Fe(III) AND V(V) AMINO TRIPHENOLATE COMPLEXES AS CATALYSTS FOR THE
CONVERSION OF RENEWABLE CARBON FEEDSTOCKS

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Chapter 1

General Introduction
1.1 Introduction

The design and study of metal catalysts able to mimic the activity of biological systems is of considerable interest nowadays. This can be achieved through the modulation of the electronic properties and the steric volume around the metal modes using synthetic ligands. This translates in the control of the catalytic behaviour and coordination chemistry of the resulting system. Among the different strategies, the use of multi-dentate ligands is emerging as the leading route for the synthesis of stable and active metal catalysts.\(^1\) The nearly complete filling of all vacant coordination sites around the metal by a single ligand results in intrinsic thermodynamic stability and it allows the use of low catalyst concentrations to prevent the formation of multi-meric species during catalyst turnover. In addition, the presence of single mononuclear species greatly facilitates mechanistic studies and catalyst optimization, particularly in stereoselective processes.

While \(C_2\) symmetric bi-dentate ligands have been extensively studied, ligands with a \(C_3\) symmetric axis have attracted attention only recently.\(^2\) These systems have attracted the interest to a substantial number of research groups concerning their synthesis, complexation behaviour and catalysis.

In this context, triphenolamines Figure 1, have proven to be excellent ligands due to the particular stability, and catalytic abilities of their corresponding metal complexes.\(^3\) The tripodal ligand system bearing a central amino and three phenoxide donors (NO\(_3\) donor ligand) has attracted great interest (triphenolamines, Figure 1).

In view of this thesis work, different approaches used for their synthesis will be reported, followed by some examples of their coordination chemistry and subsequently their use in catalysis.

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1.1.1 Synthesis of Triphenolamines

Triphenolamines molecules have traditionally been synthesized by reaction of ortho/para-disubstituted phenols with hexamethylenetetramine Scheme 1. This synthetic pathway (Mannich reaction) involves only one-step from the phenol to the ligand. This procedure however, requires long reaction times (2-7 days), harsh reaction conditions and high temperatures. In addition, this strategy allows the formation of corresponding ligand only when the phenol moiety is substituted in either the ortho- and para-positions.

An alternative route has been reported based on the nucleophilic substitution (S\textsubscript{N}2) of a 2-methoxybenzylamine with two equivalents of 2-methoxybenzylbromide Scheme 2. This strategy has the advantage of giving access to asymmetric triphenolamine 13 Scheme 3.

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This strategy allows also access to enantiopure triphenolamines. The key step is the stereoselective reduction of a chiral imine 9. Subsequently, this is converted to the primary amine by oxidation in the presence of Pb(OAc)$_4$, followed by hydrolysis.$^6$ Finally, the enantiopure triphenolamine 4d is obtained by reacting the amine with two equivalents of 2-benzylxy-3-bromomethyl-biphenyl, followed by the hydrogenolysis of the benzyl group Scheme 3.

A third synthetic approach has been developed to synthesize $C_3$ symmetric ortho-substituted triphenolamine ligands as depicted in Scheme 4. This synthesis is based on a three-fold reductive amination starting from ortho-substituted salicyl aldehydes using a nitrogen source such as NH$_4$OAc and a reducing agent NaBH(OAc)$_3$. Most of the salicylaldehyde derivatives are commercially available but they can also be easily prepared from their corresponding phenols. The phenoxy group is usually protected with an ether moiety, typically a benzyl group, during the reductive amination step. Finally, the ligand is obtained in good yield by removing the ether group via hydrogenolysis. The easy availability of the starting materials and the possibility to have direct access to this important class of ligands, make this strategy an efficient route for the preparation of ortho-substituted triphenolamines.


1.2 Coordination chemistry of amine triphenolate complex

Amino triphenolate ligands are able to form metal complexes with early transition metals and main group elements in high oxidation states. The coordination of these ligands to metal ions affords highly robust complexes. In these complexes, the ligand usually binds to the metal as a tetradentate ligand with the three anionic oxygen atoms in the equatorial positions and the tertiary amine in one of the axial positions. Generally, upon complexation with metal ions, mononuclear complexes with a ratio of 1:1 ligand–metal are obtained. As reported previously, a crucial role for their stability is given by the substituents in ortho and para positions to the phenoxy moiety of the ligand. For instance ortho groups, which are in close proximity to the metal center, can affect directly their stability and therefore the reactivity of the corresponding metal complexes. As examples, complexes bearing bulky substituents such as t-Bu groups are highly stable to hydrolysis in comparison to complexes having small groups such as Me or H.\textsuperscript{3b,3c,8,9} Such complexes have the tendency to form di-nuclear complexes or aggregates after exposure to moisture.\textsuperscript{10} Para substituents


to the phenoxy groups are able to modify the electronic properties of the ligand and therefore can directly affect the catalytic properties of the corresponding complex.

In the majority of the reported examples the usual geometry assumed by the complexes are trigonal bipyramidal (TBP) and octahedral (OCT), whereas tetra-coordinate complexes with trigonal monopyramidal (TMP) geometry are less observed as depicted in Figure 2.

![Common geometries of the complexes](image)

Moreover, amino triphenolate ligands can form stable metal complexes with a wide range of metal ions and main group elements such as Ti, Zr, Hf, V, Nb, Ta, Mo, W, Al, Ga, In, and Fe. However, in view of this thesis work, the attention will be focused on the coordination chemistry and the reactivity of vanadium and iron amino triphenolate complexes in order to compare and identify new opportunities in catalysis.

### 1.3 Vanadium amino triphenolate complexes and their reactivity in catalysis

Vanadium complexes belong to the group V in which usually the octahedral geometry predominates, except for the vanadium species. Generally vanadium (V) complexes assume a trigonal bipyramidal (TBP) geometry, however different binding behaviour was found upon complexation with very electron-poor ligands such as dichloro-substituted ortho/para amino triphenolate (R₁=R₂=Cl).¹¹ In this example, a hexa-coordinate octahedral crystal structure was obtained with the oxo moiety present in the *trans*-position to the amine group and a molecule of water as ligand in the apical position of the complex Figure 3.

![Vanadium complex](image)

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The first synthesis of vanadium amino triphenolate complexes was reported by Kol et al.\textsuperscript{11} The synthesis was carried out mixing equimolar amounts of ortho/para di-substituted amino triphenolate ligand with VCl$_3$-THF affording, vanadium complexes with C$_3$-TBP in which in the apical position is occupied with a labile ligand such as THF.

Also when other metal precursors are used in the synthesis of vanadium complexes, such as V(O)(OR)$_3$, the same geometry was obtained with an oxo moiety in the trans position to the nitrogen of the amino triphenolate ligand.\textsuperscript{12} Vanadium oxo complexes have a much longer distance between the amino donor group (N) and the metal centre (V), in comparison to the distance found for the V(III) species.

The catalytic behaviour of V(V) amino triphenolate complexes was also investigated in the oxidation of styrene to styrene oxide, in the presence of t-butyl hydrogen peroxide (t-BuOOH) as oxidant. In these catalytic studies reported by Kol, Goldschmidt and others,\textsuperscript{11} the oxidation reaction was carried out using 5% mol of V(V) catalysts in a solution of benzene and t-BuOOH. Under these conditions, the catalysts showed poor reactivity and the evolution of side products were observed.

More recently, the catalytic studies of V(V) amino triphenolate complexes, were focused on sulfoxidation and halogenation reactions.\textsuperscript{13} In these studies, vanadium complexes were obtained by the reaction of ligands with an equimolar amount of vanadium precursor VO(Ot-Pr) in dry THF in an inert atmosphere affording mononuclear complexes in high yield (92-94%) as deep red crystalline solids Scheme 5. All (V) amino triphenolate complexes where characterized by $^1$H-NMR, $^{51}$V-NMR spectroscopy and X-ray diffractometric analysis, the results are reported in Table 1 and Figure 4.

![Scheme 5. Synthesis of V(V) complexes 18e-h](image)

Table 1. $^{51}$V NMR chemical shift (ppm) of 18e-h in CDCl$_3$ solvent.

![Table 1](image)

Chapter 1

Complexes bearing Me and t-Bu groups in the ortho position have shown highly symmetric $^1$H-
NMR proton spectra in accordance with the presence of a mononuclear species having C$_3$ symmetry
and singlet signals in the $^{51}$V-NMR spectrum were detected (-381.90 ppm and -389 ppm
respectively recorded in CDCl$_3$). Whereas for the complex 18e, a non-symmetric $^1$H-NMR spectra
with different signals in $^{51}$V-NMR spectrum was observed, suggesting the formation of aggregates
or the presence of a mixture of species. This confirms the strong importance of bulky ortho
substituents for the formation of stable metal complexes.

As mentioned previously, the catalytic activity of amino triphenolate complexes was studied in the
sulfoxidation reaction. The complexes firstly were tested in sulfoxidation of thioanisol, using
hydrogen peroxide as oxidant at room temperature. V(V) catalysts were found to efficiently
catalyze the reaction in fast and highly selective manner to the corresponding sulfoxide, reaching
quantitative yields in the case of the complex 18g (R= t-Bu). Further optimization of the reaction
conditions was obtained by decreasing the catalyst loading to 0.01 mol%. In this case, high
selectivity of methyl phenyl sulfoxide with respect to methyl phenyl sulfone was obtained reaching
high TONs and TOFs (up to 8000h$^{-1}$). The optimized procedure was then extended to other
sulphides Table 2. In this case, the catalytic systems based on vanadium complexes were found to
be extremely active with high selectivity, confirming the efficiency of these catalysts in oxygen
transfer reactions. The results obtained employing complex 18g as catalysts are reported in Table 2.

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$^{51}$V NMR - δ (ppm), CDCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18e</td>
<td>-396.83, -428.78</td>
</tr>
<tr>
<td>18f</td>
<td>-381.90</td>
</tr>
<tr>
<td>18g</td>
<td>-389.07</td>
</tr>
</tbody>
</table>

Table 2. Oxidation of sulphides catalysed by 18g.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>Yield (%)</th>
<th>SO/SO$_2$</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Me</td>
<td>98</td>
<td>99:1</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>p-Tol</td>
<td>Me</td>
<td>&gt; 99</td>
<td>&gt; 99:1</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>p-Tol</td>
<td>n-Bu</td>
<td>96</td>
<td>99:1</td>
<td>120</td>
</tr>
</tbody>
</table>
In general, the mechanism is believed to proceed through the addition of hydrogen peroxide to the metal centre affording a metal peroxide species, which is the active species in the sulfoxidation reaction. The sulfide acts as nucleophile and can attack the electrophilic oxygen of the peroxo moiety to subsequently give cleavage of the O-O bond leading the oxidized product and the formation of the di-oxo species. Finally, this complex, in the presence of H^+, can form again the initial species.

