{Me}_2$ (**21a**) and $\text{Pt}(\text{dtbpe})\text{Me}_2$ (**21b**) were synthesized by reduction of the respecting platinum dichloride complexes with methyllithium. They were reacted with 3 bar of CO_2 in an NMR tube, however no insertion of CO_2 into the platinum-methyl bond was observed even after several hours at 70°C .

The reaction of Pt(dtbpe)Br₂ with hydrogen over mercury amalgam afforded Pt(dtbpe)H₂ (**22b**) with moderate yield. 3 bar of CO₂ were pressurized over **22b**, and a reaction was observed. However, it led to the formation of numerous byproducts, and no pure CO₂-containing compound could be isolated. The same phenomenon was observed with Pt(dcpe)H₂ (**22a**), which was synthesized in-situ from the reduction of Pt(dcpe)Br₂ with Li[BET₃H].

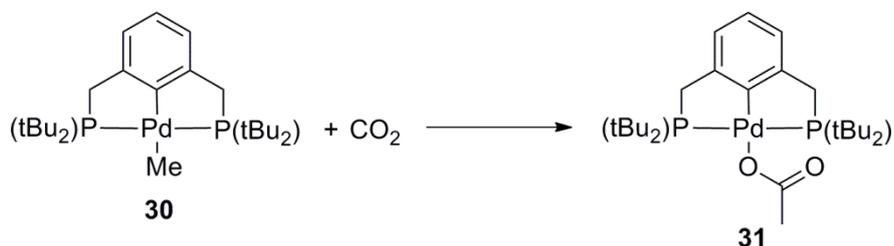
The synthesis of palladium (II) bis-NHC complexes bearing methyl groups was intended through two routes. First, the reduction of Pd(bis-NHC)Br₂ with MeLi was studied by NMR, and it was observed that MeLi attacks preferentially the acidic protons of the bridge linking the two imidazole rings rather than reducing the bromide ligands. The second route proceeded through the in-situ formation, or the isolation, of the free carbene and its reaction with Pd(tmeda)Me₂. The desired compound as well as the free carbene were however never isolated.

The reduction of Pd(bis-NHC)Br₂ to the dihydride Pd(bis-NHC)H₂ was intended with different reducing agents. The formation of the desired complexes was never observed, probably due to the high instability of such dihydride compounds. A [Pd(bis-NHC)(CH₃CN)Br]⁺ PF₆⁻ complex was synthesized and its reduction to the monohydride was performed. An in-situ NMR study at low temperature showed the formation of the hydride at -78 °C and its decomposition at temperatures higher than -20 °C.

6 Synthesis of palladium (II)-methyl complexes with CNC pincer ligands and their reaction with carbon dioxide

6.1 Introduction

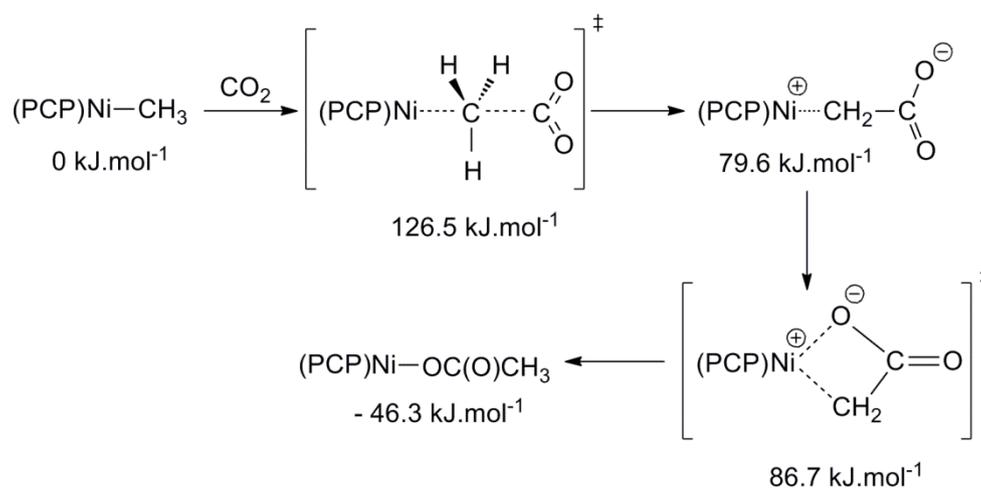
An important number of publications relate the insertion of CO₂ into palladium-carbon bonds, these reactions proceeding for the large majority through the insertion into palladium-allyl or aryl complexes.^[112a, 142] One insertion has even been made recently into palladium-bridging allyl dimers.^[143] Even if the CO₂ insertion into metal-methyl complexes is known for several metals such as Co^[144], Fe^[130], Rh^[145] and Ru^[131], Wendt et al. published the only paper up to date where a CO₂ insertion into a palladium-methyl bond has occurred.^[119d] By using a PCP tridentate pincer ligand, they labilized the palladium-carbon enough to permit the CO₂ insertion. Complex **30** displays indeed the longest palladium-carbon σ -bond reported in a mononuclear complex: 2.199(3) Å. This shows the high trans influence from the aryl ring.



Scheme 6.1. Wendt's first insertion of CO₂ into a Pd-CH₃ bond^[119d]

Complex **30** reacted with thirty equivalents of CO₂ in an NMR tube at 80 °C, leading to the normally inserted complex **31**. However, under the same conditions, the PNP-palladium complex bearing phenyl groups on the phosphorous atoms did not react with CO₂. It is therefore clear that the ancillary ligand plays a crucial role in this insertion reaction. The same complex was later designed with a hydroxyl group rather than a methyl and the insertion of CO₂ proved to be much easier: it proceeds within minutes at 4 bar of CO₂ and room temperature.^[142f]

Raskatov et al. synthesized the nickel-complex bearing the same PNP-ligand.^[146] It displays a shorter nickel-methyl bond of 2.026(4) Å and reacts at 150 °C under 1 atmosphere of CO₂ to afford the carboxylate Ni-CO₂Me. Both Wendt et al. and Raskatov et al. performed DFT calculations and arrived to the same conclusion: no interaction exists between the metal and carbon dioxide due to the bulky tert-butyl groups. The pathway as described by Raskatov et al. is summarized in Scheme 6.2.



Scheme 6.2. DFT calculations on the insertion of CO₂ into a Ni-CH₃ bond^[146]

The insertion proceeds through a S_E2 mechanism: the CO₂ attacks the metal bound carbon from the opposite face to the nickel-methyl bond to form a five coordinate carbon.^{[146]-[147]} Kinetic data show the reaction is first order in palladium and in CO₂.^[147]

A theoretical study about the insertion of CO₂ into Rh(I)-methyl bonds with different pincer ligands was performed by Leitner et al.^[148] They concluded that several structural factors influence the reactivity of the complexes:

- Ionic complexes are more reactive than neutral ones
- The central donor atom of the pincer ligand has a major influence, with the reactivity decreasing in the order N > C > O
- Basic side arms ligands bring higher reactivity to the complex

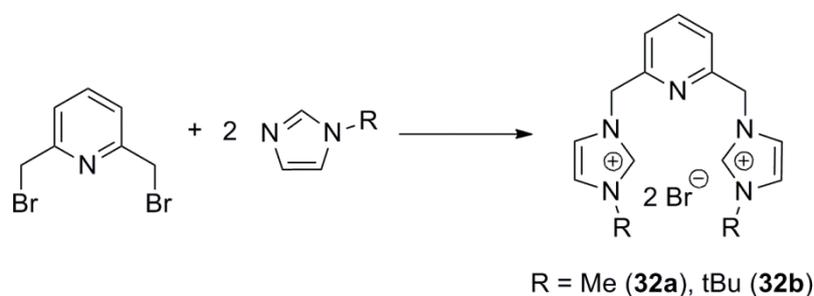
Our interest was to synthesize palladium complexes bearing a methyl bond and a CNC pincer ligand, and to study its insertion with CO₂. Complexes with CNC pincer are more current than

the one with PCP. A review summarizing all complexes bearing CNC ligands has been published recently.^[149]

6.2 Synthesis of palladium(II)-methyl complexes

6.2.1 Synthesis of the CNC ligands

Two CNC pincer ligands were synthesized: **32a** and **32b**. The difference between them is the group on the pending arm: for **32a** it is a methyl group, whereas **32b** has a bulky tert-butyl group.



Scheme 6.3. Synthesis of CNC pincer ligands

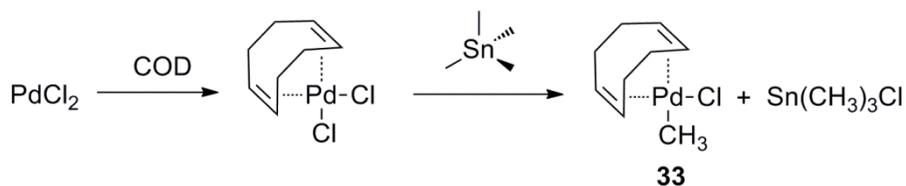
The procedure for the synthesis of **32a** and **32b** was fully repeated according to the method reported by Cavell et al.^[150] (Scheme 6.3.). The yields obtained were satisfactory (respectively 85 and 67 %), close to what was reported in the literature. The purity of the complexes was verified by ¹H and ¹³C NMR spectroscopy. The bis-imidazolium salts were stored under air at room temperature.

6.2.2 Synthesis of the palladium precursor

The compound Pd(COD)(CH₃)Cl (**33**) was synthesized according to the method reported by Vrieze et al.^[151] (Scheme 6.4.). The reaction between Pd(COD)Cl₂ and Sn(CH₃)₄ proceeded smoothly at room temperature in one day. Sn(CH₃)₄ is a well-known methylating agent^[152]; it

Synthesis of palladium complexes with CNC pincer ligands and their reaction with carbon dioxide

is however a very toxic compound which has to be handled with great care. Compound **33** was obtained with 74 % yield, its separation for the tin compounds was performed by simple washings with ether.



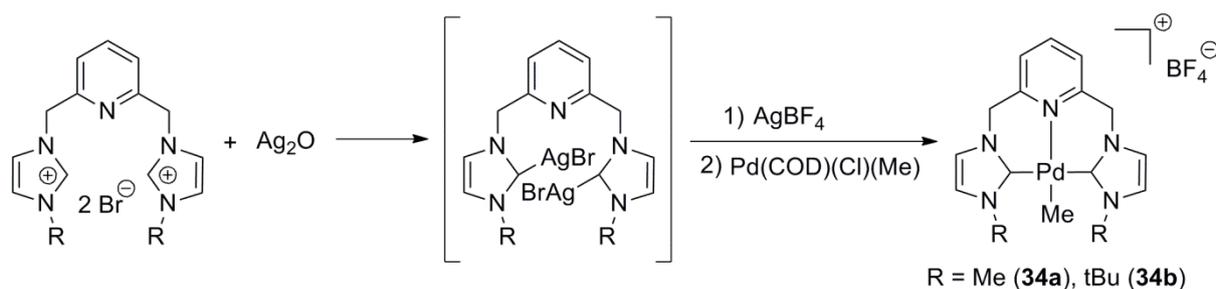
Scheme 6.4. Synthesis of Pd(COD)(CH₃)(Cl)

The purity of the compound was verified by ¹H and ¹³C NMR. It was stored under argon at room temperature in exclusion of light. After some months, the complex has turned to a grey color due to the slow dissociation of COD from the metal.

6.2.3 Synthesis of the palladium(II) complexes

The synthesis of complexes **34a** and **34b** was slightly changed from the procedure published by Cavell et al.^[150] The yield of **34b** was lower than the one of **34a**, probably because of the steric hindrance of the tert-butyl groups. Both complexes were characterized by ¹H, ¹³C and ¹⁹F NMR.

In a first step, an Ag(I) complex was formed in situ by deprotonation of the bis-imidazolium salt with the mild base Ag₂O. In a second step, a transmetalation was performed to transfer the NHC ligand to the palladium(II) complex.



Scheme 6.5. Synthesis of **34a** and **34b**

The methyl groups linked to the palladium in complex **34a** and **34b** exhibit singlet peaks at respectively 0.70 and 0.65 ppm in ^1H NMR and at -14.6 and -8.1 ppm in ^{13}C NMR, in the range of other Pd-CH₃ complexes^[119a-c], and slightly downfield as compared to complex **30** (peak at 0.47 ppm in ^1H , not reported in ^{13}C).^[119d] The complexes show a remarkable stability, requiring respectively 15 h at 150 °C and 9 h at 105 °C in d₆-DMSO to completely remove the palladium-methyl signal from the ^1H NMR spectrum.^[150a] The effect of the tert-butyl ligand is particularly noticeable in the geometry of the molecule. While the C-Pd-C bond is close to linearity in complex **34a** (173 °), it is more twisted in complex **34b** (169 °). This twist and the steric hindrance from the tert-butyl groups explain the lengthening of the Pd-Me bond in complex **34b** (2.061(4) Å) as compared to complex **34a** (2.044(1) Å).^[150b]

6.3 Reaction of **34a** and **34b** with carbon dioxide

In a typical experiment, 30 mg of complex **34a** or **34b** were dissolved in d₆-DMSO in a NMR tube. 3 bar of CO₂ were pressurized at room temperature and NMRs (^1H , ^{13}C , ^{19}F) were recorded after 3 h, 1 day and 2 days. As no change could be observed in the NMR spectra, **34a** and **34b** were heated at respectively 100 °C and 60 °C for two weeks and NMR were recorded regularly. Even under such condition, no reaction could be observed (see Figures 6.1. to 6.5.).