Vanadium-based complexes have also attracted recently the interest as biomimetic systems, as some of these catalytic systems are able to mimic vanadium haloperoxidases. These enzymes, which catalyse the oxidation of halides to the corresponding "X^+" halonium species in the presence of hydrogen peroxides, can generate halogenated compounds. These vanadium-dependent enzymes, have shown a five coordinate V(V) centre with a trigonal bipyramidal geometry. The most reported vanadium dependent enzymes are bromoperoxidases VBrPO, which are able to catalyse the oxidation of bromide by hydrogen peroxides. Generally, the catalytic cycle, proceeds towards the formation of a peroxovanadium species, which represents the active oxidant in the cycle. The peroxo derivatives are able to oxidize the bromide ion to a brominating intermediate, which subsequently reacts with the substrate, generally a nucleophile, affording the brominated product.

V(V) amino triphenolate complexes can be considered to be good candidates for structural and functional models of vanadium haloperoxidase enzymes and for these reasons they have been studied in halide oxidations, for example; bromination reactions. In these catalytic systems, the ligands play an important role in order to stabilize the monomeric vanadium complex preventing the formation of oligomeric species under acidic conditions. The catalytic performance of vanadium (V) amino triphenolate complexes were tested in the bromination of 1,3,5-trimethoxybenzene using tetrabutyl ammonium bromide (TBAB) as a halogen source, in the presence of an oxidant, hydrogen peroxide (1 eq.) and in acidic conditions (1 eq.), according to the stoichiometry of the reaction. The

<table>
<thead>
<tr>
<th>4</th>
<th>Ph</th>
<th>Bn</th>
<th>&gt; 99</th>
<th>&gt; 99:1</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>n-Bu</td>
<td>n-Bu</td>
<td>99</td>
<td>&gt;99:1</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>p-MeO-C_6H_4</td>
<td>Me</td>
<td>98</td>
<td>99:1</td>
<td>100</td>
</tr>
</tbody>
</table>

* Reaction conditions: Reactions carried out at 28 °C with a 1:1 molar ratio of substrate aq H_2O_2; 0,1 catalyst.
* Conversion determined by ^1H-NMR (CD_3OD), 300MHz). Yield determined by GC analysis on the crude reaction mixture after total oxidant consumption.

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brominated product 2,4,6-trimethoxybromobenzene was afforded in high yield, up to 92%, reaching TONs up to 1260 Scheme 6.

![Scheme 6. Bromination of 1,3,5-trimethoxybenzene using 18g as catalyst](image)

**1.4 Iron amino triphenolate complexes and their use in catalysis**

Iron (III) complexes bearing amino triphenolate ligands were originally reported by Koch and co-workers more than 10 years ago. The ligand was synthesized by the reaction of two equivalents of 2-methoxybenzyl bromide with commercially available 2-methoxybenzylamine in refluxing CH$_3$CN and K$_2$CO$_3$ affording tris (2-methoxybenzyl) amine in 80–85% yield. The protecting groups were removed by refluxing the compound in toluene with five equivalents of AlCl$_3$ yielding triphenolamine which was reacted with FeCl$_3$ leading to a penta-coordinate TBP structure having 1-methylimidazole in apical position. Crystal structures demonstrated that Fe (III) is able to bind an extra ligand which confers an octahedral geometry Figure 5. The catalytic activity of these complexes was not exploited at that time.

![Figure 5. Structure and crystal structure of Fe(III) amino triphenolate having 1-methylimidazole in apical position](image)

More recently, Kleij and co-workers reported an iron(III) amino triphenolate complex to be an efficient catalyst for the cycloaddition of carbon dioxide to a wide variety of oxiranes and oxetanes to yield the corresponding cyclic carbonate products under mild reaction conditions. The

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ligand was synthesized following the Scheme 1 (Mannich reaction) starting from ortho/para dimethyl substituted phenol.

The Fe (III) amino triphenolate complex was prepared by mixing a solution of the ligand with three equivalents of NaH and FeCl₃ as the metallic precursor. The corresponding complex was characterized by X-ray crystallographic analysis showing a di-meric form Figure 6. The synthesis of the complex and the crystal structures obtained are reported in Scheme 7.

As mentioned above, the complex was employed as catalyst in cycloaddition of carbon dioxide to oxirane and oxetanes to yield the corresponding cyclic carbonate. The synthesis of these compounds from epoxides and CO₂ catalysed by metal complexes has been widely investigated and nowadays represents a successful example of carbon dioxide utilization. In these metal-based complexes, catalysis is made possible by the combination of a binary system, which consists commonly of quaternary ammonium halide salt (tetrabutyl ammonium chloride, bromide TBAB and iodide TBAI) or phosphonium halide salts and a metal complex. In this context, Fe(III) amino triphenolate complexes together with a presence of a co-catalyst (TBAI or TBAB), have shown good performance for the synthesis of cyclic carbonates. The reactions were carried out employing 0.5 mol% of Fe (III) catalyst, 5 mol% of co-catalyst using methylethyl ketone as solvent at 10 bar of CO₂. Some of the results are summarized in Table 3.

\[ \text{Scheme 7. Synthesis complex 19a} \]

\[ \text{Figure 6. X-Ray complex 19a}^{16} \]

\[ \text{As mentioned above, the complex was employed as catalyst in cycloaddition of carbon dioxide to oxirane and oxetanes to yield the corresponding cyclic carbonate. The synthesis of these compounds from epoxides and CO₂ catalysed by metal complexes has been widely investigated and nowadays represents a successful example of carbon dioxide utilization. In these metal-based complexes, catalysis is made possible by the combination of a binary system, which consists commonly of quaternary ammonium halide salt (tetrabutyl ammonium chloride, bromide TBAB and iodide TBAI) or phosphonium halide salts and a metal complex. In this context, Fe(III) amino triphenolate complexes together with a presence of a co-catalyst (TBAI or TBAB), have shown good performance for the synthesis of cyclic carbonates. The reactions were carried out employing 0.5 mol% of Fe (III) catalyst, 5 mol% of co-catalyst using methylethyl ketone as solvent at 10 bar of CO₂. Some of the results are summarized in Table 3.} \]


Table 3. Cycloaddition of CO₂ to terminal epoxides.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Co-cat</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TBAI</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBAB</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBAI</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBAB</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBAI</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBAI</td>
<td>70</td>
</tr>
</tbody>
</table>

Reaction conditions: substrate ($2.0 \times 10^{-3}$ mol), catalyst ($1.0 \times 10^{-5}$ mol, 0.5 mol%), co-catalyst ($1.0 \times 10^{-4}$ mol, 5 mol%) methyl ethyl ketone (5 mL), pCO₂=0.2 MPa, 25 °C, 18 h. Conversions based on $^1$H NMR analysis of reaction mixture aliquots using mesitylene as an internal standard. [c] The selectivity toward the cyclic carbonates was~99% as determined by $^1$H NMR.

All the cyclic carbonate products were obtained in good yields using either an iodide or a bromide salt as co-catalyst. In general, the iron complex acts as Lewis Acid which has the role of activating the epoxide towards ring opening by the nucleophile, followed by the insertion of CO₂ into the activated intermediate. The carbonate intermediate can either undergo a ring-closure reaction leading to formation of the cyclic carbonate or react further through the alternating insertion of epoxide and CO₂ molecules, yielding a polycarbonate.
More recently, three different ortho/para substituted Fe(III) amino triphenolate complexes were reported and their catalytic activity in the synthesis of cyclic and polymeric cyclohexane carbonates were described.\textsuperscript{20,21} In this work, it has been shown that the selectivity towards formation of either the cyclic carbonate or the polycarbonate can be controlled by using Fe(III) catalysts and a carefully combination of the reactions conditions, such as temperature and pressure.

1.5 Aim of the thesis work

This thesis has the aim to search for and develop catalytic systems based on metal complexes for different uses in catalysis. In particular, catalysts based on amino triphenolate complexes, which have shown to be highly stable and reactive, will be reported. Furthermore, an extension toward the synthesis of their analogues will be described.

In this respect, Chapter 2 will report a new strategy for the synthesis of the analogues tris-thiophenol amine.

In Chapter 3 and 4 the results obtained with Fe(III) amino triphenolate and V(V) amino triphenolate for the synthesis of small molecules from a renewable carbon feedstock such as carbon dioxide will be discussed.

In particular, Chapter 3 will describe novel reactivity of V(V) amino triphenolate complexes as catalysts for the aerobic oxidation of diols and ether compounds in order to investigate their use for the transformation of lignin into valuable chemicals.

In Chapter 4 the reactivity of Fe(III) amino triphenolate complexes as a catalyst for the synthesis of cyclic organic carbonates, starting from epoxides and CO\textsubscript{2}, is reported.


Chapter 2

Synthesis of ortho-Substituted Trithiophenol Amines by Miyazaki–Newman–Kwart Rearrangement
Abstract

In this chapter, the synthesis of ligands analogous of triphenolamines is described. An efficient synthetic pathway of ortho-substituted trithiophenol amines via Miyazaki–Newman–Kwart rearrangement followed by reductive amination is reported. This project has the aim to affect directly a modification of the binding and electronic properties of the parent ligand in order to have access to different metal complexes and consequently different catalysis.

This chapter has been published.1

2.1 Introduction

Owing to the numerous publications on the topic, it is clear that the use of polydentate ligands, and in particular C₃ symmetric complexes, is emerging as one of the leading strategies for the formation of catalytically stable complexes.² As discussed in the first chapter, these ligands are used to control the environment of the metal, modulate the electronic and steric properties around the metal centre and therefore control their catalytic properties. In the last decade, many studies have been carried out for the synthesis of triphenolamines, their complexation with a wide variety of transition metals and main group elements³ and catalytic activity⁴ (triphenolamine Figure 1 right).

Figure 1. Triphenolamine (left) and trithiophenol amine (right).

Usually the synthesis of triphenolamines is performed via a one-step Mannich reaction of ortho/para disubstituted phenols with HMTA (hexamethylenetetramine) but this synthetic pathway requires long reaction times and harsh conditions. As previously reported, an effective synthesis based on a three-fold reductive amination starting from protected salicyl aldehydes was employed to achieve ortho-substituted triphenolamines.\textsuperscript{5} This synthesis has been shown to be a successful methodology to build a large family of complexes with various functionalities in a multi-gram scale.

Taking advantage of this synthetic approach work proceeded in the study of the analogous trithiophenol amines (Figure 1, left). Ligands based on thiophenolate systems coordinated to transition metals can be efficiently employed in homogeneous catalysis and bioinorganic chemistry, although they are still rare and unexplored compared to their related phenolate derivatives.

In view of the results obtained with triphenolamines and inspired by the trigonal FeS\textsubscript{3} coordination sites present in the Fe Mo-cofactor of nitrogenase, the study was extended to trithiophenol amine in order to understand if the variation of the environment around the metal center would lead to different reactivity and therefore different applications in catalysis and in coordination chemistry. Very little has been reported on ligands-based on thiophenolate and the first synthesis of such ligand (R =H) was reported by Koch \textit{et al}. nearly 20 years ago. It was employed for the preparation of the corresponding iron(II) and iron(III) complexes.\textsuperscript{6} The catalytic behaviour of iron complexes was not explored at that time.

The ligand was synthesized starting from thiol-protected benzylamine, which was reacted with 2 equiv of the corresponding benzyl bromide using K\textsubscript{2}CO\textsubscript{3} as base in acetonitrile (ACN), yielding the corresponding protected trithiophenol amine in 80\% yield. After the removal of the protecting group, the ligand was obtained as a salt in 40\% yield. The synthetic pathway is depicted in Scheme 1.


This synthetic route opened the way for the study of a new class of ligands however this strategy (Scheme 1), provided only non-substituted trithiophenol amine ligand in quite low yield involving the preparation of the two reagents separately.

In view of these results others have been investigated amino trithiophenolate when coordinated with Ga(III) and In(III).\textsuperscript{7} In particular, Ga(III) amino trithiophenolate complexes have shown promising applications in the radiolabelling of large biomolecules such as peptides for use in receptor-based imaging. The tripodal ligand for Ga(III) was found to be stable to enzymatic hydrolysis, neutral and able to pass the BBB (blood-brain barrier). Although extensive theoretical studies have been carried out on amino trithiophenolate (R= H) complexes with iron,\textsuperscript{8} ortho-substituted trithiophenol amine derivatives and their coordination chemistry with different metals have not been intensively investigated.

As consequence, the development of a general and efficient synthesis for this type of ligand is desirable and it will offer the opportunity to extend their application in catalysis. In light of our experience in the synthesis of triphenolamines and in their use as ligands for complexation and catalysis, we planned to prepare trithiophenol amine molecules \textit{via} a similar methodology, i.e. the use of reductive amination as the key step for the preparation of the amino skeleton and Miyazaki–Newman–Kwart (MNK) rearrangement for the preparation of the thiophenol salicaldehyde monomers Scheme 2.


2.1.1 Miyazaki-Newman-Kwart Rearrangement

MNK rearrangement is a tautomeric rearrangement, which allows the migration of the aryl group of an O-aryl thiocarbamate from the oxygen to the sulfur atom through a four membered transition state, which forms an S-aryl thiocarbamate. Because the sulphur atom has a stronger nucleophilicity compared to the oxygen atom, it becomes the driving force of the reaction toward the displacement of the oxygen as depicted in Scheme 3.

The electronic and sterical properties of substituents, in either the aromatic ring or N-substituent, are important in the rearrangement in order to stabilize both the negative and positive charge. For example, it was shown that electron withdrawing groups such as NO$_2$ in para position to the thiocarbamate have a positive effect in stabilizing the negative charge. On the other hand, N-alkyl substituents strongly affected the yield in rearranged product. Investigations also of the sterical effects have been carried out, showing that hindered groups at the ortho position generally favoured the rearrangement except in the case of t-Bu groups.

Taking account of these considerations, the work proceeded by planning the synthesis of a series of ortho-substituted trithiophenol amines, which can be easily and effectively prepared by reductive amination of the corresponding MNK rearranged S-thiocarbamoyl salicaldehydes. The key issue that makes this method successful is the use of the thiocarbamoyl group both as a rearranging agent and protecting group during the reductive amination carried out in the presence of NaBH(OAc)$_3$ and

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NH₄OAc. This strategy allows the effective construction of the ligand skeleton and differently substituted trithiophenol amines.

Initially a synthetic approach was examined, which proceeded toward the preliminary protection of the H group of substituted salicaldehydes 2a–d (R = H, Me, Ph, tBu, respectively), followed by MNK rearrangement of the resulting O-thiocarbamate esters 3a–d, a threefold reductive amination of the thiosalicaldehyde S-thiocarbamates 4a–d, and finally the reductive removal of the protecting carbamoyl groups, yielding 1a–c (Scheme 4). The starting materials are commercially available (2a–c) or easily accessible from the corresponding phenol using paraformaldehyde and MgCl₂ (2d).⁵

2.2. Synthesis of S-thiocarbammate compounds

Treatment of 2a–d with N,N-dimethylthiocarbamoyl chloride (DMTCl) in acetonitrile in the presence of potassium carbonate gave the desired O-thiocarbamates 3a–d in good yields after purification (75–77%). The compounds were purified by either column chromatography or crystallization. Alternative procedures with different bases, such as 1,4-diazabicyclo[2.2.2] octane or NaH in N,N-dimethylformamide, did not furnish satisfactory yields for all of the products.

Reaction conditions for the MNK rearrangement were optimized for 3a (R = H, Table 1). The rearrangement was performed initially using the Lewis acid catalyst BF₃·OEt₂ as reported by Brooker et al.⁶ Although the reaction proceeded smoothly in high yield, it requires long reaction times 3d and strictly anhydrous reaction conditions. To obtain a more reliable method the classical thermal rearrangement was attempted (Table 1, Entry 2).

Table 1. Optimisation of MNK rearrangement reaction conditions for 3a.

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<thead>
<tr>
<th>#</th>
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<th>Solvent[b]</th>
<th>Temp °C</th>
<th>Time (min)</th>
<th>Conversion[%]</th>
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The reaction was performed at 300 °C and 25% of the desired product 4a was obtained, in a very short time. However, under these conditions, extensive hydrolysis of the reagent to 2a (56%) was observed. On the contrary, the reaction carried out using microwave (MW) induced heating, after dissolving the sample in N-methylpyrrolidone (NMP), enables the tuning and optimization of the reaction conditions and the maximization of conversion of 3a into 4a without reagent or product hydrolysis (Table 1, Entries 3–6). The best reaction conditions were obtained, using anhydrous NMP at 230 °C for 10 min (Table 1, Entry 5). Shorter reaction times did not permit complete conversion of the reagent, and longer reaction times resulted in the partial hydrolysis of the S-thiocarbamoyl group yielding thiosalicaldehyde (6a, 10%, Table 1, Entry 6). The best reaction conditions obtained with 3a were also applied to 3b–d (Table 2). As mentioned previously, the presence of an ortho substituent to the thiols moiety is known to strongly influence the MNK rearrangement. Preliminary tests showed that, although a clean and quantitative rearrangement was obtained for the phenyl substituted aldehyde 4c, the presence of an aliphatic group in the ortho position, as the methyl group 3b or tert-butyl 3d systems, resulted in extensive reagent and/or product hydrolysis, lowering the final yield of 4. Therefore, irradiation times were decreased to 5 min and under this conditions a good yield of 3c was obtained (95% conversion, Table 2, Entry 4), whereas 3b, with 97% conversion, gave a rearrangement yield of 78% for S-thiocarbamate 4b (54%) and the hydrolyzed 6b (24%, Table 2, Entry 2 and 4). For 3d, reagent and product hydrolysis were even more evident. The MNK rearrangement furnished 10% yield of 4d and 50% of 6d. It seems likely that the aliphatic substituent is not responsible for the reduced yield in the rearrangement reaction rather the starting material 3d and the thiocarbamate product 4d are more susceptible to hydrolysis. Further variation of the reaction times and reaction temperatures under MW induced heating conditions or the use of BF3·OEt2 did not result in better yields.

Table 2. MNK rearrangement for 3a–d.

---

Compounds 3b and 3d were also irradiated without solvent and an increased yield of rearranged product was obtained for 3b (90%, Table 2 Entry 3), whereas 3d gave a higher yield of 4d (25%) with an amount of 6d (48%). Because of the low yields of 4d, the synthesis of trithiophenol amine 1d was not further investigated. However, it must pointed out that the MNK rearrangement is effective (60% of rearranged product as 4d and 6d) and can still be synthetically useful. Moreover, 2b and 2d can be recycled. S-thiocarbamoyl aldehydes 4a–c were purified by column chromatography after removal of the solvent by distillation at low pressure.

2.3 Synthesis of ortho-trithiophenol amines

The resulting S-thiocarbamoyl aldehydes 4a–c were subsequently used for reductive amination in the presence of NaBH(OAc)₃/NH₄OAc. The yields of 5a–c after purification were satisfactory (ca. 50%). The only product of the reaction was the benzylic alcohol arising from the reduction of the corresponding aldehyde. The final step can be driven to completion under reductive conditions (lithium aluminium hydride), whereas hydrolytic methods (KOH/EtOH) gave only partial deprotection. The desired 1a–c ligands were obtained in good yields after aqueous work up (60–65 %) Scheme 4. These compounds are known to have low stability under oxidative or basic
conditions (formation of disulfides and dibenzo[1,5] dithiocines)\textsuperscript{13} and, for these reasons, they were usually used directly for the synthesis of the corresponding metal complexes without further purification.\textsuperscript{14}

![Scheme 4](image)

Scheme 4. Synthetic procedure for the synthesis of 1a-c

The synthesis can be further optimized by carrying out the reductive amination and deprotection in a one-pot procedure. This strategy has been tested on 4c affording the product in quite good yields. Therefore, only three steps are required to obtain the trithiophenol amines from the commercially available salicaldehydes.

Furthermore, in parallel with the synthetic pathway described above, another synthetic approach was attempted. To achieve directly the ligand, firstly it was prepared using a threefold reductive amination, as presented above, followed by the Miazaki-Newmann–Kwart rearrangement of the ligand itself. Although the threefold introduction of the thiocarbamoyl groups proceeded smoothly, the rearrangement did not take place and a mixture of either rearranged or non-rearranged products was observed. The synthesis is depicted in Scheme 5.

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2.4 Conclusions

In conclusion, the synthetic methodology reported allows the synthesis of ortho-substituted trithiophenolamines 1a-c with very satisfactory yields via a three step procedure starting from commercially available aldehydes. This approach led us to the possibility, for the first time, to access this important class of ligands in a systematic way using either commercially or readily available building blocks. Moreover, the synthesis of thio-aldehydes could be important for the preparation of salan, salen and salalen ligands. This methodology will be employed for the synthesis of a large library of this class of ligands for applications in coordination chemistry and catalysis.

2.5 Experimental Section

General methods: Chemicals and solvents were purchased from commercial suppliers and used as supplied. Starting materials such as 3-substituted salicyl aldehydes 2a-d are commercially available or easily accessible from the corresponding phenols. $^1$H-NMR spectra were recorded on a Bruker AC 250 (250.18 MHz) or Bruker Avance DRX 300 (300.13 MHz) spectrometer, using partially deuterated solvent or TMS as internal references (TMS = 0.00 ppm, CHCl$_3$= 7.26 ppm). ESI-MS and EA

Synthesis of substituted O-2-formylphenyl dimethylthiocarbamate (3a-d).

Substituted salicyl aldehydes 2a-d, (0.05 mol) were dissolved in dry acetonitrile (20 ml) under nitrogen at room temperature. K$_2$CO$_3$ (26.25g, 0.2 mol) was added to the stirred solution. After 10
min solid dimethylthiocarbamoyl chloride (7.4 g, 0.06 mol) was added and the mixture heated at 80°C. After 24 hours the mixture was cooled at room temperature, the solid residue was filtered and washed with EtOAc (25 ml). The organic layer was washed with water (3 x 15 ml), dried over Na₂SO₄ and concentrated under reduced pressure. The product was purified by flash chromatography (SiO₂, Petroleum Ether:EtOAc 8:2).