Synthesis of palladium complexes with CNC pincer ligands and their reaction with carbon dioxide

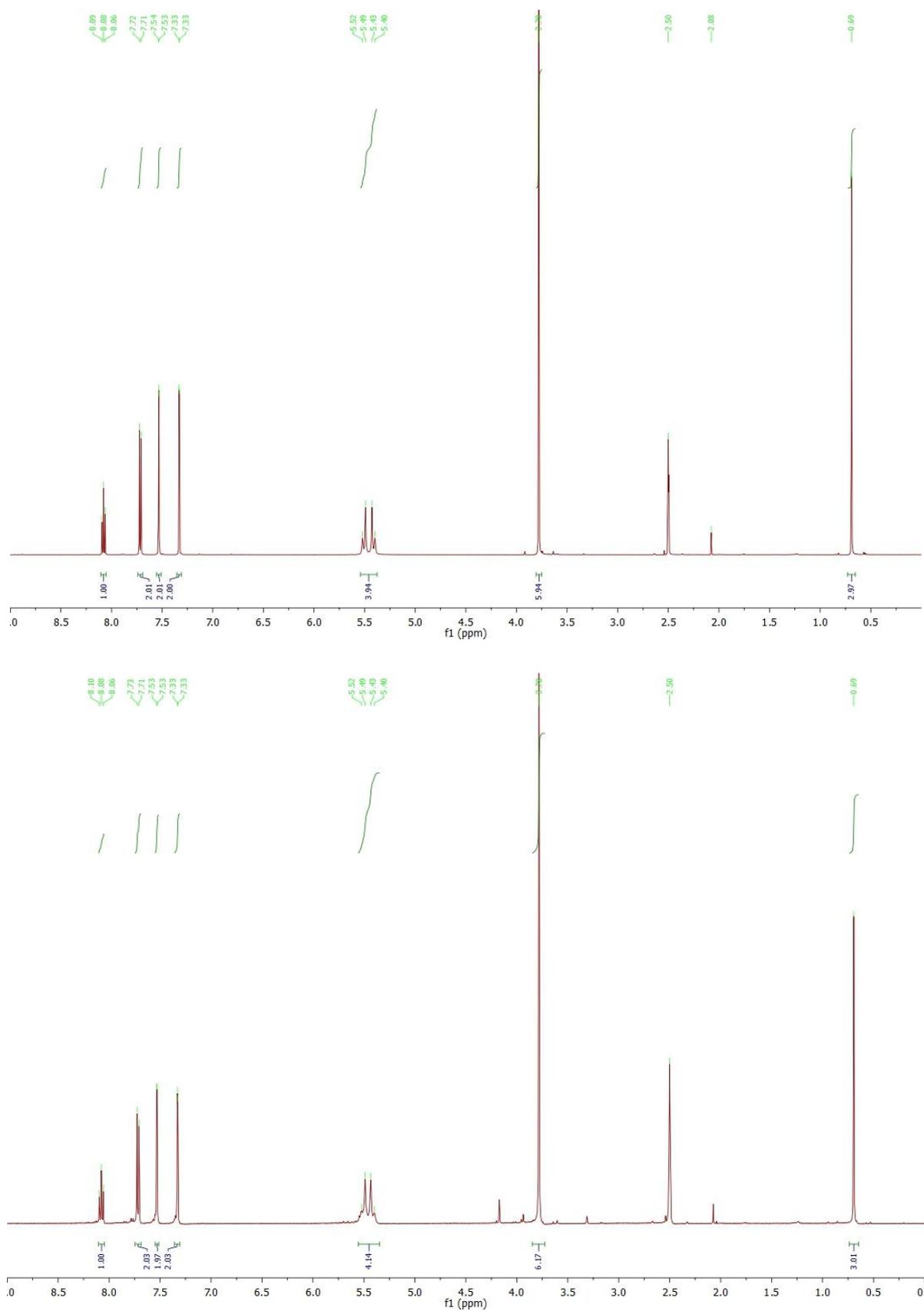


Figure 6.1. ^1H spectra of **34a** (top) and **34a** at 3 bar of CO_2 after 2 days at r.t. and one week at 110 °C (bottom)

Chapter 6

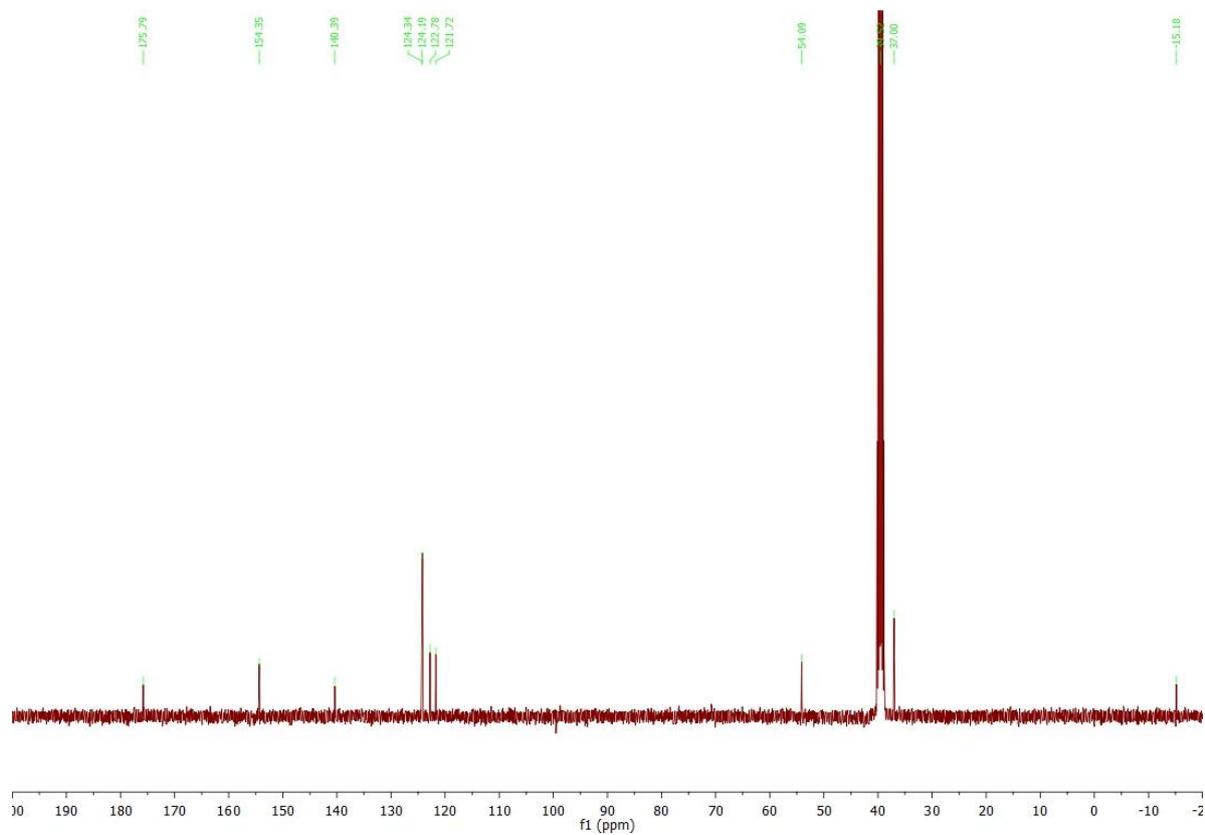
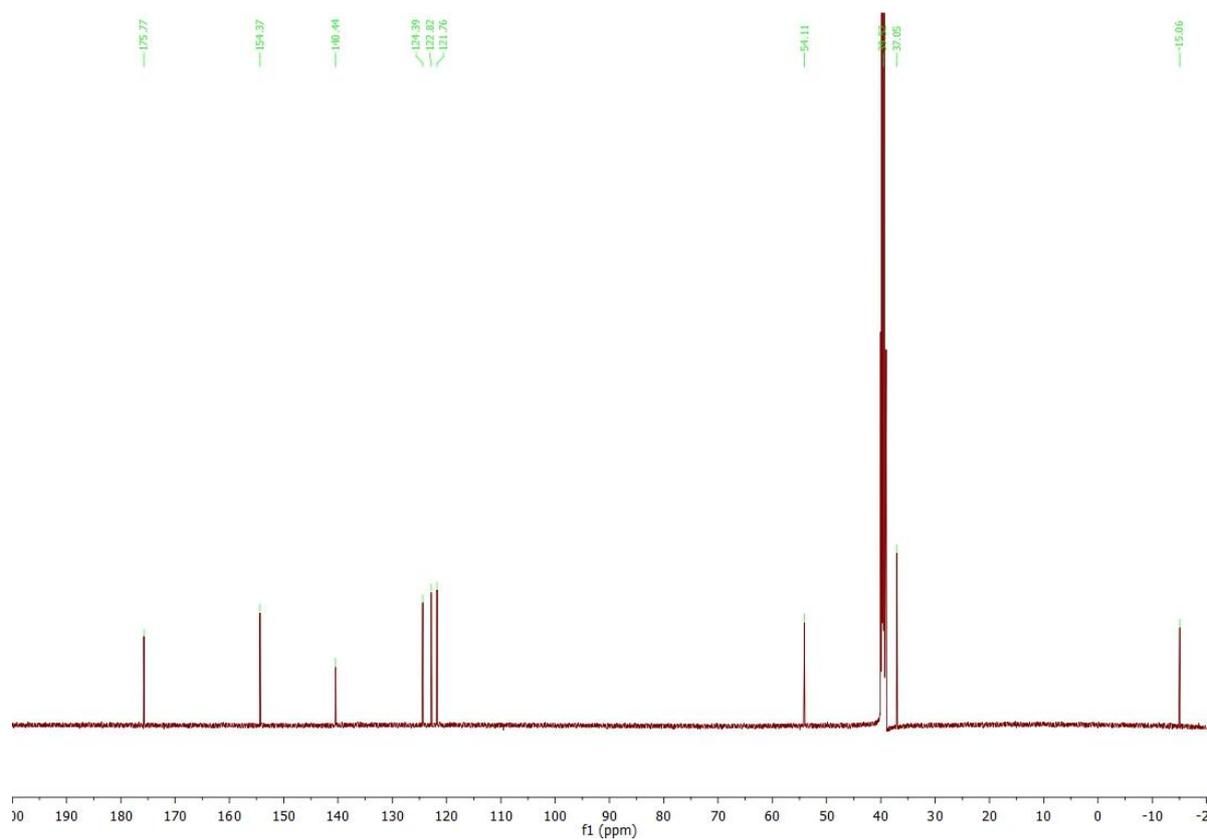


Figure 6.2. ^{13}C spectra of **34a** (top) and **34a** at 3 bar of CO_2 after 2 days at r.t. and one week at 110 °C (bottom)

The ^1H NMR spectra of **34a** and of **34b** under three bar of CO_2 after two days at r.t. and one week at $110\text{ }^\circ\text{C}$ are comparable. The compound is perfectly stable, and the peak of the palladium-methyl bond has not decreased in intensity. Apart from the presence of the peak of free CO_2 in solution at 124.2 ppm, no change is observed in the ^{13}C NMR spectra. The peak of the methyl group is still present at -14.6 ppm and no peak from an acetate group could be detected.

The same results are found for complex **34b**. Therefore, it can be concluded that those compounds are unreactive towards carbon dioxide.

6.4 Conclusion

Two palladium-methyl complexes with tridentate CNC pincer ligand were synthesized and their reaction with carbon dioxide was studied by NMR spectroscopy.

The synthesis of complexes **34a** and **34b** proceeds via the reaction between (η^2, η^2 -cycloocta-1,5-diene)chloromethylpalladium(II) ($\text{Pd}(\text{COD})(\text{Cl})(\text{Me})$) and the salt of the pincer ligand in presence of silver oxide and silver tetrafluoroborate. Those complexes were submitted to three bar of CO_2 at high temperature for a week but displayed no reaction with this compound.

7 Experimental Section

7.1 General procedures

7.1.1 Inert gas atmosphere

All preparations and manipulations were carried out under argon atmosphere using standard Schlenk techniques. All commercial compounds were purchased from Acros Organics, ABCR, Aldrich and Strem Chemicals unless otherwise stated. All chemicals were used as received by the supplier. The glassware was washed in an isopropanol/KOH bath followed by diluted HCl bath to remove traces of base and then rinsed with distilled water. All glassware was dried in an oven at 100 °C overnight and further heated at ca. 300 °C *in vacuo* before use.

7.1.2 Solvents

All solvents were dried and stored under argon and molecular sieves (4 Å or 3 Å for acetonitrile and methanol). Hexane, pentane, dichloromethane, diethyl ether and toluene were dried in a Grubbs apparatus. THF was dried with sodium wires; acetone with MgSO₄ and methanol with Mg or CaH₂. The water content of all solvents (except methanol and acetone) was analyzed by a Karl-Fisher titrator. Deuterated solvents were dried under molecular sieves and degassed prior to use.

7.1.3 Characterization Methods

Elemental analyses were measured at Mikroanalytisches Labor of the TU München. Metal analyses were determined with a Vario EL metal analyzer.

FT-IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using KBr pellets or Nujol as matrix.

NMR Measurements (^1H , ^{13}C , ^{19}F , ^{27}Al) were made with a 400 MHz Bruker Avance DPZ-400, a 500 MHz Bruker Avance DRX-500 and a 400 MHz Jeol-GX 400.

^1H NMR and ^{13}C NMR spectra were recorded in deuterated chloroform on a 400 MHz (100 MHz for ^{13}C) or on a 500 MHz (125 MHz for ^{13}C) instrument, chemical shifts are reported in ppm (δ , relative to TMS) using CHCl_3 residual peak ($\delta = 7.26$ ppm) in CDCl_3 as an internal standard. In situ IR spectroscopy was performed on a Mettler Toledo ReactIR 45/MultiMax RB04-50 station mounting 50 mL stainless steel autoclaves equipped with a *DiComp* diamond probe on the vessel bottom as a multiple reflection ATR element.

For the catalysis experiments, the vessels were connected to a CO_2 cylinder through a Mettler Toledo LMPress60 pressure controller. Trace metal analysis was performed on a Varian ICP OES 720 ES spectrometer, GC analysis of the reaction products was carried out on a Agilent Technologies 7890A GC system, equipped with a 19091j-413 column (bonded 5% phenyl, 95% dimethylpolysiloxane) 0.25 μ .

7.2 Chapter 2

Epoxides other than ethylene oxide were stirred for at least 6 hours over CaH_2 before distillation. Ethylene oxide (99.9%, liquefied gas, containing 200 ppm water, purchased from the AHG company) was used as received. Tetra-*n*-butylammonium bromide and tetra-*n*-butylammonium chloride (99%) were melt at 100-150 $^\circ\text{C}$ in a Schlenk tube, stirred under vacuum for five hours and stored under a protective atmosphere.

In a typical experiment (Table 2.1., entry 6), a stainless steel autoclave was charged under a protective atmosphere with propylene oxide (7 mL, 100 mmol), NbCl_5 (67.5 mg, 0.25 mmol) and DMAP (61.1 mg, 0.5 mmol) at 25 $^\circ\text{C}$. The solution was stirred at 300 r.p.m for five minutes and the temperature was raised to 50 $^\circ\text{C}$ at a rate of 5 $^\circ\text{C}/\text{min}$. Simultaneously, the pressure of the reactor was allowed to rise to five bar at a rate of 0.5 bar/min through the progressive addition of CO_2 controlled by a pressure regulator connected to a CO_2 cylinder (Figure 7.1.). The pressure in the reactor was kept constant at five bar for five hours with the drop in CO_2 pressure being continuously compensated by the pressure regulator. After five hours the reaction autoclave was cooled to 20 $^\circ\text{C}$ and the pressure slowly released through

the exhaust valve. A sample of reaction mixture was withdrawn and analyzed by ^1H NMR to determine conversion.

Experimental procedure for the synthesis of propylene carbonate (2a) at 50 °C and 5 bar

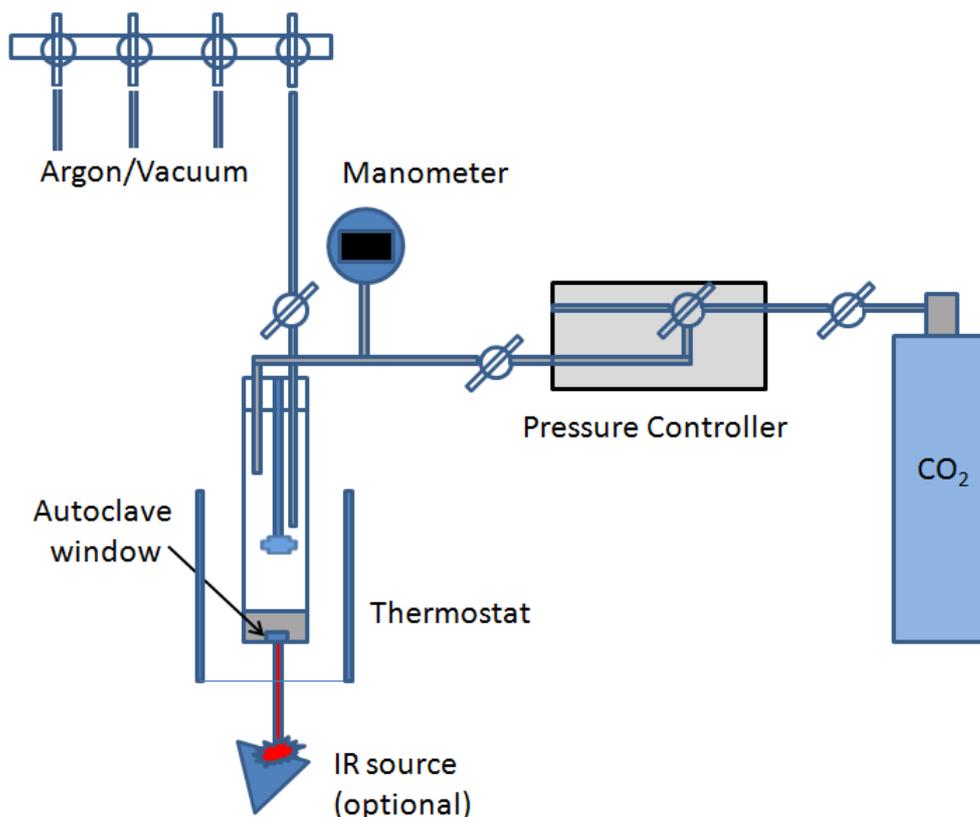


Figure 7.1. Experimental set up for the synthesis of cyclic carbonates from CO₂ and epoxides

Experimental procedure for the synthesis of 2a at room temperature and at low CO₂ concentration

In a typical experiment (Table 2.3., entry 4), a stainless steel autoclave was charged under a protective atmosphere with propylene oxide (7 mL, 100 mmol), NbCl₅ (270.2 mg, 1 mmol) and TBAB (644.7 mg, 2 mmol) at 25 °C. The solution was stirred at 500 r.p.m for ten minutes with the internal reactor pressure rising to 1.10 bar. CO₂ was added through a pressure regulator connected to a CO₂ cylinder till the internal pressure reached 2.10 bar. The pressure in the reactor was kept constant at this value for four hours with the drop in CO₂ pressure being continuously compensated by the pressure regulator. After four hours the

overpressure was slowly released through the exhaust valve. A sample of reaction mixture was withdrawn and analyzed by ^1H NMR to determine conversion.

Experimental procedure for the synthesis of ethylene carbonate (2b)

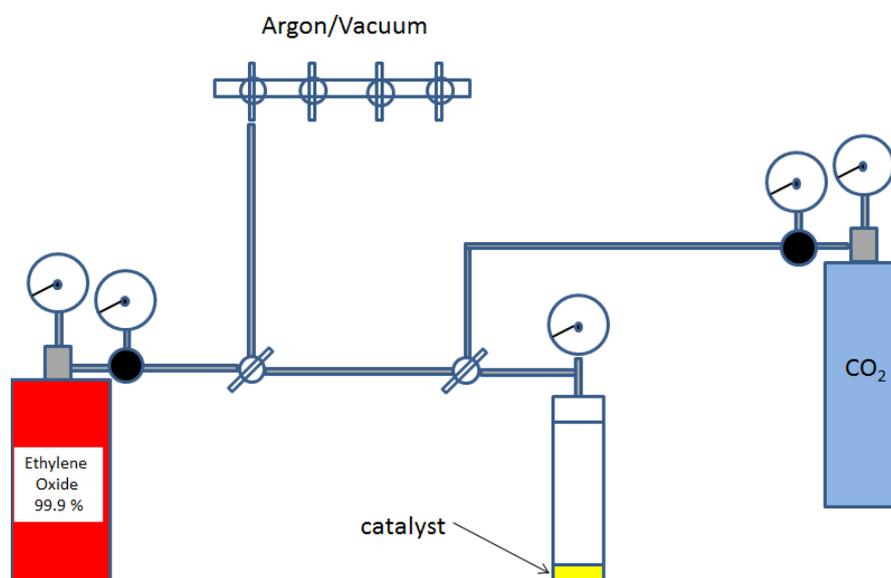


Figure 7.2. Experimental set up for the synthesis of ethylene carbonates from CO₂ and ethylene oxide

In a typical experiment (Table 2.5., entry 3), a 100 mL stainless steel autoclave was charged under a protective atmosphere with NbCl₅ (270.2 mg, 1 mmol) and TBAB (644.7 mg, 2 mmol). The autoclave was placed in an ice bath and evacuated. Ethylene oxide (99.9%, containing 200 ppm water) was introduced through a valve (25.0 g, 568 mmol) and the system was allowed to warm to room temperature (23 °C). The internal pressure of the system was 110 KPa (1.1 bar). The system was connected to a CO₂ cylinder and a slight overpressure (120 KPa) of CO₂ was applied. The system was stirred mechanically at 800 r.p.m for 12 hours. Subsequently, the reaction vessel was opened to the air and the residual ethylene oxide was allowed to evaporate and subsequently completely removed through rotary evaporation under reduced pressure at 35 °C. The pale yellow liquid was rapidly poured over a plug of silica gel that was washed with 1:1 EtO₂/EtOAc mixture affording 32.0 g (363.4 mmol, 64%) of pure ethylene carbonate after evaporation under reduced pressure. Spectroscopic data were consistent with literature (CAS: 96-49-1):

1-3-dioxolan-2-one (2b): ^1H NMR (400 MHz, CDCl₃, 20 °C): δ = 4.51 (s, 4H) ppm. ^{13}C NMR (100 MHz, CDCl₃, 20 °C): δ = 155.7 (C=O), 65.2 (CH₂) ppm.

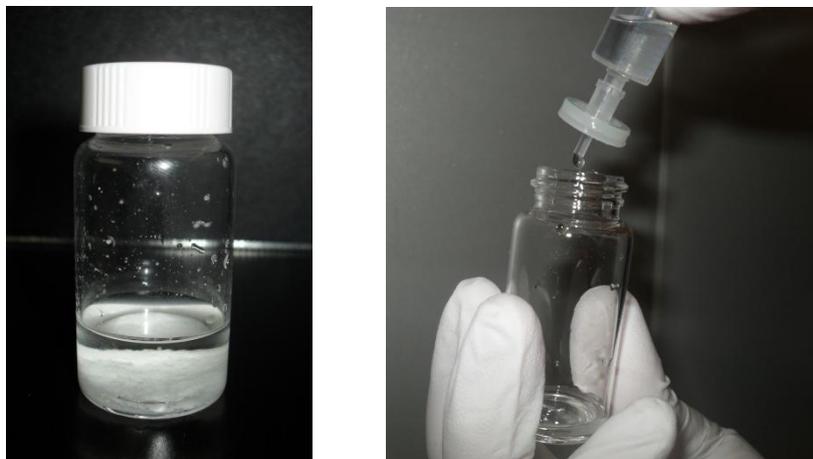
Product isolation:

Figure 7.3. Precipitation of insoluble salts from PC after exposure to air (left) and purification via filtration (right)

In the case when DMAP/NbCl₅ was used as a catalytic pair, facile propylene or butylene carbonate isolation was achieved with no need of distillation. In a typical experiment (Table 5.4., entry 1) the liquid, homogeneous phase obtained at the end of the reaction was evaporated under reduced pressure to remove the residual propylene oxide. After exposing the liquid obtained to air for one to three hours an abundant white precipitate formed that was removed through filtration on a Pall Acrodisc syringe filter (0.2 μm, nylon membrane, figure 7.3.) affording 9.19 g (90 mmol, 90%) of clean **2a**. Given the almost total absence of DMAP and Nb compounds in the carbonates obtained and the presence of nitrogen in the elemental analysis of the precipitate, the formation of insoluble pyridinium niobate salts can be assumed. The following techniques were used to assess the purity of the products:

NMR spectra were consistent with literature (propylene carbonate, CAS No: 108-32-7; butylene carbonate, CAS No: 4437-85-8):

4-Methyl-1,3-dioxolan-2-one (2a): ¹H NMR (400 MHz, CDCl₃, 20 °C): δ = 4.82 (m, 1H, OCH), 4.55 (t, 1H, J = 8.3 Hz, OCH₂), 4.01 (dd, 1H, J = 7.8, 7.9 Hz, OCH₂), 1.49 (d, 3H, J = 6.3 Hz, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ = 155.2 (C=O), 74.6 (CHO), 70.6 (OCH₂), 19.2 (CH₃) ppm.