**O-(2-formylphenyl)dimethylthiocarbamate (3a):** white solid; yield: 75%; ¹H-NMR (250MHz, CDCl₃): δ= 10.07 (s, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.89 (t, J = 9.0 Hz, 1H), 7.4 (t, J = 13.0 Hz, 1H), 7.13 (d, J = 13.0 Hz, 1H), 3.44 (d, J = 15.0 Hz, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ= 187.92, 154.81, 134.43, 129.23, 128.69, 126.00, 123.96, 111.49, 43.40, 38.92 ppm.

**O-(2-Formyl-6-methylphenyl) dimethylthiocarbamate (3b):** orange oil; yield: 77%; ¹H-NMR (250MHz, CDCl₃): δ= 10.02 (s, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.30 (t, J = 7.5, 1H), 3.46 (d, J = 10 Hz, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ= 188.77, 153.45, 136.70, 132.38, 129.13, 127.55, 126.12, 111.84, 43.33, 38.69, 15.51 ppm.

**O-(3-Formyl-biphenyl-2-yl) dimethylthiocarbamate (3c):** white solid; yield: 75%; ¹H-NMR (250MHz, CDCl₃): δ= 10.09 (s, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.5, 1H), 7.49 (s, 1H), 7.41 (m, 5H), 3.21 (d, J = 18Hz, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ= 188.49, 152.45, 136.44, 130.19, 129.17, 128.39, 127.85, 126.47, 43.40, 38.63 ppm.

**O-(2-Formyl-6-t-butylphenyl) dimethylthiocarbamate (3d):** yellow solid; yield: 75%; ¹H-NMR (250MHz, CDCl₃): δ= 9.92 (s, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 3.48 (s, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ= 188.52, 153.30, 142.51, 133.20, 130.64, 128.53, 125.98, 126.47, 43.40, 39.05, 30.83 ppm.

**Synthesis of substituted S-2-formylphenyl dimethylthiocarbamate (4a-d).**

Microwave reactions were performed in 10 ml sealed tubes in a regularly calibrated CEM Discover focused 300 W microwave reactor with IR temperature monitoring and non-invasive pressure transducer. In a typical procedure O-thiocarbamate 3a-d (1 mmol) was dissolved in NMP (2.5 ml) and heated to the required temperature with stirring for a fixed time. The heating time to reach the set temperature was typically 60 s, depending on the scale, the maximum wattage supplied (100–300 W) and the temperature required. The heating time is not included in the quoted hold time for any given procedure. The S-thiocarbamate (4a-c) products were isolated either directly by aqueous drown-out from NMP solutions, or by extraction into EtOAc followed by flash silica gel chromatography.

**S-(2-formylphenyl) dimethylthiocarbamate (4a):** Irradiation time 230°C, 5 min. After extraction with EtOAc, the crude material was purified by flash (SiO₂, Petroleum Ether: Ethyl Acetate 8:2). Bright yellow oil; yield 85% ¹H-NMR (250MHz, CDCl₃): δ= 10.35 (s, 1H), 8.02 (d, J = 5.7 Hz, 80.0 (d, J = 13.0 Hz, 1H), 3.44 (d, J = 15.0 Hz, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ= 187.92, 154.81, 134.43, 129.23, 128.69, 126.00, 123.96, 111.49, 43.40, 38.92 ppm.
1H), 7.55 (m, 3H), 3.07 (s, 6H) ppm; 13C NMR (62.9 MHz, CDCl3): δ = 191.82, 165.23, 148.24, 140.08, 138.58, 135.31, 129.58, 127.75, 37.09 ppm.

S-(2-Formyl-6-methylphenyl) dimethylthiocarbamate (4b): Irradiation time 230℃, 2 min. After extraction with EtOAc, the crude material was purified by flash (SiO2, Petroleum Ether: Ethyl Ether 7:3). Orange oil; yield: 52%; 1H-NMR (250MHz, CDCl3): δ = 10.42 (s, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.40 (m, 2H), 2.97 (s, 6H) ppm; 13C NMR (62.9 MHz, CDCl3): δ = 192.06, 164.61, 143.97, 138.39, 135.47, 130.75, 129.60, 127.77, 36.96 ppm.

S-(3-Formyl-biphenyl-2yl) dimethylthiocarbamate (4c): Irradiation time 230℃, 5 min. After extraction with EtOAc, the crude material was purified by flash (SiO2, Petroleum Ether: Ethyl Acetate 8:2). Bright yellow oil; yield 94%. 1H-NMR (250MHz, CDCl3): δ = 10.36 Hz (s, 1H), 8.0 (m, 1H), 7.52 (m, 2H), 7.34 (m, 3H), 2.97 (s, 6H) ppm; 13C NMR (62.9 MHz, CDCl3): δ = 191.69, 165.10, 148.26, 140.10, 138.59, 135.34, 130.75, 129.60, 127.77, 36.96 ppm.

Synthesis of Tri-(2-N-dimethylthiocarbamoylbenzyl) amine (5a-c):
Rearranged aldehydes 4a-c (3 mmol) were mixed with ammonium acetate (80 mg, 1 mmol) in THF (20 ml) under nitrogen atmosphere. After 2h sodium triacetoxy borohydride (920 mg, 4 mmol) was added. The mixture was stirred overnight at room temperature and evaporated to dryness. The residue was dissolved in EtOAc and washed twice in ammonium chloride and brine. The organic layer was dried over Na2SO4 and concentrated under reduced pressure. The product was purified by flash chromatography. (SiO2, Petroleum Ether: EtOAc:TEA 8:2:0.01).

Tri-(2-N-dimethylthiocarbamoylbenzyl) amine (5a): 55%. Bright yellow oil; yield 55%. 1H-NMR (250MHz, CDCl3): δ = 7.53 Hz (d, J = 7.5, 3H), 7.42 (d, J = 5.0 Hz, 3H), 7.31 (t, J= 5.0 Hz, 3H), 7.21 (t, J = 7.5 Hz, 3H), 3.69 (s, 6H), 2.98 (s, 18H) ppm; 13C NMR (62.9 MHz, CDCl3): δ = 166.50, 142.82, 136.93, 130.96, 129.02, 128.74, 126.96, 56.95, 36.72 ppm. MS (ESI): calcd for C30H36N4O3S3 [M+H]+, 596.1, found 596.2.

Tri-(2-N-dimethylthiocarbamoyl-3-methylbenzyl) amine (5b): 50%. Bright yellow oil; 1H-NMR (250MHz, CDCl3): δ = 7.80 (d, J =7.5 Hz, 3H), 7.40 (m, 6H), 3.73(s, 6H), 3.04 (s, 18H), 2.43 (s, 9H) ppm; 13C NMR (62.9 MHz, CDCl3): δ = 165.70, 147.97, 140.39, 138.30, 133.70, 131.44, 128.30, 37.04, 20.84 ppm. MS (ESI): calcd for C33H42N4O3S3 [M+H]+, 639.2, found 639.2.

Tri-(2-N-dimethylthiocarbamoyl-3-phenylbenzyl) amine (5c): 53% Yellow oil; 1H-NMR (250MHz, CDCl3): δ= 7.80 Hz (d, J = 7.5 Hz, 3H), 7.30 (m, 3H), 7.27 (m, 15H), 2.85 (s, 18H) ppm; 13C NMR (62.9 MHz, CDCl3): δ = 166.29, 147.85, 144.74, 142.12, 129.53, 129.37, 129.04, 128.89, 127.32, 126.72, 57.65, 37.19 ppm. MS (ESI): calcd for C48H48N4O3S3 [M+H]+, 825.3, found 825.3.
Synthesis of Tris-(2-mercaptobenzyl) amine (1a-c): To a solution of compound 5a-c (0.16 mmol) in dry THF (2 ml) was slowly added at -70°C LiAlH₄ (1.34 ml 1.0 M in THF, 1.34 mmol). After 5 min the mixture was warmed to room temperature and refluxed for 3 hours. The excess of LiAlH₄ was quenched by careful addition of EtOAc (3 ml) at 0°C. This operation was followed by the addition of a solution of H₂SO₄ (10% water, 2 ml). The mixture was extracted with EtOAc (5 ml), washed with water and dried over Na₂SO₄. The resulting solution was concentrated under reduced pressure. Due to the instability of the ligands, the products were not purified.

Tris-(2-mercaptobenzyl) amine (1a). Bright yellow oil; yield 60%. ¹H-NMR (250MHz, CDCl₃): δ = 7.33 Hz (d, J = 7.5 Hz, 3H), 7.3 (d, J = 5.0 Hz, 3H), 7.17 (t, J = 5.0 Hz, 3H), 7.21 (t, J = 7.5 Hz, 3H), 3.69 (s, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ = 142.82, 136.93, 130.76, 129.02, 128.74, 126.96, 56.95 ppm. MS (ESI): calcd for C₂₁H₂₁N₃S₃ [M+H]⁺, 384.1, found 384.0.

Tris-(2-mercapto-3-methylbenzyl) amine (2a) Bright yellow oil; yield 60% ¹H-NMR (250MHz, CDCl₃): δ = 7.60 (d, J =7.5 Hz, 3H), 7.25 (m, 6H), 3.73 (s, 6H), 2.41 (s, 9H) ppm; ¹³C NMR (62.9 MHz, CDCl₃): δ =145.97, 140.39, 138.30, 133.70, 131.44, 128.30, 57.04, 21.84 ppm. MS (ESI): calcd for C₃₃H₄₂N₄O₃S₃ [M+H]⁺, 426.1, found 426.2.

Tris-(2-mercapto-3-phenylbenzyl) amine (3a): bright yellow oil 65%. ¹H-NMR (250MHz, CDCl₃): δ= 7.38 Hz (m, 3H), 7.35 (m, 3H), 7.30 (m, 15 H), 7.10 (m, 3H), 3.80 (s, 6H), ppm; ¹³C NMR (62.9 MHz, CDCl₃): 147.85, 144.74, 142, 12, 129.53, 129.37, 129.04, 128.89, 127.32, 126.72, 57.65, ppm. MS (ESI): calcd for C₃₉H₃₃NS₃ [M+H]⁺, 612.2, found 612.1.
Chapter 3

V(V) amino triphenolate as catalyst for C-C bond cleavage under aerobic conditions
Abstract

In this chapter, an exploration into new reactivity of V(V) amino triphenolate complexes will be described. In particular the activity in oxidative C-C bond cleavage of 1,2-diols and, in a preliminary way, β-hydroxy ethers has been investigated. These studies were carried out in order to develop catalysts capable of controlled oxidative degradation of more challenging substrates, such as lignin models to demonstrate the feasibility of producing fine chemicals from a renewable carbon feedstock.