4-Ethyl-1,3-dioxolan-2-one (2c): ^1H NMR (400 MHz, CDCl_3 , 20 °C): δ = 4.70 (m, 1H, OCH), 4.52 (t, 1H, J = 8.3 Hz, OCH_2), 4.07 (dd, 1H, J = 6.9 8.5 Hz, OCH_2), 1.80 (m, 2H, CH_2), 1.02 (t, 3H, J = 7.5 Hz, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 20 °C): δ = 156.3 (C=O), 78.6 (CHO), 69.1 (OCH_2), 26.7 (CH_2), 8.9 (CH_3) ppm.

Trace metal analysis (IPC-OES) on samples of propylene or butylene carbonate obtained through this procedure showed a concentration of Nb lower than 1 ppm.

GC analysis of samples of propylene carbonate obtained according to this procedure was carried out using the system mentioned in the general information (gradient: 40 °C for 5 min, 5 °C/min up to 200 °C, hold for 5 min; propylene carbonate retention time: 15.8 min; DMAP retention time 24.4 min, peaks were assigned through injection of pure samples of propylene carbonate and DMAP). All samples showed purity $\geq 99.8\%$ and only trace amounts of DMAP.

Kinetic studies on the propylene carbonate formation using NbCl_5 /DMAP or NbCl_5 / $n\text{Bu}_4\text{Br}$ as catalysts

Online IR spectroscopy was used to follow the time dependent formation of the reaction products or to photograph the reaction intermediates at a given time using the experimental setup reported in Figure 7.1. and the components specified in the general information.

NbCl_5 (135.1 mg, 0.5 mmol) and the cocatalyst (0.5 mmol) were dissolved under a protective atmosphere in 7 mL (100 mmol) of propylene oxide in a stainless steel autoclave equipped with a mechanical stirrer and a diamond probe on its bottom to allow for IR measurements (setup as in figure 7.1.). After the time interval of choice, 5 bar CO_2 were added into the reaction vessel through a pressure regulator connected to a CO_2 cylinder. The pressure in the vessel was kept constant through the whole experiment. An IR spectrum of the solution was taken at each minute after reaction beginning and the evolution of the carbonyl band at 1810 cm^{-1} was monitored.

7.3 Chapter 3

Mechanistic studies in the pyridine asymmetric ring stretching (ARS) region (1600 - 1700 cm^{-1})

In a typical experiment, DMAP, 61.1 mg (0.5 mmol) and NbCl_5 , 135.1 mg (0.5 mmol) were dissolved under a protective in 7 mL (100 mmol) of dry propylene oxide in a stainless steel autoclave equipped with a mechanical stirrer and a diamond probe on its bottom to allow for IR measurements. The mixture was stirred at 200 r.p.m. and a IR spectrum was recorded every minute for two hours. No IR measurements were carried out for the first five minutes to allow for proper mixing of the reagents and in order to suppress artifacts arising from the presence of undissolved material on the autoclave window.

The signal at 1600 cm^{-1} corresponds to the asymmetric ring stretching for the pyridine ring of DMAP as reported in the literature¹³ and as measured by us in propylene oxide on a sample of 0.5 mmol of DMAP in 7 mL of PO (figure 7.4.).

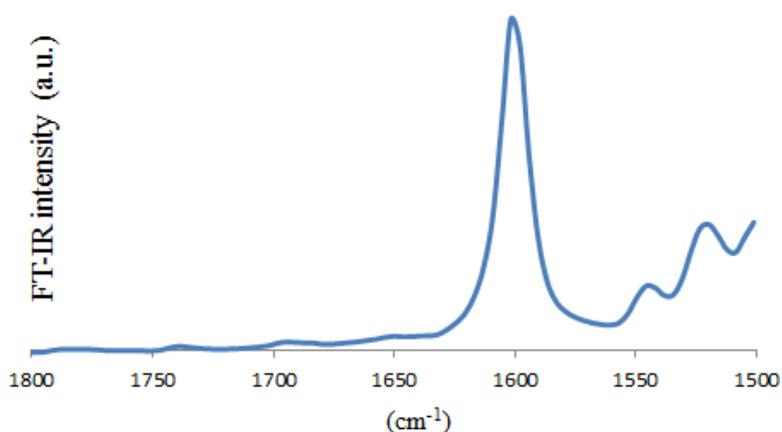


Figure 7.4. IR spectrum of DMAP in propylene epoxide in the ARS region.

The IR spectra of the DMAP- NbCl_5 complex **3** has been measured in DCM according to the following procedure:

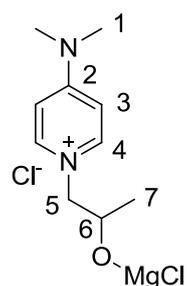
Under a protective atmosphere, dry dichloromethane (7 mL) was placed in a stainless steel autoclave. After one minute DMAP (61.1 mg, 0.5 mmol) was added under stirring (300 r.p.m). After five minutes NbCl_5 (135.1 mg, 0.5 mmol) was added to the solution. The development of the IR intensities of the signals belonging to the ARS region was monitored.

Synthesis of the DMAP-NbCl₅ complex (3)

DMAP (125 mg, 1 mmol) and NbCl₅ (270 mg, 1 mmol) were added in a Schlenk flask in the glove box. Upon addition of CH₂Cl₂ (20 mL) a dark violet suspension formed which was stirred at r.t. for 40 minutes. 60 mL of dry hexane were added to give a brown precipitate, which was collected by filtration, washed with hexane and dried *in vacuo*. Yield: 338 mg (86 %). ¹H NMR (400 MHz, CDCl₃) δ [ppm] 8.83 (d, *J* = 6.7 Hz, 2H), 6.50 (d, *J* = 7.5 Hz, 2H), 3.19 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm] 155.5, 152.8, 105.6, 40.0. Elemental Analysis: calculated C 21.43, H 2.57, N 7.14%, found C 21.66, H 2.69, N 6.84%.

Synthesis of the DMAP-epoxide-MgCl₂ complex (4)

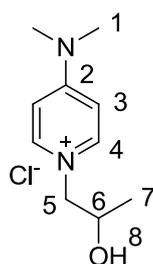
A stainless steel autoclave was charged with DMAP (310 mg, 2.54 mmol), MgCl₂ (238 mg, 2.50 mmol) and propylene oxide (8 mL, 114 mmol) at 25 °C. The solution was stirred at 300 r.p.m for five minutes and the temperature was raised to 60 °C at a rate of 5 °C/min. The reaction is followed by in-situ IR and is performed until the intensity of the band at 1654 cm⁻¹ was stabilized. The autoclave was cooled to 20 °C and the reaction mixture is collected. Acetone is added to ensure the precipitation of a white solid collected by filtration and washed with ethyl acetate and ether. Yield: 652 mg (95 %). ¹H NMR (400 MHz, DMSO) δ [ppm] 8.23 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 4.23 (dd, *J* = 12.9, 2.5 Hz, 1H), 4.00-3.86 (m, 2H), 3.18 (s, 6H), 1.09 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (100 MHz, DMSO) δ [ppm] 156.0, 142.8, 107.1, 65.5, 63.0, 39.5 (not observed because of the solvent peaks), 20.4. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$ 1647, 1616, 1562, 1438, 1347, 1219, 1050, 999, 807. MS: *m/z*: 181 [DMAP-epoxide]⁺.

HMBC (^1H - ^{13}C)

| Entry | δ_{H} | δ_{C} | HMBC (^1H - ^{13}C) |
|-------|---------------------|---------------------|---|
| 1 | 3.18 (s, 6H) | 39.5 | 2 |
| 2 | | 156.0 | |
| 3 | 7.03 (d, 2H) | 107.1 | 2, 3 |
| 4 | 8.23 (d, 2H) | 142.8 | 2, 3, 4, 5 |
| 5 | 4.00-3.86 (m, 2H) | 63.0 | 4, 6, 7 |
| 6 | 4.23 (dd, 1H) | 65.5 | 4, 7 |
| 7 | 1.09 (d, 3H) | 20.4 | 5, 6 |

Synthesis of the DMAP-epoxide-OH complex (5)

Complex **4** (50 mg, 0.18 mmol) was stirred for 10 minutes in 5 mL of distilled water. **5** was collected by filtration, washed with water and dried under air. Yield: 32 mg (99 %). ^1H NMR (400 MHz, DMSO) δ [ppm] 8.20 (d, $J = 7.8$ Hz, 2H), 7.02 (d, $J = 7.8$ Hz, 2H), 5.17 (d, $J = 5.1$ Hz, 1H), 4.23 (d, $J = 12.4$, 1H), 3.98-3.90 (m, 2H), 3.18 (s, 6H), 1.09 (d, $J = 6.0$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ [ppm] 155.9, 142.7, 107.1, 65.5, 63.0, 39.5 (not observed because of the solvent peaks), 20.4. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3195, 1646, 1538, 1444, 1399, 1205, 1180, 1131, 1073, 837, 817. MS: m/z : 181 [DMAP-epoxide] $^+$.

HMBC (^1H - ^{13}C)

| Entry | δ_{H} | δ_{C} | HMBC (^1H - ^{13}C) |
|-------|---------------------|---------------------|---|
| 1 | 3.18 (s, 6H) | 39.5 | 1, 2 |
| 2 | | 155.9 | |
| 3 | 7.02 (d, 2H) | 107.1 | 3, 4 |
| 4 | 8.20 (d, 2H) | 142.7 | 2, 3, 4, 5 |
| 5 | 3.98-3.90 (m, 2H) | 63.0 | 4, 6 |
| 6 | 4.23 (d, 1H) | 65.5 | 4, 6, 7 |
| 7 | 1.09 (d, 3H) | 20.4 | 5, 6, 7 |
| 8 | 5.17 (d, 2H) | | 5, 6, 7 |

7.4 Chapter 4

Synthesis of Pd(COD)Cl₂

To a suspension of PdCl₂ (4.90 g, 27.6 mmol) in 150 mL of methanol was added 1,5-cyclooctadiene and the mixture was stirred for 46 h at room temperature. The yellow suspension which formed was filtrated, washed with methanol and dried *in vacuo* to afford Pd(COD)Cl₂ as a yellow solid. Yield: 97 % (7.63 g).

Synthesis of Pd(P(o-tolyl)₃)₂ (8)^[114]

A solution of 1.48 g (37 mmol) of NaOH in methanol (8 mL) was added to Pd(COD)Cl₂ (5.23 g, 18 mmol) suspended in toluene (27 mL) at -5 °C. The resulting solution was stirred for 5 min under an atmosphere of argon until an off-white solid (corresponding to NaCl) forms. A solution of P(o-tolyl)₃ (11.15 g, 37 mmol) in toluene (55 mL) was added to this solution at -5 °C and stirred for 2 h. The resulting solution was then brought to room temperature and filtrated. The residue was washed twice with 25 mL of methanol and this solution was added to the filtrate to ensure the precipitation of the product. After stirring overnight, the suspension was filtrated, washed twice with 10 mL of methanol and dried *in vacuo* to afford

the final product as a yellow powder. Yield: 8.05 g (63 %). ^1H NMR (250 MHz, C_6D_6) δ [ppm] 7.28 (s, 18H, CH), 6.95 (m, 6H, CH), 3.09 (s, 18H, CH_3). ^{31}P NMR (100 MHz, C_6D_6) δ [ppm] -7.40. A small peak at -29.59 is also observed. It corresponds to the free phosphine $\text{P}(\text{o-tolyl})_3$ as complex **1** slowly dissociates in solution.

Synthesis of glyoxal-bis-(2,4,6-trimethylphenyl)imine^[116]

To a solution of 18.15 g of a 40 % aqueous solution of glyoxal (0.125 mmol) in 50 mL of 1-propanol and 25 mL of water was added a solution of 33.80 g (0.250 mmol) of 2,4,6-trimethylphenylamine in 150 mL of 1-propanol. This mixture was stirred overnight at room temperature and then for 4 h at 60 °C. Upon addition of 100 mL of water, a yellow solid precipitated which was collected by filtration, washed with water and dried *in vacuo*. Yield: 27.23 g (75 %). ^1H NMR (400 MHz, CDCl_3) δ [ppm] 8.12 (s, 2H, NCH), 6.93 (s, 4H, m-CH), 2.30 (s, 6H, p- CH_3), 2.17 (s, 12H, o- CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ [ppm] 163.5 (NCH), 145.9 (ipso-C), 134.2 (p-C), 129.3 (m-C), 125.8 (o-C), 20.6 (p- CH_3), 17.4 (o- CH_3).

Synthesis of glyoxal-bis-(2,6-diisopropylphenyl)imine^[116]

To a solution of 49.20 g (0.28 mmol) of 2,4,6-trimethylphenylamine in 200 mL of 1-propanol was added a solution of 18.15 g of a 40 % aqueous solution of glyoxal (0.125 mmol) in 20 mL of 1-propanol and 50 mL of water. This mixture was stirred for 3 h at 70 °C. Upon addition of 200 mL of water, a yellow solid precipitated which was collected by filtration, washed with water and dried *in vacuo*. Yield: 36.65 g (78 %). ^1H NMR (400 MHz, CDCl_3) δ [ppm] 8.11 (s, 2H, NCH), 7.10-7.28 (m, 6H, aryl-CH), 2.96 (sept, $J = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, $J = 6.9$ Hz, 24H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ [ppm] 163.2 (NCH), 147.9 (ipso-C), 136.2 (o-C), 125.3 (p-C), 122.8 (m-C), 28.4 ($\text{CH}(\text{CH}_3)_2$), 22.4 (CH_3).

Synthesis of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride^[116]

To a solution of 9.17 g (92.15 mmol) of chloromethylethyl ether (95 %) in 30 mL of THF was added a solution of glyoxal-bis-(2,4,6-trimethylphenyl)imine (27.00 g, 92.40 mmol) in 300 mL of THF, and the resulting mixture was stirred for 4 days at room temperature. The precipitated solid was collected by filtration, washed with THF, and dried *in vacuo*. Yield: 22.50 g (72 %). ^1H NMR (400 MHz, DMSO-d_6) δ [ppm] 9.75 (s, 1H, $\text{imC}_2\text{-H}$), 8.29 (s, 2H, $\text{imC}_{4,5}\text{-H}$), 7.20 (s, 4H, m-CH), 2.35 (s, 6H, p-CH), 2.12 (s, 12H, o-CH). ^{13}C NMR (100 MHz,

DMSO- d_6) δ [ppm] 140.5 (imC_2), 138.5, 134.2, 131.0 and 129.3 (aryl C), 124.8 ($imC_{4,5}$), 20.6 (o- CH_3), 16.9 (p- CH_3).

Synthesis of 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride^[116]

To a solution of 9.70 g (97.5 mmol) of chloromethylethyl ether (95 %) in 20 mL of THF was added a solution of glyoxal-bis-(2,6-diisopropylphenyl)imine (36.65 g, 97.40 mmol) in 200 mL of THF, and the resulting mixture was stirred for 24 hours at 40 °C. The precipitated solid was collected by filtration, washed with THF, and dried *in vacuo*. Yield: 30.20 g (73 %). 1H NMR (400 MHz, DMSO- d_6) δ [ppm] 10.15 (s, 1H, imC_2-H), 8.52 (s, 2H, $imC_{4,5}-H$), 7.67 (t, $J = 7.8$ Hz, 2H, p- CH), 7.53 (d, $J = 7.8$ Hz, 4H, m- CH), 2.35 (sept, $J = 6.9$ Hz, 4H, $CH(CH_3)_2$), 1.24 (d, $J = 6.9$ Hz, 12H, CH_3), 1.15 (d, $J = 6.9$ Hz, 12H, CH_3). ^{13}C NMR (100 MHz, DMSO- d_6) δ [ppm] 142.5 (imC_2), 143.5 (o-C), 138.2 (ipso-C), 129.0 and 128.3 (aryl C), 124.8 ($imC_{4,5}$), 28.4 ($CH(CH_3)_2$), 20.6 (o- CH_3), 23.9 and 23.2 (CH_3).

Synthesis of 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene^[116]

A suspension of 7.49 g (22.0 mmol) of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride in 80 mL of THF was stirred for 15 minutes at room temperature. Potassium tert-butoxide (2.59 g, 23.0 mmol) was added to the suspension which immediately turned to an orange solution. It was stirred for 20 minutes and the solvent was removed *in vacuo*. The residue was extracted with two times 50 mL of warm (70 °C) toluene leading to a light brown solution. The solvent volume was decreased *in vacuo* to one third, and the desired compound recrystallized at -30 °C. Yield: 4.89 g (73 %). 1H NMR (500 MHz, C_6D_6) δ [ppm] 6.81 (s, 4H, m- CH), 6.48 (s, 2H, $imC_{4,5}-H$), 2.17 (s, 12H, o- CH), 2.16 (s, 6H, p- CH). ^{13}C NMR (125 MHz, C_6D_6) δ [ppm] 219.4 (imC_2), 139.3, 137.2, 129.1 and 128.3 (aryl C), 120.5 ($imC_{4,5}$), 21.1 (o- CH_3), 18.1 (p- CH_3).

Synthesis of 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene^[116]

Same procedure as for the synthesis of 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene with: 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride (6.38 g, 15.0 mmol), potassium tert-butoxide (1.99 g, 17.7 mmol). Yield: 3.79 g (65 %). 1H NMR (500 MHz, C_6D_6) δ [ppm] 7.29 (t, 2H, $J = 7.7$ Hz, p- CH), 7.18 (d, 4H, $J = 7.8$ Hz, m- CH), 6.60 (s, 2H, $imC_{4,5}-H$), 2.96 (sept, 4H, $J = 6.9$ Hz, $CH(CH_3)_2$), 1.29 (d, $J = 6.9$ Hz, 12H, $CH(CH_3)_2$), 1.18 (d, $J = 6.9$ Hz, 12H, $CH(CH_3)_2$).

^{13}C NMR (125 MHz, C_6D_6) δ [ppm] 220.5 (imC_2), 146.3 (o-C), 139.0 (ipso-C), 129.0 and 128.3 (m- and p-C), 121.5 ($\text{imC}_{4,5}$), 28.8 ($\text{CH}(\text{CH}_3)_2$), 24.8 and 23.6 (CH_3).

Synthesis of Pd(IMes) $_2$ (9a) ^[115]

A solution of 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene (2.68 g, 8.80 mmol) in 30 mL toluene was added to a solution of Pd[P(o-tolyl) $_3$] $_2$ (2.47 g, 3.45 mmol) in 30 mL of toluene. It immediately gave an orange suspension which was stirred for 40 minutes. After 10 minutes, the suspension had become a clear solution. The solvent was removed *in vacuo*, and the orange residue was washed several times with small amounts of cold hexane until no more free phosphine was detected in ^{31}P NMR. Yield: 1.65 g (67 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm] 6.82 (s, 8H, CH-m), 6.14 (s, 4H, CH_{imid}), 2.34 (s, 12H, CH₃-p), 2.04 (s, 24H, CH₃-o). ^{13}C NMR (100 MHz, C_6D_6) δ [ppm] 198.9 (imC_2), 139.2, 136.5, 136.1 and 129.0 (aryl C), 119.1 (imC_4), 21.7 (o-CH $_3$), 19.1 (p-CH $_3$).

Synthesis of Pd(IPr) $_2$ (9b) ^[115]

Same procedure as for **9a** with: Pd[P(o-tolyl) $_3$] $_2$ (541 mg, 0.76 mmol), 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (2.68 g, 8.80 mmol). Yield: 385 mg (58 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm] 7.29 (t, $J = 8.0$ Hz, 4H, CH-p), 7.09 (d, $J = 7.5$ Hz, 8H, CH-m), 6.27 (s, 4H, CH_{imid}), 2.89 (sept, $J = 6.9$ Hz, 8H, CH(CH $_3$) $_2$), 1.20 (d, $J = 6.9$ Hz, 24H, CH(CH $_3$) $_2$), 1.11 (d, $J = 7.1$ Hz, 24H, CH(CH $_3$) $_2$). ^{13}C NMR (100 MHz, C_6D_6) δ [ppm] 198.6 (imC_2), 144.2 (o-C), 139.5 (ipso-C), 128.5 and 126.2 (m- and p-C), 121.1 ($\text{imC}_{4,5}$), 28.7 (CH(CH $_3$) $_2$), 24.8 and 23.8 (CH $_3$).

Synthesis of Pd(PCy $_3$) $_2$ (10b) ^[114]

A solution of 0.94 g (23.5 mmol) of NaOH in methanol (5 mL) was added to Pd(COD)Cl $_2$ (1.67 g, 5.9 mmol) suspended in toluene (10 mL) at -20 °C. The resulting solution was stirred for 20 min under an atmosphere of argon until an off-white solid (corresponding to NaCl) forms. A solution of PCy $_3$ (3.29 g, 11.7 mmol) in toluene (10 mL) was added at -20 °C and the solution was stirred for 1 h at this temperature, followed by 1h at 0 °C. The solution was filtrated, the residue was washed twice with 25 mL of methanol and this solution was added to the filtrate to ensure the precipitation of the product. After stirring for 10 minutes, the suspension was filtrated, washed twice with 10 mL of methanol and dried *in vacuo* to afford the final product as a yellow powder. Yield: 2.36 g (61 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm]

2.34 (d, 12H), 1.94 (m, 18H), 1.80 (m, 18H), 1.39 (m, 18H). ^{31}P NMR (160 MHz, C_6D_6) δ [ppm] 39.0 (s).

Synthesis of Pd(PtBu₃)₂ (10a)^[114]

Same procedure as for **10b** with: Pd(COD)Cl₂ (1.52 g, 5.4 mmol), NaOH (0.86 g, 21.5 mmol), PtBu₃ (2.18 g, 10.8 mmol). Yield: 1.60 g (58 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm] 1.59 (t, J = 7.8 Hz, 54H). ^{31}P NMR (160 MHz, C_6D_6) δ [ppm] 86.4 (s).

Synthesis of Pd(IMes₂)(Me)(I) (11a)

To a solution of Pd(IMes)₂ (496 mg, 0.69 mmol) in 10 mL benzene was added a solution of CH₃I (0.05 mL, 0.76 mmol). The orange solution turned immediately to light yellow. It was stirred at room temperature for 10 minutes. The solvent was removed *in vacuo*, the collected residue was washed with acetonitrile to remove the excess of methyl iodide and the product was further dried *in vacuo*. Yield: 557 mg (94 %). ^1H NMR (400 MHz, CDCl₃) δ [ppm] 6.93 (s, 4H, CH-m), 6.88 (s, 4H, CH-m), 6.77 (s, 4H, CH_{imid}), 2.44 (s, 12H, CH_{3-p}), 2.12 (s, 12H, CH_{3-o}), 1.78 (s, 12H, CH_{3-o}), -0.34 (s, 3H, Pd-CH₃). ^{13}C NMR (100 MHz, CDCl₃) δ [ppm] 198.9 (imC₂), 137.4, 137.1, 136.8, 134.7, 129.7 and 128.3 (aryl C), 122.5 (imC_{4,5}), 21.9 and 21.3 (CH_{3-o}), 18.8 (CH_{3-p}), -5.4 (Pd-CH₃). E.A.: calculated C 60.11, H 6.22, N 6.52%, found C 60.52, H 5.97, N 6.72% and mass spectroscopy. MS: m/z : 730 [Pd(IMes)₂(CH₃)⁺].

Synthesis of Pd(PCy₃)₂(Me)(I) (11b)

To a solution of Pd(PCy₃)₂ (500 mg, 0.75 mmol) in 10 mL toluene was added a solution of CH₃I (0.05 mL, 0.80 mmol). It was stirred at room temperature for 25 minutes, then 20 mL of dry Et₂O were added and the solution was stirred for 30 minutes until a yellow solid precipitated. It was collected by filtration, washed with ether and dried *in vacuo*. Yield: 0.53 g (87 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm] 2.76 (br s, 6H), 2.11 (d, 12H), 1.73 (m, 30H), 1.30 (m, 18H), 0.8 (t, 3H). ^{31}P NMR (160 MHz, C_6D_6) δ [ppm] 24.1 (s). ^{13}C NMR (100 MHz, C_6D_6) δ [ppm] 34.4, 31.0, 28.1, 27.1, -1.8 (s, Pd-CH₃).