3.1 Introduction

The development of efficient catalytic systems able to transform biomass into useful chemicals is of great interest in the chemical world because biomass is considered to be the only renewable carbon feedstock available.1 Both cellulose and lignin are constituents of non-food based biomass and therefore potential sources of complex organic building blocks. Several methods have been reported for the conversion of cellulose whereas little progresses have been made for the transformation of lignin into valuable compounds. This is related to its highly intricate structure; lignin is a polymer organized in irregular carbon-carbon and carbon-oxygen phenolic subunits and the abundance of these subunits linkages is different in each type of wood. Despite the diversity of lignin, the most common unit includes the β-O-aryl ether (β-O-4) linkages featured in Figure 1.

This subunit represents a significant percentage of all the linkages, thus is a target of lignin depolymerization. For this reason, the development of catalysts that can effectively cleave β-O-4 bonds under mild reaction conditions could provide the utilization of lignin for high-value applications. Aside from the difficulty related to its structural complexity, there are three main problems for the efficient use of lignin compounds: firstly the reaction conditions required for its degradation such as temperature, pressure and solubility, secondly the selectivity of the transformation in delivering valuable aromatic compounds and finally the cost of the entire degradation process which has to be convenient in terms of both price and waste products. The primary pathway by which lignin is naturally depolymerized is oxidation using enzymes such as lignin peroxidases in the presence of oxidants such as hydrogen peroxide or oxygen. Oxidation in aerobic conditions has shown to be advantageous since no added reagents are required. Furthermore, it could preserve a high degree of the functionalities present in the original lignin polymer.

A series of recent works report that homogeneous catalysis using non-toxic, abundant and cheap metals could provide a selective cleavage of lignin linkages, which as mentioned above, is highly desirable under mild and inexpensive conditions.

In general, the homogeneous catalysts employed for lignin oxidation can be summarized into five classes of compounds: Schiff base catalysts, metalloporphyrins, tetraamidomacrocyclic iron
catalysts,\textsuperscript{10,11} polyoxometalates\textsuperscript{12} and Co(III)\textsuperscript{13} and Mn(III)\textsuperscript{14} salts. For each system reported stoichiometric amounts of oxidants, \textit{e.g.} hydrogen peroxide or oxygen, were employed.

### 3.1.1 Vanadium(V) as catalysts for lignin degradation

Among these catalytic systems developed in the last few years and in view of this thesis work, attention will be focused on homogeneous catalysis based on vanadium complexes, that have been shown to be able to degrade lignin model compounds under aerobic oxidation conditions. Son and Toste reported the V(V) tridentate Schiff-base catalyst 1 that effectively and selectively cleaves β-O-4′ bonds in lignin substructures as depicted in Scheme 1.\textsuperscript{15,16}

![Scheme 1. Lignin model degradation by 1](image)

The reaction was carried out using 10% catalyst 1 loading, at 80°C in MeCN and after 24 h it was possible to obtain almost complete conversion of lignin model compound (95%), yielding the products 3, 4 and 5. It was found that after 24 h under anaerobic conditions the same products were obtained, albeit in reduced yield. This demonstrates that the V(V) is reduced to V(IV) species during the reaction, but oxygen is not fundamental for catalyst turnover. For this catalytic system, a non-oxidative C-O bond cleavage was proposed which proceeds through one-electron process as depicted in Scheme 2.

\begin{itemize}
\item \textsuperscript{15} S. Son, F. D. Toste. \textit{Angew. Chem. Int. Ed.} \textbf{2010}, 49, 3791.
\end{itemize}
The first step involves the exchange of the alcholate ligand on the vanadium(V) complex 1 with the benzylic hydroxyl group, followed by the abstraction of the hydrogen to form a ketyl radical which subsequently eliminates the aryloxyradical. The reaction proceeds with the elimination of the hydroxyl group from the resulting enolate yielding an enone product and the reduced species of vanadium (IV) which can be re-oxidized into vanadium (V) species by the aryloxyradical. These latter results are supported by thermodynamic studies of hydrogen atom transfer reaction between phenol derivatives and vanadium–oxo species.\(^{17}\) The same authors inspired by these promising results obtained with vanadium(V) catalyst \(^{1}\), proceeded toward the extension of this catalytic system into lignin derived from *Miscanthus giganteus*. The reactions were followed by GPC and it was found that V(V) catalyst \(^{1}\) remained active and can efficiently perform the cleavage of the β-O-4 linkage yielding valuable aromatic compounds.

More recently, Hanson *et al.* reported other vanadium complexes as catalysts for oxidative C-C bond cleavage of a phenolic lignin compound.\(^{18}\) These studies had the aim to identify catalysts able to control the selectivity toward C-C or C-O bond cleavage of lignin in aerobic oxidation. Both in catalytic aerobic oxidation conditions and the cleavage of specific linkages represent a challenge in homogeneous catalysis, as this strategy would provide the production of fine chemicals without the use of stoichiometric reagents. As previously mentioned, lignin is composed by irregular


phenolic subunits, each containing 1,2-hydroxy ether substituents. In these studies the reactivity of 8-quinolinate vanadium(V) complex 6 was investigated with the phenolic lignin model compound 7 (Scheme 3). In previous work, it was found that complex 6 is able to catalyze the aerobic oxidation of benzylic and allylic alcohols when an additive, generally a base, is used. The reaction was carried out using 10 mol% of catalyst 6 in the presence of triethylamine and the results are presented in Scheme 3.

Under these conditions the reactions affords the products derived from cleavage of the C-C bond: compound 8 (2,6-dimethoxybenzoquinone 40%), an acrolein derivative 9 (38%), and the corresponding oxidized ketone 10 (38%) (Scheme 3). According to the authors, the formation of the acrolein product 9 was unexpected as the cleavage of C-C bond between alkyl and phenyl moieties is a rare reaction. The cleavage observed with the formation of the acrolein product, which differs from the non-oxidative C-O cleavage reported by Toste, indicates that the reaction selectivity depends upon the catalyst used. When the same lignin model was tested with Toste’s catalyst the products derived from C-O bond cleavage were observed. This confirms that selectivity in cleavage sites can be achieved using different catalysts. The role played by the phenoxy group in the lignin model compound in selectivity was highlighted when the experiment was carried out using a non-phenolic lignin model compound. In this case, products derived from the C-C bond cleavage were not detected.

According to the authors, the mechanism of the oxidative C-C bond cleavage may involve the formation of a phenoxy radical intermediate. This pathway has been also proposed for metal complexes based on cobalt.\textsuperscript{20}

More recently, the same group reported a vanadium complexes based on bis-(phenolate) ligands (Scheme 4). These complexes were employed as catalysts in the aerobic oxidation of lignin model compounds and in the oxidation of 1,2-diols and benzyl alcohol.\textsuperscript{21} In this case, for lignin transformation, vanadium complexes have shown different selectivity toward the cleavage of C-O and C-H bond and lower reactivity in comparison with the V(V) 8-quinolinate previously discussed. For example, it was found that complex 10, employing phenolic lignin model compound 7, gave only 20% of conversion, whereas for 11, a non-phenolic lignin model, 84% of conversion was obtained with a mixture of C-O and C-H bond cleavage products, as reported in Scheme 4.

![Scheme 4. Lignin model 11 degradation catalyzed by 10.\textsuperscript{21}](image)

In view of the latest studies obtained with V(V) complexes and in the light of the promising results achieved previously with V(V) amino triphenolate catalysts in oxidation reactions,\textsuperscript{22} we tested the potential reactivity of V(V) amino triphenolate complexes in the oxidative carbon-carbon bond cleavage in aerobic conditions of diols and β-hydroxy ether compounds.

The work here presented will be focused on the reactivity of a vanadium (V) amino triphenolate complex in the oxidative C-C bond cleavage under aerobic conditions of both 1,2-diols and one ethereal derivative.


3.2 V(V) Amino Triphenolate Complex

The V(V) amino triphenolate complex used in this study was synthesized as depicted in Scheme 5 and characterized as reported previously. 22

Equimolar amounts of the ligand 15 with the precursor VO(Oi-Pr) in dry THF in inert atmosphere afforded complex 16 in high yield (90%).

3.2.1 Electrochemical and UV-Vis Studies

To evaluate the potential of V(V) amino triphenolate to be employed as oxidant, cyclic voltammetry experiments were performed in dichloromethane for the complex 16 which exhibits quasi-reversible waves at -625 mV (vs Ag/AgCl) corresponding to a vanadium (IV) species and at -1.024 mV (vs Ag/AgCl) corresponding to a vanadium (III) species, as reported in Figure 2.

Figure 2. Cyclic voltammograms of V(V) complex 16 (5·10⁻⁴ M) in CH₂Cl₂ at 298 K (scan rate = 100 mV s⁻¹) using 0.1 M NBu₄PF₆ as supporting electrolyte, glassy carbon working electrode, platinum wire auxiliary electrode, and Ag/AgCl/NaCl (sat) reference electrode.

In order to further characterize the vanadium species at different oxidation states, the UV-vis spectra of the three different oxidation states corresponding to V(V), V(IV) and V(III) of 16 were recorded in CH₂Cl₂. This was performed by measurement of UV-Vis spectrum during electrochemical reduction of the V(V) complex 16 (Figure 3).
The red curve, corresponding to the V(V) species 16 has a maximum at 460 nm, was recorded at initial time at equilibrium potential. After the application of a -700 mV (vs Ag/AgCl) potential, the UV-vis spectrum of a different species was recorded, with a maximum of adsorption at 470 nm. This spectrum can be assigned to the corresponding V(IV) species (green curve, Figure 3). Finally, applying a potential of -1025 mV (vs Ag/AgCl), a third spectrum was obtained, with a maximum of absorption at 567 nm, that we could assign to the V(III) species (blue curve).

3.3 Catalytic reactivity of vanadium (V) catalyst: Pinacol aerobic oxidation

Investigations to assess the potential of the V(V) amino triphenolate complex 16 to catalyze an oxidative C-C bond cleavage reaction were performed. The reactions were carried out using pinacol as substrate in different solvents and were monitored in order to detect the consumption of the pinacol and formation of the products. The results obtained are summarized in Table 1.

![UV-Vis spectra of V(V) complex 16 (5·10^{-4} M) in CH_2Cl_2 at 298 K. Red Curve V(V) species at equilibrium potential, green curve at -625 mV potential and blue curve at -1025 mV potential.](image)

Table 1. Aerobic oxidation of pinacol catalyzed by 16 (10%).

<table>
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<th>Solvent</th>
<th>Time (h)</th>
<th>Conversion%</th>
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<td>8</td>
<td>&gt;98</td>
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<tr>
<td>2</td>
<td>Toluene</td>
<td>4</td>
<td>&gt;98</td>
</tr>
<tr>
<td>3</td>
<td>Pyridine</td>
<td>2</td>
<td>&gt;98</td>
</tr>
<tr>
<td>4</td>
<td>NMP</td>
<td>2</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>
It was found that complete consumption of pinacol after 2 h in >98% 1H-NMR yield was observed using pyridine and NMP as solvent. Toluene and DCE afforded reaction slightly slower (4 and 8 h respectively to go to completion). Having established that pyridine has a positive effect on the rate of the reaction, we also investigated the effect of another base such as triethylamine (20%). In the presence of triethylamine, it was possible to observe a significant decrease of the rate of the reaction resulting in longer reaction time (24 h Table 1 entry 5). Due to the less problematic handling of toluene, in respect to pyridine and NMP, it was chosen as optimal solvent for the further studies and the reactions were carried out without the presence of any additives.