Synthesis of Pd(IMes₂)(H)(Cl) (12)

To a solution of Pd(IMes)₂ (220 mg, 0.31 mmol) in 10 mL benzene was added a solution of HCl (0.16 mL, 2M in Et₂O, 0.32 mmol). The orange solution turned immediately to light yellow. It was stirred at room temperature for 10 minutes. The solvent was removed *in*

vacuo, the collected residue was washed with ether to afford **12** as a white solid. Yield: 213 mg (91 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm] 6.80 (s, 8H, CH-m), 6.09 (s, 4H, CH_{imid}), 2.35 (s, 12H, $\text{CH}_3\text{-p}$), 2.09 (s, 24H, $\text{CH}_3\text{-o}$), -14.84 (s, 1H, Pd- H). ^{13}C NMR (100 MHz, C_6D_6) δ [ppm] 186.0 (imC_2), 136.9, 136.5, 135.9 and 128.7 (aryl C), 120.9 (imC_4), 21.0 (o- CH_3), 18.4 (p- CH_3). E.A.: calculated C 67.10, H 6.57, N 7.45%, found C 66.76, H 6.52, N 7.14%) and mass spectroscopy. MS: m/z : 715 [$\text{Pd}(\text{IMes})_2(\text{H})$] $^+$.

Synthesis of $\text{Pd}(\text{IMes})_2\text{O}_2$ (**15**)^[123]

To a solution of $\text{Pd}(\text{IMes})_2$ (17 mg, 23.7 μmol) in 0.5 mL of C_6D_6 was pressurized 3 bar of O_2 . In 10 min, the solution had turned to light green and a ^1H NMR show that the reaction was complete. Yield: 18 mg (100 %). ^1H NMR (400 MHz, C_6D_6) δ [ppm] 6.66 (s, 8H, CH-m), 6.03 (s, 4H, CH_{imid}), 2.28 (s, 12H, $\text{CH}_3\text{-p}$), 2.05 (s, 24H, $\text{CH}_3\text{-o}$).

7.5 Chapter 5

Synthesis of $\text{Pt}(\text{COD})\text{Cl}_2$ (**18**)^[153]

To a solution of K_2PtCl_4 (4.97 g, 11.97 mmol) in 50 mL of water was added 35 mL of 1-propanol followed by 10 mL of COD and 37 mg of SnCl_2 . The red solution was stirred for 3 days until it turned to a white suspension. The suspension was filtrated, washed successively with water, ethanol and small quantities of cold ether, and dried *in vacuo* affording **18** as a white solid. Yield: 4.25 g (95 %). ^1H NMR (400 MHz, CDCl_3) δ [ppm] 5.60 (t due to ^{195}Pt satellites, $J = 66.2$ Hz 4H, CH), 2.70 (s, 4H, CH_2), 2.25 (m, 4H, CH_2), 1.30 (m, 18H), 0.8 (t, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ [ppm] 100.2 (s with ^{195}Pt satellites, $J = 151.9$ Hz, CH), 31.0 (CH_2).

Synthesis of $\text{Pt}(\text{COD})\text{Me}_2$ (**19**)^[154]

Copper(I) iodide (0.721 g, 1.92 mmol) was pre-dried overnight *in vacuo* at 100 °C. To it was added 15 mL of diethylether to give a white suspension which was cooled at -20 °C. MeLi (5mL, 1.6M in diethylether, 8.59 mmol) was added to give first a yellow precipitate which turned to a transparent solution. $\text{Pt}(\text{COD})\text{Cl}_2$ was added, and the solution became immediately brown. It was warmed to room temperature over 30 minutes. The brown mixture was cooled to -20 °C and hydrolyzed with few drops of water. The solution became

greenish and was warmed to r.t., where 15 mL of water were added, followed by 15 mL of ether. The solution was stirred for 15 min and filtrated. The organic layer was extracted, dried over K_2CO_3 and the solvent was removed *in vacuo* to afford **19** as a white powder. Yield: 0.50 g (69 %). 1H NMR (400 MHz, $CDCl_3$) δ [ppm] 4.82 (t due to ^{195}Pt satellites, $J = 40.8$ Hz, 4H, CH), 2.30 (m, 8H, CH_2), 2.25 (t due to ^{195}Pt satellites, $J = 81.1$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm] 99.2 (s with ^{195}Pt satellites, $J = 55.3$ Hz, CH), 30.0 (CH_2), 4.7 (s with ^{195}Pt satellites, $J = 770.2$ Hz, CH_3).

Synthesis of dichloro[bis(dicyclohexylphosphino)ethane]platinum(II) $Pt(dcpe)Cl_2$ (**20a**)^[155]

To a solution of $Pt(COD)Cl_2$ (0.334 g, 0.89 mmol) in 60 mL of dichloromethane was added a solution of dcpe (0.452 g, 1.07 mmol) in 15 mL of dichloromethane. The resulting solution was stirred for 5 h at r.t., and the solvent was removed *in vacuo* to lead to a white solid. **20a** was recrystallized as a white solid at -10 °C from a CH_2Cl_2 /pentane mixture. Yield: 259 mg (72 %). 1H NMR (400 MHz, $CDCl_3$) δ [ppm] 2.42-2.11 (m, 8H), 1.98-1.77 (m, 20H), 1.40-1.15 (m, 20H). ^{31}P NMR (160 MHz, $CDCl_3$) δ [ppm] 59.9 (t with ^{195}Pt satellites, $J = 3572$ Hz).

Synthesis of ditert-butylphosphino ethane dtbpe^[132]

A solution of tert-butyllithium (50 mL, 1.6 M in pentane, 80.0 mmol) was added dropwise at -78 °C to a solution of $Cl_2P(C_2H_4)PCl_2$ (3.0 mL, 4.61 g, 19.9 mmol) in 8 mL of ether. The solution was slowly warmed to r.t. over 4 hours and filtrated. The solvent was removed *in vacuo* to lead to a yellow solid. Dtbpe was crystallized as a white solid from a pentane solution. Yield: 1.58 g (25 %). 1H NMR (400 MHz, CD_2Cl_2) δ [ppm] 1.56 (m, 4H, PCH_2), 1.12 (m, 36H, $(CH_3)_3$). ^{31}P NMR (160 MHz, CD_2Cl_2) δ [ppm] 36.4 (s).

Synthesis of dichloro[bis(ditert-butylphosphino)ethane]platinum(II) $Pt(dtbpe)Cl_2$ (**20b**)^[156]

$Pt(COD)Cl_2$ (0.70 g, 1.86 mmol) and dtbpe (0.60 g, 1.88 mmol) were dissolved in 50 mL of THF and refluxed overnight at 100 °C. The solvent is removed *in vacuo* leading to a yellow solid which is washed several times with hexane and dried *in vacuo*. Yield: 0.92 g (85 %). 1H NMR (400 MHz, CD_2Cl_2) δ [ppm] 1.85 (m, 4H, PCH_2), 1.47 (d, $J = 14.0$ Hz, 36H, $(CH_3)_3$). ^{31}P NMR (160 MHz, CD_2Cl_2) δ [ppm] 75.3 (t due to ^{195}Pt satellites, $J = 3647$ Hz).

Synthesis of dimethyl[bis(dicyclohexylphosphino)ethane]platinum(II) Pt(dcpe)Me₂ (21a)^[157]

Route 1: A solution of Pt(COD)Me₂ (0.156 g, 0.47 mmol) in 10 mL of toluene was added to a solution of dcpe (0.197 g, 0.47 mmol). The resulting solution was stirred for 45 min, the solvent was removed *in vacuo* to lead to a white solid which was washed with 2 times 5 mL of hexane, and dried *in vacuo*. Yield: 0.237 g (78 %).

Route 2: To a suspension of Pt(dcpe)Cl₂ (0.150 g, 0.22 mmol) in 10 mL of ether at -40 °C was added dropwise MeLi (0.5 mL, 1.6 M in Et₂O, 0.80 mmol). The suspension was let warm to r.t. over 45 min and filtrated. The solvent was removed *in vacuo* to lead to a white solid which was washed with 2 times 5 mL of hexane and dried *in vacuo*. Yield: 0.090 g (63 %). ¹H NMR (400 MHz, CDCl₃) δ [ppm] 2.53-2.19 (m, 8H), 2.02-1.78 (m, 20H), 1.41-1.19 (m, 20H), 0.68 (m, 6H, PtCH₃). ³¹P NMR (160 MHz, CDCl₃) δ [ppm] 61.2 (t with ¹⁹⁵Pt satellites, *J* = 3631 Hz).

Synthesis of dimethyl[bis(ditert-butylphosphino)ethane]platinum(II) Pt(dtbpe)Me₂ (21b)^[158]

To a suspension of Pt(dtbpe)Cl₂ (0.245 g, 0.42 mmol) in 15 mL of ether at 0 °C was added dropwise MeLi (0.6 mL, 1.6M in Et₂O, 0.96 mmol) and the solution was stirred for 2 h at 0 °C. A few drops of a NH₄Cl saturated solution in water were added, the solution was let warm to r.t. and extracted. The organic phase was collected and the solvent was removed *in vacuo* to afford **5b** as a white solid. Yield: 0.148 g (65 %). ¹H NMR (400 MHz, CD₂Cl₂) δ [ppm] 1.65 (m, 4H, PCH₂), 1.26 (d, *J* = 14.0 Hz, 36H, (CH₃)₃), 0.65 (tt, *J* = 69.8, 6.3 Hz, 6H, PtCH₃). ³¹P NMR (160 MHz, CD₂Cl₂) δ [ppm] 76.3 (t due to ¹⁹⁵Pt satellites, *J* = 3612 Hz).

Synthesis of Pt(dtbpe)H₂ (22b)^[134]

A solution of Pt(dtbpe)Cl₂ (0.30 g, 0.51 mmol) in 20 mL of THF was added via syringe to mercury amalgam which was prepared by a mixture of 19 g of Hg (94.7 mmol) and 0.19 g (8.26 mmol) of Na powder. The solution immediately turned to dark yellow, and 36 psi (2.5 bar) of H₂ were pressurized for 24h until it became light brown. The solution was filtrated, the solvent removed *in vacuo* to give a yellow solid. 10 mL of hexane was added, the suspension was filtrated to lead to a transparent liquid, from which Pt(dtbpe)H₂ was recrystallized at -30 °C as a white solid. Yield: 0.13 g (51 %). ¹H NMR (400 MHz, THF-d₃)

δ [ppm] 1.85 (m, 4H, PCH₂), 1.28 (d, J = 12.3 Hz, 36H, (CH₃)₃), -1.48 (dd, J = 15.0, 180.3 Hz, 2H, Pt-*H*). ³¹P NMR (160 MHz, THF-d₈) δ [ppm] 106.7 (t due to ¹⁹⁵Pt satellites, J = 2024 Hz).

Synthesis of 2,4,6-trimethylphenyl imidazole (**23a**)^[136]

10 mL glacial acetic acid, 3 mL aqueous formaldehyde and 4.6 mL aqueous glyoxal were heated to 70 °C. A solution of 10 mL glacial acetic acid, 3.30 g (42.8 mmol) ammonium acetate in 2 mL water and 6 mL (5.78 g, 42.7 mmol) 2,4,6-trimethylaniline was added dropwise over a period of 30 min. The reaction system was continuously stirred at 70 °C for 18 h. After cooling to room temperature, the black suspension was added dropwise to a sodium bicarbonate solution (29.4 g in 400 mL water) to obtain a dark brown precipitate. The crude product was filtrated and washed 3 times with water leading to **23a** as a white solid. Yield: 5.96 g (75 %). ¹H NMR (400MHz, CDCl₃) δ [ppm] 7.40 (s, 1H, NCHN), 7.19 (s, 1H, NCH), 6.93 (s, 2H, *m-H*), 6.85 (s, 1H, N-CH), 2.30 (s, 3H, *p-CH*₃), 1.95 (s, 6H, *o-CH*₃).

Synthesis of 2,6-diisopropylphenyl imidazole (**23a**)^[136]

Same procedure as for **23a**, except that the purification was made with a column chromatography (ethyl acetate:hexane = 1:1). Ammonium acetate 2.45 g (31.8 mmol), 2,6-diisopropylaniline (6 mL, 5.64 g, 31.8 mmol). Yield: 4.06 g (56 %). ¹H NMR (400MHz, CDCl₃) δ [ppm] 7.50 (s, 1H, NCHN), 7.42 (t, J = 7.2 Hz, 1H, *p-H*), 7.26 (s, 1H, NCH), 7.24 (d, J = 8.0 Hz, 2H, *m-H*), 6.93 (s, 1H, NCH), 2.39 (m, 4H, CH_{isoprop}), 1.12 (d, 12H, CH₃).

Synthesis of 1,1'-di(2,4,6-trimethylphenyl)-3,3'-methylendiimidazolium dibromide (**24a**)^[137]

2.305 g (12.4 mmol) of **23a** and 1.16 g (6.2 mmol) CH₂Br₂ were added into an ACE pressure tube, and dissolved in 5 ml THF. The reaction mixture was stirred for 72 h at 130 °C. After cooling to room temperature, the suspension was filtrated and the desired product was obtained as a white solid, which was washed with THF until no change in color and dried under air. Yield: 3.29 g (97 %). ¹H NMR (400MHz, CDCl₃) δ [ppm] 11.39 (s, 2H, NCHN), 9.87 (d, J = 7.2 Hz, 2H, NCH), 7.95 (s, 2H, NCH₂N), 7.18 (d, J = 7.2 Hz, 2H, NCH), 7.02 (s, 4H, *m-H*), 2.34 (s, 6H, *p-CH*₃), 2.03 (s, 12H, *o-CH*₃). MS: m/z : 465 (**24a**).

Synthesis of 1,1'-di(2,6-diisopropylphenyl)-3,3'-methylendiimidazolium dibromide (24b)^[137]

Same procedure as for 24a with: 23b 2.30 g (10.0 mmol) and CH₂Br₂ 0.94 g (5.0 mmol). Yield: 2.78 g (88 %). ¹H NMR (400MHz, CDCl₃) δ [ppm] 11.38 (s, 2H, NCHN), 9.96 (d, J = 7.5 Hz, 2H, NCH), 7.97 (s, 2H, NCH), 7.56 (t, J = 7.2 Hz, 2H, p-H), 7.30 (d, J = 7.5 Hz, 4H, m-H), 7.23 (s, 2H, NCH₂N), 2.20 (m, 4H, CH_{isoprop}), 1.16 (d, J = 7.2 Hz, 24H, CH₃).

Synthesis of 1,1'-di(2,4,6-trimethylphenyl)-3,3'-methylendiimidazolin-2,2'-diyilden-palladium (II) dibromide (25a)^[138]

Palladium acetate (0.20 g, 0.92 mmol) and **24a** (0.50 g, 0.92 mmol) were dissolved in 10 ml DMSO. The reaction system was stirred for 1 h at 40 °C, 1 h at 60 °C, 2 h at 80 °C, 2 h at 100 °C and 1 hour at 130 °C. After cooling to room temperature, 20 ml dichloromethane was poured into the solution followed by 80 ml ether, and the resulting suspension was stirred for 20 min at room temperature. The desired product was obtained after filtration and dried *in vacuo*. Yield: 0.39 g (65 %). ¹H NMR (400MHz, DMSO-d₆) δ [ppm] 7.90 (d, 2H, NCH), 7.39 (d, J = 7.2 Hz, 2H, NCH), 6.96 (s, 4H, m-H), 6.52 (s, 2H, NCH₂N), 2.27 (s, 6H, p-CH₃), 2.02 (s, 12H, o-CH₃).

Synthesis of Pd(tmeda)Cl₂ (26)^[159]

A suspension of PdCl₂ (1.78 g, 10.0 mmol) in acetonitrile was refluxed until it became a clear orange solution. An orange solid precipitated under cooling of the solution at room temperature. N,N,N',N'-tetramethylethylenediamine (2.4 mL, 16.1 mmol) was added and the yellow precipitate that formed was filtrated, washed with diethyl ether, and dried *in vacuo*. Yield: 2.52 g (97 %).

Synthesis of Pd(tmeda)Me₂ (27)^[159]

To a suspension of Pd(tmeda)Cl₂ (2.52 g, 8.6 mmol) in 30 mL of diethylether at – 30 °C was added dropwise a solution of MeLi (11.5 mL of a 1.6 M solution in diethylether, 18.4 mmol). The mixture was allowed to warm slowly to 0 °C and was kept for 30 min at that temperature until a grayish suspension formed. 10 mL of ice cold water was slowly added until the solution formed a clear organic layer and a black water layer. The organic layer was extracted, dried over Na₂SO₃, and the solvent was removed *in vacuo* to give Pd(tmeda)Me₂ as a white solid. Pd(tmeda)Me₂ is stored under argon and at exclusion of light to prevent the

dissociation of the tmeda ligand. Yield: 1.56 g (72 %). ^1H NMR (400 MHz, CD_3COCD_3) δ [ppm] 2.57 (s, 2H, CH_2), 2.40 (s, 6H, N- CH_3), -0.34 (s, 3H, Pd- CH_3). ^{13}C NMR (100 MHz, CD_3COCD_3) δ [ppm] 60.1 (CH_2), 48.3 (N- CH_3), -9.1 (Pd- CH_3).

7.6 Chapter 6

Synthesis of 2,6-Bis[(3-methylimidazolium-1-yl)methyl]pyridine dibromide (**32a**)^[150a]

To a solution of 2,6-bis(bromomethyl)pyridine (2.0 g, 7.54 mmol) in 50 mL THF was added 1-methylimidazole (1.32 mL, 1.36 g, 16.5 mmol). A white solid began to precipitate after several minutes, and the solution was kept stirring for 5 days at room temperature. 50 mL of Et_2O was added, and the white precipitate that formed upon addition of the solvent was collected by filtration, washed with Et_2O and dried *in vacuo*. Yield: 2.75 g (85 %). ^1H NMR (500 MHz, d_6 -DMSO) δ [ppm] 9.24 (s, 2H, $\text{imC}_2\text{-H}$), 7.97 (t, $J = 7.8$ Hz, 1H, $\text{pyrC}_4\text{-H}$), 7.77 (t, $J = 1.6$ Hz, 2H, $\text{imC}_4\text{-}$ or $\text{C}_5\text{-H}$), 7.71 (t, $J = 1.6$ Hz, 2H, $\text{imC}_4\text{-}$ or $\text{C}_5\text{-H}$), 7.49 (d, $J = 7.7$ Hz, 2H, $\text{pyrC}_{3,5}\text{-H}$), 5.57 (s, 4H, CH_2), 3.92 (s, 6H, N- CH_3). ^{13}C NMR (125 MHz, d_6 -DMSO) δ [ppm] 153.7 ($\text{pyrC}_{2,6}$), 138.8 (pyrC_4), 137.2 (imC_2), 123.4 ($\text{pyrC}_{3,5}$), 123.1 and 122.1 ($\text{imC}_{4,5}$), 52.5 (CH_2), 36.0 (N- CH_3).

Synthesis of 2,6-Bis[(3-tert-butylimidazolium-1-yl)methyl]pyridine dibromide (**32b**)^[150b]

2,6-bis(bromomethyl)pyridine (2.0 g, 7.54 mmol) and 1-tert-butylimidazole (2.05 g, 16.5 mmol) were refluxed in 50 mL THF for 5 days leading to a brown solid. The crude product was collected by filtration, the solvent removed *in vacuo* and **3b** was crystallized as a light brown solid from an acetonitrile/ether solution. Yield: 2.59 g (67 %). ^1H NMR (500 MHz, d_6 -DMSO) δ [ppm] 9.47 (t, $J = 1.6$ Hz, 2H, $\text{imC}_2\text{-H}$), 8.07 (t, $J = 1.9$ Hz, 2H, $\text{imC}_4\text{-}$ or $\text{C}_5\text{-H}$), 7.98 (t, $J = 7.9$ Hz, 1H, $\text{pyrC}_4\text{-H}$), 7.77 (t, $J = 1.9$ Hz, 2H, $\text{imC}_4\text{-}$ or $\text{C}_5\text{-H}$), 7.47 (d, $J = 8.0$ Hz, 2H, $\text{pyrC}_{3,5}\text{-H}$), 5.53 (s, 4H, CH_2), 1.60 (s, 18H, N- CMe_3). ^{13}C NMR (125 MHz, d_6 -DMSO) δ [ppm] 153.8 ($\text{pyrC}_{2,6}$), 139.0 (imC_2), 135.2 (pyrC_4), 123.4 ($\text{pyrC}_{3,5}$), 122.2 and 120.3 ($\text{imC}_{4,5}$), 59.7 (CMe_3), 52.8 (CH_2), 29.0 (N- CMe_3).

Synthesis of η^2,η^2 -cycloocta-1,5-diene)chloromethylpalladium(II) (33)^[151]

1.5 mL (1.94 g, 10.8 mmol) of tetramethyltin was added to a solution of Pd(COD)Cl₂ (2.64 g, 9.2 mmol) in 50 mL of dichloromethane and the resulting solution was stirred at room temperature for 24 h, until the yellow color of the precursor had vanish. The solution was filtered and the solvent removed *in vacuo* while the temperature of the solution was kept at 0 °C with an ice bath. The off-white powder was washed twice with small amounts of diethyl ether to remove the trimethyltin chloride formed. Yield: 2.15 g (88 %). ¹H NMR (400 MHz, C₆D₆) δ [ppm] 5.81 (s, 4H, COD), 4.32 (s, 4H, COD), 0.29 (s, 3H, CH₃).

Synthesis of [PdMe(CNC_{Me})]BF₄ (CNC_{Me} = C,N,C'-2,6-bis-[(3-methylimidazolin-2-yliden-1-yl)methyl]pyridine) (34a)^[150a]

The bis-imidazolium salt **3a** (416 mg, 0.97 mmol) was stirred with Ag₂O (228 mg, 0.98 mmol) in 15 mL of DMSO at 60 °C for 3 days giving a grey suspension. AgBF₄ (198 mg, 1.02 mmol) was added at room temperature followed by **4** (257 mg, 0.97 mmol). The suspension was stirred for 40 minutes and the solvent was removed *in vacuo*. The grey residue was taken up in CH₃CN and filtrated. The solvent was evaporated, the residue washed with Et₂O to lead to a light red solid which is dried *in vacuo*. Yield: 296 mg (64 %). ¹H NMR (500 MHz, d₆-DMSO) δ [ppm] 8.09 (t, *J* = 7.6 Hz, 1H, _{pyr}C₄-H), 7.71 (d, *J* = 8.2 Hz, 2H, _{pyr}C_{3,5}-H), 7.53 (d, *J* = 1.8 Hz, 2H, _{im}C-H), 7.33 (d, *J* = 1.8 Hz, 2H, _{im}C-H), 5.45 (dd, *J* = 46.5, 14.9 Hz, 4H, CH₂), 3.78 (s, 6H, N-CH₃), 0.70 (s, 3H, Pd-CH₃). ¹³C NMR (125 MHz, d₆-DMSO) δ [ppm] 176.2 (_{im}C₂), 154.8 (_{pyr}C_{2,6}), 140.9 (_{pyr}C₄), 124.8 (_{pyr}C_{3,5}), 123.3 and 122.2 (_{im}C_{4,5}), 54.5 (CH₂), 37.5 (N-CH₃), -14.6 (Pd-CH₃). ¹⁹F NMR (470 MHz, d₆-DMSO) δ [ppm] -148.2.

Synthesis of [PdMe(CNC_{tBu})]BF₄ (CNC_{tBu} = C,N,C'-2,6-bis-[(3-tert-butylimidazolin-2-yliden-1-yl)methyl]pyridine) (34b)^[150b]

Same procedure as for **5a**, unless that the reaction is only performed for 1 day at 60 °C. **3b** (380 mg, 0.74 mmol), Ag₂O (174 mg, 0.75 mmol), AgBF₄ (153 mg, 0.78 mmol), Pd(COD)(Cl)(Me) (199 mg, 0.75 mmol). Yield: 194 mg (47 %). ¹H NMR (400 MHz, d₆-DMSO) δ [ppm] 8.01 (t, *J* = 7.5 Hz, 1H, _{pyr}C₄-H), 7.67 (d, *J* = 8.4 Hz, 2H, _{pyr}C_{3,5}-H), 7.57 (d, *J* = 1.8 Hz, 2H, _{im}C-H), 7.51 (d, *J* = 1.8 Hz, 2H, _{im}C-H), 5.50 (dd, *J* = 25.5, 15.0 Hz, 4H, CH₂), 1.70 (s, 18H, N-CMe₃), 0.65 (s, 3H, Pd-CH₃). ¹³C NMR (100 MHz, d₆-DMSO) δ [ppm] 175.0 (_{im}C₂), 154.3

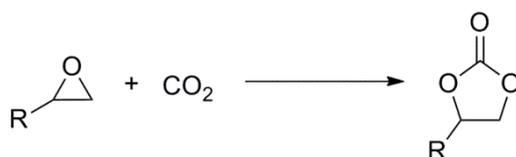
Experimental section

(_{pyr}C_{2,6}), 140.2 (_{pyr}C₄), 123.5 (_{pyr}C_{3,5}), 121.8 and 119.8 (_{im}C_{4,5}), 58.4 (N-CMe₃), 55.2 (CH₂), 31.3 (N-CMe₃), -8.1 (Pd-CH₃).

8 Summary

This thesis is divided in two main parts. The synthesis of cyclic carbonates, especially propylene carbonate, from propylene oxide and CO₂ and its mechanistic study are found in chapter 2 and 3. The second part, covered in chapter 4 to 6, focuses on the synthesis of palladium and platinum complexes and their interaction with CO₂.

Chapter 2 describes the screening of different metal halides catalysts and nucleophilic co-catalysts for the synthesis of cyclic carbonates from propylene oxide and CO₂.