The catalyticity of the system was tested as well by decreasing the catalyst loading down to 0.2 %. The results are reported in Table 2.

<table>
<thead>
<tr>
<th>#</th>
<th>16 (%)</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>Toluene</td>
<td>4</td>
<td>80</td>
<td>&gt;98</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Toluene</td>
<td>8</td>
<td>80</td>
<td>&gt;98</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>Toluene</td>
<td>48</td>
<td>80</td>
<td>&gt;98</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>Neat</td>
<td>24</td>
<td>80</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>

Even using a lower catalyst loading (2 mol%) we obtained a complete conversion of the reagent into product in 4 only hours, indicating that the system is able to performed 100 TON. When the reaction was performed using 1 mol% and 0.2 mol% of catalyst in toluene complete consumption of pinacol was obtained after 8 h and 48 h respectively (entry 2, 3 Table 2). The reaction was also carried out in neat conditions and after 24 h using 0.2 mol% of catalyst complete conversion of pinacol was obtained.

To further investigate the scope of the reaction, two different substrates were studied: 1,1-2,2–tetraphenylethandiol and 1,2-diphenyl-1,2-ethandiol. The results are summarized in Table 3.
When the reactions were performed using 1 mol% of catalyst 16, complete consumption of the starting material was observed after 8 h and 4 h, respectively. Complete conversion into the corresponding carbonyl derivatives was obtained also working at lower catalyst loading (0.2%) after 24 h. It is worth of mention that for 1,2-diphenyl-1,2-ethandiol in both cases the only product obtained was benzaldehyde (Table 3 entry 2 and 4) without any further oxidation to the corresponding benzoic acid.

### 3.5 Aerobic C-C bond cleavage of 1,2-hydroxyethers.

The catalytic activity of complex 16 has been preliminary tested with an 1,2-hydroxyether compound, 1,2-diphenyl-2-methoxyethanol, a compound that contains a β-hydroxy linkage. The aerobic oxidation of 1,2-diphenyl-2-methoxyethanol in the presence of complex 16 (10%) was tested both in toluene and DCE, in presence or absence of a base. The results obtained are reported in Table 4.
Table 4. Aerobic oxidation of 1,2-diphenyl-2-methoxyethanol catalysed by 16 (10\%).

<table>
<thead>
<tr>
<th>Entry</th>
<th>mol% 16</th>
<th>Solvent</th>
<th>Additive</th>
<th>Time (h)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>DCE</td>
<td>Et$_3$N</td>
<td>48</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>Toluene</td>
<td>Et$_3$N</td>
<td>4 days</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>DCE</td>
<td>_</td>
<td>48</td>
<td>&gt;98</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>Toluene</td>
<td>_</td>
<td>3 days</td>
<td>&gt;98</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>DCE</td>
<td>_</td>
<td>36</td>
<td>&gt;98</td>
</tr>
<tr>
<td>6</td>
<td>--</td>
<td>DCE</td>
<td>_</td>
<td>48</td>
<td>--</td>
</tr>
</tbody>
</table>

Reaction conditions: 1-0.2 mol\% of catalyst 16, [substrate]$_0$= 0.05M at 80 ºC, performed in air. Yield determined by $^1$H-NMR (%) analysis of the crude reaction mixture after complete consumption of substrate using 1,3,5-tri-tert-butyl benzene as internal standard.

From the data reported in the Table 4, it is possible to observe that also in this case catalyst 16 is able to perform the oxidative C-C cleavage in both toluene and DCE under aerobic conditions. The products obtained by substrate cleavage are mainly benzoic acid (up to 77\%), benzaldehyde (7\%) and benzoin methyl ether (16\%) determined via $^1$H-NMR (internal standard, 1,3,5-tri-tert-butyl benzene) (Table 4 entry 5).

Also in this case, the presence of the base inhibits the reactions (Table 4 entry 1 and 2). Reactions are faster in DCE and the complete consumption of the starting material was obtained after 36 h (1\% catalyst loading entry 5) or 48 h (0.2\% catalyst loading entry 6).

In order to determine if the oxidation occurs via oxidation to the corresponding ketone and subsequent C-C bond cleavage, as suggested in some recent work reported by Hanson et al.,\textsuperscript{24} we attempt the oxidation of (2-methoxy-2-phenylacetophenone) (Scheme 6). Even after 48 h no products originating from C-C bond cleavage could be detected (benzaldehyde or benzoic acid/ester). The reaction has been monitored via $^1$H-NMR and $^{51}$V-NMR spectroscopy and no changes on the NMR signals of the substrate/catalyst were registered.

Scheme 6. Oxidation of 2-methoxy-2-phenylacetophenone under aerobic conditions.
This result, even if very preliminary, indicate that V(V) catalyst 16 operates with a different mechanism in respect to the ones studies by Hanson et al. Further investigation on different substrates and reaction conditions will be performed in the future, in order to elucidate the reaction mechanism and apply the method to lignin itself.

3.5 Conclusions

V(V)/TPA complex 16 has been found to be a very effective catalyst for the aerobic oxidative C-C cleavage of tertiary and secondary vicinal diols. The mild reaction conditions and high yields achieved for 1,2-diols and an ethereal derivative make this catalyst not only competitive to those previously reported but also good candidate for lignin model compounds transformation.

3.6 Experimental part

General methods: All chemicals and solvents were purchased from commercial suppliers and used as supplied. Triphenolamine23 and its corresponding V(V) complex were synthetized as previously reported.22 1H-NMR spectra were recorded on Bruker Avance DRX 300 (300.13 MHz) spectrometer, using partially deuterated solvent, CHCl3 = 7.26 ppm. 51V NMR spectra have been recorded at 301 K with 10000 scans at 78.28 MHz with a broadband probe. V(V) complex 16, once prepared in Glove-Box under inert atmosphere, can be handled in open air.

UV-Vis measurements were carried out on a Shimadzu UV-1700PC spectrophotometer equipped with a photomultiplier detector, double beam optics, and D2 and W light source. All oxygen or moisture sensitive compounds have been handled under controlled atmosphere in a glove-box Mbraun MB 200MOD, equipped with a MB 150 G-I recycling system. UV-Vis spectra was recorded using a quartz cell with a 1 cm of path length, of a solution of 16 (5X10⁻⁴ M) in CH2Cl2 at 298 K.

Cyclic voltammetry experiments were performed using a BAS EC-epsilon potentiostat. A standard three-electrode electrochemical cell was used. Glassy carbon electrode from BAS and a Pt wire

were used respectively as working and auxiliary electrode. Potentials were referred to an Ag/AgCl/3 M NaCl reference electrode. The experimental data were obtained under N₂ atmosphere using V(V) complex 16 (5·10⁻⁴ M) in CH₂Cl₂ at 298 K (scan rate = 100 mV s⁻¹) and 0.1 M NBu₄PF₆ as supporting electrolyte.

**Catalytic Experiments**

In a typical experiment, the substrate (0.1 mmol of 1,2 diol or β-hydroxy compound), complex 16 (0.01 mmol) and the internal standard (0.5 mmol of 1,3,5-tri-tert-butylbenzene, dimethylsulfone or hexamethylbenzene) were dissolved in 2 mL of toluene or DCE (1,2-dichloroethane). The reactions were performed in a 5 mL glass vessel equipped with a Teflon stopcock and stirred under air. An initial ¹H-NMR spectra was recorded and afterward the vessel was closed and heated at 80°C under magnetical stirring. The reactions were monitored periodically, recording ¹H-NMR spectra by transferring an aliquot of the mixture in NMR tube after concentrating with reduced pressure. After the consumption of the starting materials, product yields were determined by integration against the internal standard.

**Compounds Determination**

Aerobic Pinacol oxidation. (Table 1 and 2) 

In a 5 mL glass vessel, the substrate 0.1 mmol and 0.01-0.002 mmol of complex 16 were dissolved in toluene under aerobic condition. To the mixture (red colour) was added 0.05 mmol of internal standard (dimethylsulfone). An initial ¹H-NMR was detected and the mixture was left stirring at 80°C. During the course of the reaction, it was possible to observe a change of colour in the solution at the end of the reaction, from deep red to slightly green and purple. After cooling and exposure of the mixture to air the reddish colour was again observed. The consumption of pinacol was revealed and quantified after recording periodically ¹H-NMR spectra.

Aerobic oxidation of 1,1-2,2–tetraphenylethandiol (Table 3, entry 1).

Same procedure followed for pinacol. In this case, to a 2 mL of toluene solution containing the substrate 0.1 mmol and the catalyst 16 1-0.2 mmol, was added 0.05 mmol of hexamethylbenzene as internal standard and the product detected was benzophenone (C₁₃H₁₀O).

¹H NMR (300 MHz, CDCl₃) δ 7.82 – 7.79 (m, 4H), 7.76-7.45 (m, 6H), 1.26 (s, 3H). MS m/z (M⁺, 182).
Aerobic oxidation of 1,2-diphenyl-1,2-ethandiol (Table 3, entry 2)
Same procedure followed for pinacol. In this case, to a 2 mL solution of toluene, containing 0.1 mmol of substrate and 1-0.2 mmol of catalyst 16, was added 0.05 mmol of 1,3,5-tri-tert-butylbenzene as internal standard and the product detected was benzaldehyde.

$^1$H NMR (300 MHz, CDCl₃) δ 10.03 (s, 1H), 7.87-7.84 (d, 2H), 7.63-7.48 (m, 3H), 1.34 (s, 9H).
MS m/z (M$^+$ H$^+$, 108)

1,2-diphenyl-2-methoxyethanol. (Table 4)
Same procedure followed for pinacol. In this case, to a 2 mL solution of DCE or toluene, containing 0.1 mmol of substrate and 1-0.2 mmol of catalyst 16, was added 0.05 mmol of 1,3,5-tri-tert-butylbenzene as internal standard and the product detected was benzaldehyde, benzoic acid and methyl benzoate. The data were compared with original spectra recorded for each sample.

Benzaldehyde: $^1$H NMR (300 MHz, CDCl₃) δ 9.97 (s, 1H), 7.87-7.84 (m, 2H), 7.63-7.48 (m, 3H), 1.34(s, 9H).

Benzoic Acid: $^1$H NMR (300 MHz, CDCl₃) δ 8.13-8.11 (d, 2H), 7.64-7.59 (t, 1H), 7.50-7.45 (t, 2H), 1.34 (s, 9H).

Methyl Benzoate: $^1$H NMR (300 MHz, CDCl₃) δ 8.04-8.01 (m, 2H), 7.54-7.52 (t, 1H), 7.50-7.4 (m, 2H), 1.34 (s, 9H).
Chapter 4

Fe(III) Amino Triphenolates as Catalysts for CO₂ Activation
Abstract
This chapter describes the synthesis and characterization of new Fe(III) amino triphenolate complexes and their use as catalysts in carbon dioxide activation, in particular the cycloaddition to epoxides and oxetanes to yield cyclic carbonates. Fe(III) amino triphenolates allows CO₂ activation under mild conditions (low temperature and CO₂ pressure) with a series of epoxides and oxetanes. Different activities have been observed depending on the substituents on the phenyl ring and the nuclearity of the complexes. The catalytic reactivity of their analogues, V(V) and Mo(VI) complexes has been also investigated.

Part of the work reported in the Chapter has been published: ¹

4.1 Introduction
In recent years, the transformation of carbon dioxide into useful chemicals has been of great interest to the scientific community because CO₂ can be considered a renewable carbon source (C₁), abundant, cheap and non-toxic.²³ Since fossil fuels (coal, oil) are limited, carbon dioxide can be considered as an alternative chemical feedstock for the production of high-value products. Despite this desire, very few industrial processes utilize carbon dioxide as sustainable carbon resource and this is mainly due to the low reactivity of CO₂. However, the annual consumption of CO₂ per year

as a synthetic building block is 110 Mtonnes.\(^2\)\(^4\) Industrial processes in which carbon dioxide is used\(^5\) include the synthesis of urea from \(\text{CO}_2\) and ammonia,\(^6\) the synthesis of salicylic acid from phenol and \(\text{CO}_2\) (the Kolbe-Schmitt reaction)\(^7\) and the synthesis of cyclic carbonates and polypropylene carbonate from \(\text{CO}_2\) and epoxides.\(^4\)\(^8\)\(^9\)

The production of urea is the largest scale chemical process currently in operation (100 Mtonnes/year).\(^10\) This is also an excellent example of the use of the waste \(\text{CO}_2\) obtained as by-product in the synthesis of hydrogen from methane.

The synthesis of salicylic acid has been already developed on an industrial scale since the 1890.\(^11\) The process used today is based on the reaction of sodium phenolate with \(\text{CO}_2\) at a pressure of 0.5 mPa at 0°C. After absorption of approximately one mole of \(\text{CO}_2\) the temperature is risen to 50°C for several hours until the reaction is completed (Scheme 1).

![Scheme 1. Industrial synthesis of salicylic acid.](image)

The transformation of carbon dioxide and epoxides/oxetanes into cyclic organic carbonates is a rather important reaction (equation 1).

\[
\text{Catalysts employed for industrial scale synthesis: KI or TBAB (tetrabutylammonium bromide)}
\]

---


These class of compounds are of interest for a wide variety of applications, including the production of aprotic polar solvents, fine chemical intermediates, starting materials for the synthesis of polymers, engineering plastics, biomedical materials and electrolytes in lithium ion batteries.\textsuperscript{12} The current production of cyclic carbonates is around 100 ktonnes/year.\textsuperscript{8} Traditionally the synthesis of these compounds was carried out using phosgene as reagent (equation 2), which is highly toxic and in addition, this methodology affords two equivalents of corrosive hydrochloric acid.

\[
\text{R} - \text{O-Cl} + \text{CO}_2 \rightarrow \text{R} - \text{O-OC-OR} + 2 \text{HCl}
\]  

The necessity to replace this conventional route with greener and safer process motivated intense research to find new effective systems for producing cyclic carbonates by using CO\textsubscript{2}.

4.1.1 Cyclic carbonate synthesis from epoxides and CO\textsubscript{2} catalyzed by metal based complex

As previously mentioned, the addition of CO\textsubscript{2} to epoxides cleanly generates cyclic carbonates,\textsuperscript{3b,7,8} which are the thermodynamically favored products or, under different reaction conditions, polycarbonates.\textsuperscript{13,14} The synthetic routes developed for the preparation of cyclic carbonates from carbon dioxide and epoxides (equation 1) are all catalytic processes. Catalysts that have been used are amines or phosphines,\textsuperscript{15} ammonium\textsuperscript{16,17} or metal halides\textsuperscript{18,19} and metal complexes. The catalysts currently


\textsuperscript{18} N. Kihara, N. Hara, T. Endo. J. Org. Chem. 193, 58, 6198.

employed for industrial production of cyclic carbonates (equation 1) are metals and ammonium halides such as KI or tetrabutylammonium bromide (TBAB).

These salts are suitable for large scale synthesis because they are stable, soluble in the reaction products (cyclic carbonate), and they do not solidify when the reaction mixture is concentrated during the purification step. In Scheme 2 a possible reaction mechanism for the synthesis of cyclic carbonates starting from epoxides and CO$_2$ catalyzed by tetrabutylammonium bromide (TBAB) is reported. This reaction proceeds through the ring opening of the epoxide by nucleophilic attack of the halide ion (Br$^-$), which leads to an oxy anion species that is transformed into the corresponding cyclic carbonate after reaction with CO$_2$.

![Scheme 2 General mechanism of cyclic carbonates synthesis catalysed by TBAB.](image)

These catalytic systems require high temperatures (100-150°C) and pressures (up to 20 bar) and the catalysts are difficult to recover and reuse. Furthermore they are active only with terminal epoxides.

Metal complexes have been found to be much more active catalysts in order to operate under milder conditions (lower temperature and CO$_2$ pressure) and with less reactive epoxides. Metal-based complexes usually are used in the presence of a co-catalyst, a quaternary ammonium halide, (tetra-butyl ammonium chloride, bromide or iodide) or phosphonium halide. Examples of co-catalysts anchored on the ligand backbone, arising a bifunctional systems, have been also reported. Generally, in the catalytic cycle, the metal complex acts as Lewis acid, activating the epoxide toward nucleophilic attack by the halide co-catalyst. Then the insertion of CO$_2$ and ring closure yields the cyclic carbonate (Scheme 3).

---

In the recent years effective catalysts for the synthesis of cyclic carbonates from epoxides have been reported. It is worth mentioning that Al, Co, Cr salen (1-3), 25 Zn(salophen) (4), 26, 27 Zn(metalloporphyrin) (5) 23 phatoxyanine (6) and Fe (7) and Al (8) amino triphenolate complexes 28 are the most successful catalysts reported in literature Figure 1.
In Table 1 are reported the results obtained using the different catalytic systems in the reaction with propylene (9) or 1-hexene oxide (10).

Table 1. Effect of different metal catalysts (1-8) on the reaction of terminal epoxides (propylene oxide (9) or 1-hexene oxide (10) with CO2.

<table>
<thead>
<tr>
<th>#</th>
<th>Sub</th>
<th>Cat (%)</th>
<th>co-cat.</th>
<th>P&lt;sub&gt;CO2&lt;/sub&gt;(bar)</th>
<th>T(°C)</th>
<th>TOF (h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>solvent</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>1 (0.125)</td>
<td>nBu&lt;sub&gt;4&lt;/sub&gt;NI</td>
<td>6</td>
<td>35</td>
<td>63.0</td>
<td>neat</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>2 (0.1)</td>
<td>nBu&lt;sub&gt;4&lt;/sub&gt;NBr</td>
<td>35</td>
<td>45</td>
<td>316</td>
<td>neat</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>3 (0.075)</td>
<td>DMAP</td>
<td>7</td>
<td>100</td>
<td>916</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>4 (0.5)</td>
<td>nBu&lt;sub&gt;4&lt;/sub&gt;NI</td>
<td>10</td>
<td>85</td>
<td>n.d.</td>
<td>MEK</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>5 (0.03)</td>
<td>nBu&lt;sub&gt;4&lt;/sub&gt;NBr</td>
<td>17</td>
<td>120</td>
<td>12.000</td>
<td>neat</td>
<td>10</td>
</tr>
</tbody>
</table>
In most of the cases the reactions can be carried out at relatively low CO₂ pressures (6-10 bar) and catalyst loadings. In the case of the reaction with porphyrine 5 as catalyst the presence of the cocatalyst in the ligand allowed to very high reactivity (TOF’s up to 12,000 h⁻¹).

More recently, effective catalytic systems based on Fe(III) and Al(III) amino triphenolate complexes have been reported.²⁶ ²⁷ Either the dinuclear Fe(III) and Al(III) amino triphenolate complexes 7 and 8 have shown excellent reactivity with a broad substrate scope and low catalyst loadings.

In the present work the reactivity of amino triphenolate complexes as catalysts for cyclic carbonate formation has been explored more in detail. In particular the effect of the nature of the ligand on the reactivity of Fe(III) amino triphenolate complexes, and the resulting nuclearity, has been investigated together with the performance of the corresponding analogous V(V) and Mo(VI) complexes.

### 4.2 Synthesis and Characterization of Iron(III) ortho-substituted Amino Triphenolate Complexes

#### 4.2.1 Synthesis

All the ligands used in this study have been synthesized by a three-fold reductive amination.³⁰ Fe(III) complexes were obtained by the reaction of the triphenolamines L₁₄H₃, ¹¹, where R = H, methyl, tert-butyl, or phenyl with 3 equiv. of sodium hydride in tetrahydrofuran and subsequent addition of 1 equiv. of FeCl₃, after filtration to remove the sodium salt, analytically pure mono- or di-iron(III) complexes were obtained. Scheme 4.

Scheme 4. Synthesis of Fe(III) complexes 12a-d

All complexes 12a-d have been characterized by Maldi-TOF-MS and elemental analysis. Crystals suitable for X-ray analysis have been obtained for all the compounds, confirming the mono and dinuclear nature of the complexes.

4.2.2 X-Ray Diffractometric Studies

Crystals for X-ray diffractometric studies were obtained by slow evaporation of tetrahydrofuran solutions of the complexes, except for 12a where crystals were grown from a concentrated toluene solution. The solid state structures of iron(III) amino triphenolate complexes are shown in Figure 2, with selected bond lengths and angles reported in Tables 2 and 3.
The molecular structure of the complex 12a consists of two iron(III) amino triphenolate complexes forming a dinuclear assembly, with one phenoxide O-atom from each individual complex acting as a bridging ligand, resulting in the formation of a central Fe₂O₂ motif. The solid state structures of the complexes 12b, 12c and 12d are mononuclear containing an apical ligand originating from the solvent media. The molecular structure 12c contains a water ligand in place of the expected tetrahydrofuran ligand, which is likely to be a consequence of ligand exchange with the water present in the solvent used during crystallization. The molecular structure of complex 12b, as has been mentioned, shows the mononuclear form of the complex, but further investigations (vide infra) indicate that a dinuclear structure may be easily formed as in the case of complex 12a. No evidence of dinuclear complexes in the cases of 12c or 12d have been found. The solid state structure of 12b displays idealized C₃ symmetry, with the corresponding angle between the amine and the oxygen atom of the tetrahydrofuran ligand (178.24(4)°) close to the ideal value of 180° expected in a perfectly C₃ symmetrical molecule. The structure also displays similar bond length values for all the Fe–O bonds with the ligand and an elongated Fe–O bond length for the bond between the tetrahydrofuran and metal. The addition of tert-butyl groups, impacts severely on the C₃ symmetry of the complex in 12c compared with 12b. It appears that the tert-butyl groups have a significant steric effect on the structure. The angles between of O(1)–Fe(1)–O(2), O(1)–Fe(1)–O(3), and O(1)–Fe(1)– O(3) are significantly different from those expected in a perfect C₃ symmetrical molecule and have values of 113.79(17)°, 115.77(17)°, and 130.41(17)°, respectively. These distortions are similar in value to those observed by Safaei and co-workers for a similar complex containing a methanol ligand in the apical position. 31 A further difference in this molecule compared to 12b is that not all the Fe–O bond lengths between the metal and the ligand have the same length, with one of them being clearly elongated. The observation of these differences in structure adds weight to the proposal that the original tetrahydrofuran ligand has exchanged with the water ligand during crystallization to form a more stable complex. Similar but less significant distortions from perfect C₃ symmetry are also observed in the case of 12d compared with 12c indicating that the phenyl groups contribute less to the steric constraints immediately around the Fe(III) center.