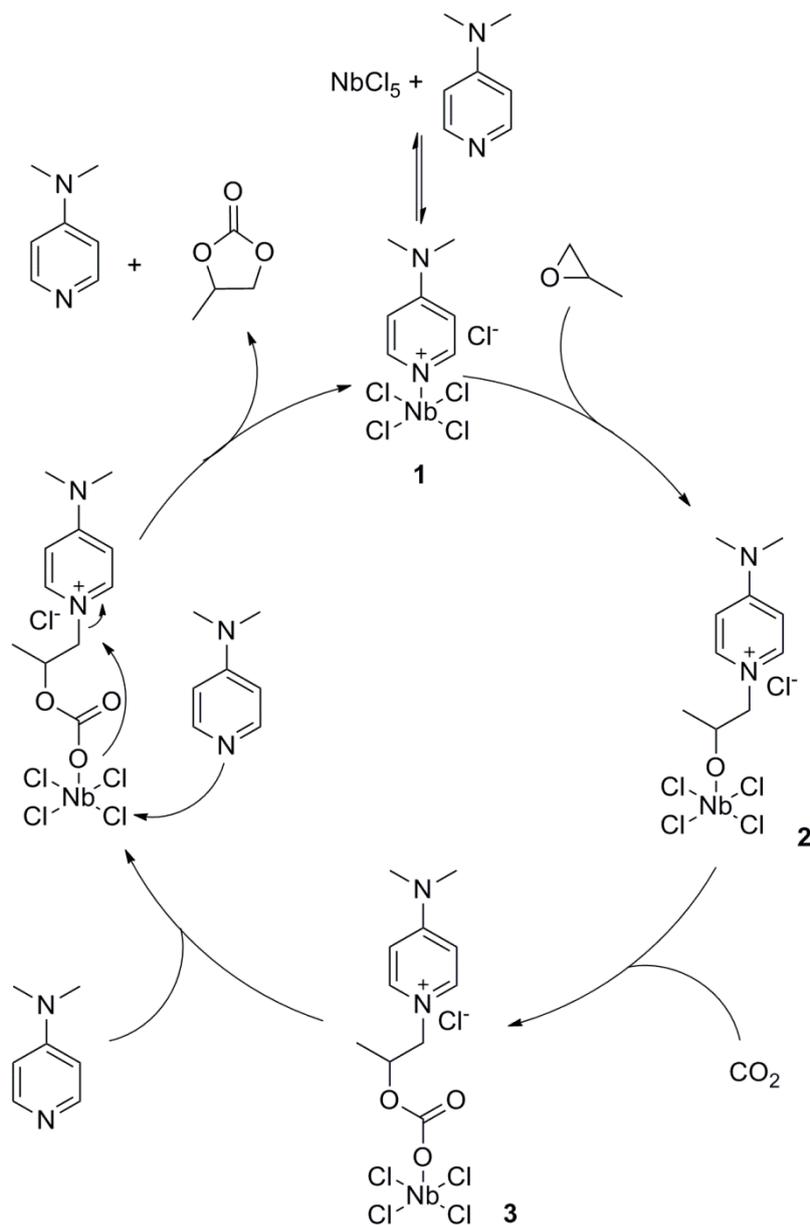
Scheme 8.1. Formation of carbonates

The best TOFs are obtained with the system NbCl₅/nBu₄Br. This system is particularly efficient under mild conditions: at room temperature and one atmosphere (or less) of CO₂. It is also active for a variety of epoxides, especially for epoxides with low steric hindrance: propylene oxide and ethylene oxide. TOFs of respectively 20 h⁻¹ and 30 h⁻¹ are obtained, which represents the best results published up to date.

The influence of the CO₂ pressure and of the catalyst:co-catalyst ratio are studied. At 50 °C, pressures of CO₂ above 3 bar do not lead to any significant improvement in the reaction rate. An ratio of catalyst:co-catalyst between 1:1.5 to 1:2 is optimal. It is observed that if the catalyst is present in higher quantity than the co-catalyst the reaction proceeds very slowly.

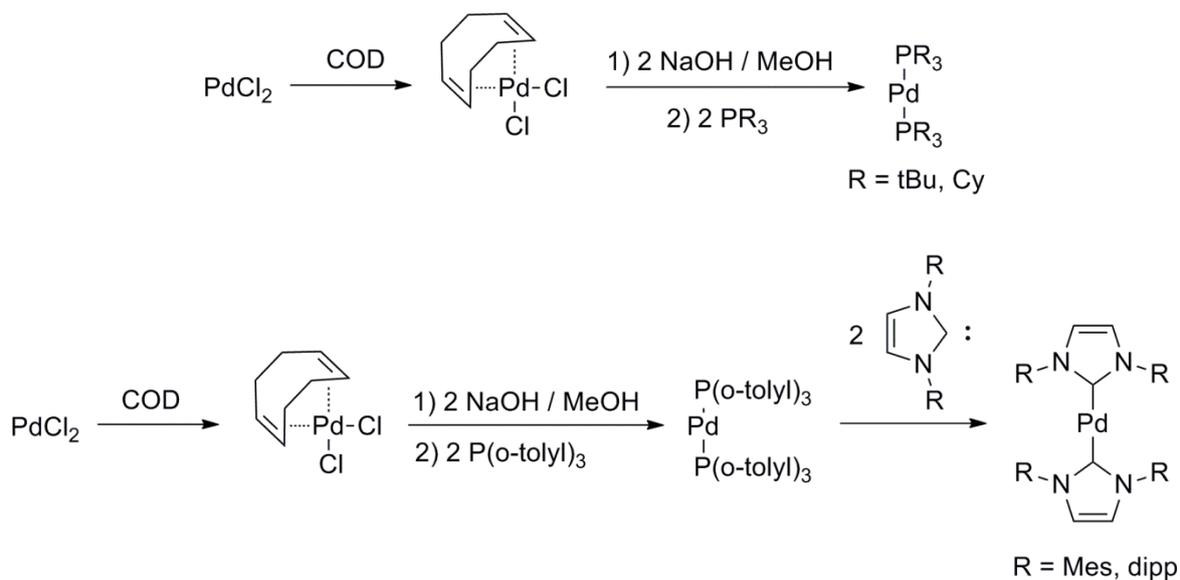
In chapter 3, a mechanistic study of the formation of propylene carbonate from epoxide and CO₂ is performed through in-situ IR spectroscopy using the NbCl₅/DMAP system. It is

determined that DMAP first reacts with NbCl_5 in an acid/base reaction forming a DMAP- NbCl_5 complex (**1**). This reaction is reversible and permits the formation in 90 minutes at room temperature of **2**, which contains the epoxide. The catalytic cycle then proceeds through the insertion of CO_2 into the niobium-oxygen bond (**3**), and the presence of free DMAP in solution is necessary to release the cyclic carbonate.



Scheme 8.2. Postulated catalytic cycle

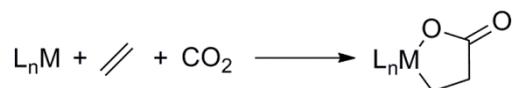
In chapter 4, different palladium (0) complexes are synthesized. They either bear two phosphine ligands (PCy_3 , PtBu_3) or two NHC ligands (IMes, Idipp).



Scheme 8.3. Synthesis of palladium (0) complexes

Those compounds unfortunately prove to be unreactive towards CO_2 activation. They serve as a basis for the synthesis of different palladium (II) complexes through their reactions with CH_3I , HCl and HCOOH . Especially, the complexes $\text{Pd}(\text{IMes})_2(\text{CH}_3)(\text{I})$ and $\text{Pd}(\text{PCy}_3)_2(\text{CH}_3)(\text{I})$ are synthesized from the reaction of respectively $\text{Pd}(\text{IMes})_2$ and $\text{Pd}(\text{PCy}_3)_2$ with CH_3I in high yields. No reaction is observed when 4 bar of CO_2 is pressurized on those compounds. The same behavior is observed with the complex $\text{Pd}(\text{IMes})_2(\text{H})(\text{Cl})$.

Palladium (0) complexes are also reacted with ethylene and CO_2 to form metallalactones.

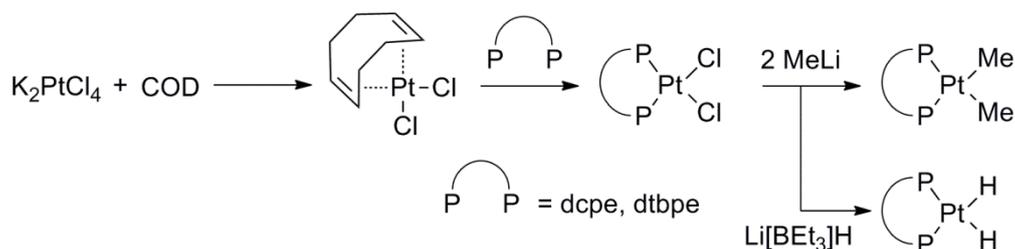


Scheme 8.4. Formation of metallalactones

Several elements tend to prove that ethylene and CO_2 have coordinated to the metal center, however a clear determination of the structure of the complex formed could not be obtained. Further research is still ongoing in the laboratory.

The synthesis of platinum and palladium methyl or hydride complexes bearing bisphosphine or bis-NHC ligands is described in chapter 5. The complexes $\text{Pt}(\text{dcpe})\text{Me}_2$ (**4**) and

Pt(dtbpe)Me₂ (**5**), as well as Pt(dcpe)H₂ (**6**) and Pt(dtbpe)H₂ (**7**) are synthesized and their reaction with CO₂ is followed by NMR.



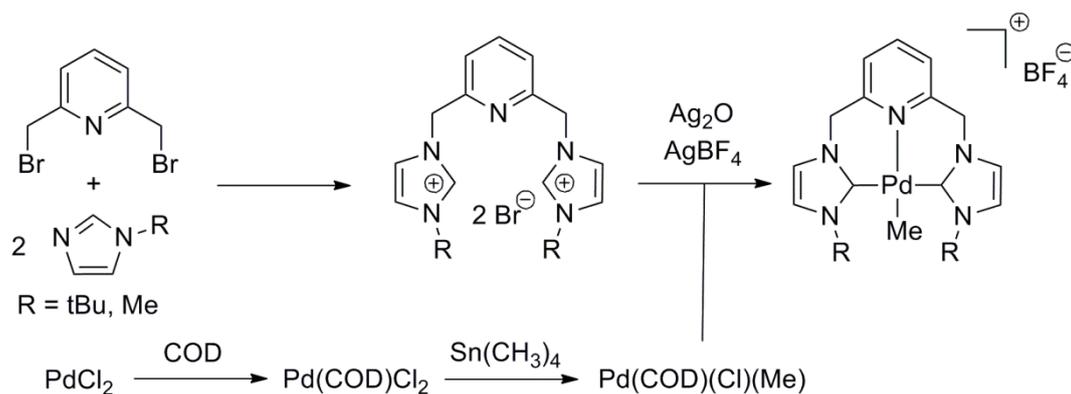
Scheme 8.5. Synthesis of platinum dimethyl and dihydroxy complexes

Complexes **4** and **5** do not react with carbon dioxide. A reaction is occurring when **6** and **7** are submitted to 3 bar of CO₂, however the formation of numerous byproducts is observed in NMR and no pure CO₂-containing compound could be isolated.

The synthesis of palladium (II) bis-NHC complexes bearing methyl groups is intended through two routes. The first one involves the reduction of Pd(bis-NHC)Br₂ with MeLi. An NMR study shows that MeLi attacks preferentially the acidic protons of the bridge linking the two imidazole rings rather than reducing the bromide ligands. The second route proceeds through the in-situ formation, or the isolation, of the free carbene and its reaction with Pd(tmeda)Me₂. Following the synthesis reported by Slaughter et al.^[139] for the in-situ formation of the free carbene never leads to the formation of the desired complexes. Several modifications of this procedure are intended however without success.

The reduction of Pd(bis-NHC)Br₂ to the dihydride Pd(bis-NHC)H₂ is intended with different reducing agents. The formation of the desired complexes is never observed, probably due to the high instability of such dihydride compounds. A [Pd(bis-NHC)(CH₃CN)Br]⁺ PF₆⁻ complex is synthesized and its reduction to the monohydride is performed. An in-situ NMR study at low temperature shows the formation of the hydride at -78 °C and its decomposition at temperatures higher than -20 °C.

Chapter 6 deals with the synthesis of palladium (II) methyl complexes bearing CNC pincer ligands.



Scheme 8.6. Synthesis of palladium complexes with CNC pincer ligands

Two different ligands were chosen, one with bulky tert-butyl groups on the pending arm, one with smaller methyl groups. Those ligands exert a strong trans influence, as can be seen by the relative length of the palladium methyl bond, which weakens the palladium-methyl bond. However, those complexes were unreactive towards 3 bar of CO_2 , even at high temperature (110 °C).

Summary

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