Table 2. Selected bond lengths (Å) of iron (III) complexes.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>12a</th>
<th>12b</th>
<th>12c</th>
<th>12d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)-O(1)</td>
<td>1.9713(18)</td>
<td>1.8643(12)</td>
<td>1.885(4)</td>
<td>1.856(3)</td>
</tr>
<tr>
<td>Fe(1)-O(2)</td>
<td>1.8611(18)</td>
<td>1.8555(12)</td>
<td>1.853(4)</td>
<td>1.859(3)</td>
</tr>
<tr>
<td>Fe(1)-O(3)</td>
<td>1.8519(19)</td>
<td>1.8685(11)</td>
<td>1.861(4)</td>
<td>1.878(3)</td>
</tr>
<tr>
<td>Fe(1)-O(4)</td>
<td>2.0642(17)</td>
<td>2.1063(11)</td>
<td>2.097(4)</td>
<td>2.055(5)</td>
</tr>
<tr>
<td>Fe(1)-N(1)</td>
<td>2.1440(20)</td>
<td>2.1795(13)</td>
<td>2.178(4)</td>
<td>2.163(4)</td>
</tr>
</tbody>
</table>

The resulting angles being 116.22(14)°, 121.82(14)°, and 121.94(14)° for O(1)−Fe(1)−O(2), O(1)−Fe(1)−O(3), and O(1)−Fe(1)−O(3), respectively. The dinuclear complex 12a displays two Fe−O bonds with lengths of 1.8611(18) Å and 1.8519(19) Å corresponding to the non-bridging phenoxide moieties and two longer Fe−O bonds with lengths of 1.9713(18) Å and 2.0642(17) Å for the bonds involving the bridging phenoxide moieties. These bond lengths are similar to those previously reported for a similar dinuclear structure. 32

Table 3. Selected angles (deg) of iron (III) complexes

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th>12a</th>
<th>12b</th>
<th>12c</th>
<th>12d</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Fe(1)-O(2)</td>
<td>120.76(8)</td>
<td>121.15(5)</td>
<td>113.79(17)</td>
<td>116.22(14)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-O(3)</td>
<td>116.00(8)</td>
<td>119.08(6)</td>
<td>130.41(17)</td>
<td>121.94(14)</td>
</tr>
<tr>
<td>O(2)-Fe(1)-O(3)</td>
<td>123.14(9)</td>
<td>119.58(5)</td>
<td>115.77(17)</td>
<td>121.82(14)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-O(4)</td>
<td>77.44(7)</td>
<td>89.28(5)</td>
<td>92.16(16)</td>
<td>93.41(18)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-N(1)</td>
<td>91.15(8)</td>
<td>91.71(5)</td>
<td>89.75(16)</td>
<td>90.11(13)</td>
</tr>
<tr>
<td>N(1)-Fe(1)-O(4)</td>
<td>168.33(8)</td>
<td>178.24(4)</td>
<td>172.98(17)</td>
<td>173.95(19)</td>
</tr>
</tbody>
</table>

4.2.3 UV−VIS Studies.

The electronic spectra of all complexes 12a-d are very similar to one another. A metal-to-ligand charge transfer band (MLCT) is observed in all the complexes around 400−450 nm. A second MLCT band is detected for all complexes around 310−360 nm and in addition, 12a displays a third MLCT band in this region as a shoulder at 358 nm which is most likely as a result of the bridging phenoxide moieties.

In order to investigate the behaviour of the Fe(III) complexes in solution, titration studies were performed. In this regard, it has been reported that complex 7, similar to 12b, can be disrupted by titration with propylene oxide. From the UV-Vis spectra of 12b a slight change in the absorption curve was observed after addition of the titrant (Figure 3, bottom), whereas titration of the remaining complexes (12a, 12c and 12d) with propylene oxide did not give rise to any significant changes in the spectra. These data suggested that the complex 12a due to its strong tendency to form dinuclear species did not show any changes in the UV-Vis spectra. On the contrary, 12c and 12d complexes because of their mononuclear nature, did not give any change upon addition of propylene oxide (Figure 4 top and bottom).

Figure 3. UV-Vis spectra of 12a (top) and 12b (bottom) (1.0 x10^-4M) titrated with propylene oxide (0 to 1000 equiv.) in toluene.
However, when the dinuclear complex 12a is titrated with pyridine (a much more basic ligand), a significant change in spectra is observed (Figure 5). For comparison the same experiment performed with the mononuclear complex 12d is reported, where the addition of an excess of pyridine causes only minor modification of the UV-Vis spectrum (Figure 5 right). These results suggest that 12a is a stable dinuclear complex also in solution and only in the presence of highly basic ligands it can form the corresponding mononuclear species.

4.2.4 1H NMR Characterization.

Paramagnetic complexes generally exhibit broad resonances with large chemical shifts. The 1H NMR spectra of all the complexes were recorded in CDCl₃ at 298 K and are shown in Figure 6, with the region between 15 and −5 ppm omitted for clarity (this region principally displays resonances for the protio-impurities of the deuterated solvents, a broad resonance for the alkyl protons of the ligand and in the case of 12c, a broad resonance for the protons of the tert-butyl
Additionally, the $^1$H NMR spectra of all complexes were obtained in a CDCl$_3$:d$_5$-Pyridine (90:10 v/v) mixture to allow for comparison with the species obtained in the solution magnetic susceptibility measurements. The paramagnetically shifted resonances have been assigned tentatively, as efforts to acquire 2D NMR spectra were unsuccessful.

In the $^1$H NMR spectra of both 12a and 12b, there are no observable strongly shifted resonances to indicate the presence of a paramagnetic species. Most likely, in the case of 12a, as a result of strong antiferromagnetic coupling between the two iron(III) centers, very broad signals were observed. Upon addition of pyridine to both of these complexes it is possible to observe the appearance of new resonances in the 90 to $-80$ ppm range, indicating the formation of paramagnetic species. In the case of 12a/pyridine, we propose that the observed resonances, shown in Figure 6, are those of the aromatic protons of the ligand.

Three of the aromatic protons appear as a pair of resonances ($H_a' = H_a''$, $H_b' = H_b''$, and $H_c' = H_c''$), with the resonance corresponding to the remaining ortho-proton of the aromatic moiety being likely present in the 0–12 ppm range. We propose that a pair of resonances is observed for each proton because of the possibility of either one or two pyridine ligands coordinating to the iron(III) center, and this is further confirmed by the presence of only a single set of resonances when the experiment is run in neat $d_5$-pyridine. In the case of a single coordinated pyridine, the complex would display trigonal bipyramidal geometry, whereas upon coordination of a second pyridine ligand the complex becomes octahedral in geometry, resulting in different
orbital overlap and therefore displaying slightly different chemical shifts. The proposed ability of 12a to bind two external ligands and form an octahedral complex is a result of lower steric constraints imposed by this ligand compared with the other ligand structures and this complex would also be similar in structure to the first iron(III) amino triphenolate complex reported by Koch and co-workers, 12a (dipyridine), containing two pyridine molecules as apical ligand Scheme 5.  

![Scheme 5. Schematic Representation of the Proposed Reaction of Pyridine with 12a](image)

In the case of 12b, the steric constraints imparted by the methyl groups of the ligand prevent the coordination of a second pyridine ligand, and hence only a single set of resonances (Ha, Hb, and Hc) are observed for each proton. The protons from the methyl group of 12b are observed as the second resonance (CH3) at around 60 ppm. Both the spectra of 12c and 12d display the paramagnetically shifted resonances for the aromatic protons (Ha, Hb, and Hc) in the absence of pyridine, further adding to the evidence that these two complexes exist in their mononuclear form. Upon addition of pyridine to 12c there is no change in the spectrum, as the pyridine is only substituting the tetrahydrofuran ligand to yield 12c (Py) in situ.

The same behaviour is not true for 12d as after addition of pyridine the resonances which we propose are assigned to the protons of the ortho-phenyl group disappear (Hd, He, and Hf). The X-ray structure of 12d (Py) has been resolved and indicates that pyridine can coordinate and act as a ligand though resulting in a reduced rotational freedom of the Ph groups of the triphenolamine ligand Figure 7 and Table 4.

4.2.5 Electrochemical Studies

Cyclic voltammetry experiments have been performed in dichloromethane for all the complexes Figure 8. The complexes 12c and 12d exhibit respectively quasi-reversible waves at -0.825 and -1.008 V. Complexes 12a and 12b have a more complex electrochemical behavior. In the case of the dinuclear species 12a, a single quasi reversible wave at -0.288 V was obtained. This value is remarkably lower than for the mononuclear species, most likely because there is an easier reduction of the metal center due to the delocalized electron density between the two iron centers. The data observed and the cyclic voltamograms are reported in Table 5 and Figure 8.

Table 4. Selected bond lengths (Å) and angles (deg) in 12d (Py).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)-O(1)</td>
<td>1.856(3)</td>
</tr>
<tr>
<td>Fe(1)-O(2)</td>
<td>1.870(3)</td>
</tr>
<tr>
<td>Fe(1)-O(3)</td>
<td>1.860(3)</td>
</tr>
<tr>
<td>Fe(1)-N(1)</td>
<td>2.182(4)</td>
</tr>
<tr>
<td>Fe(1)-N(2)</td>
<td>2.135(4)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-O(2)</td>
<td>123.40(14)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-O(3)</td>
<td>117.45(13)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-N(1)</td>
<td>88.43(13)</td>
</tr>
<tr>
<td>O(1)-Fe(1)-N(2)</td>
<td>89.76(13)</td>
</tr>
<tr>
<td>N(1)-Fe(1)-N(2)</td>
<td>177.99(13)</td>
</tr>
</tbody>
</table>
Figure 8. Cyclic voltammograms at 298 K in CH$_2$Cl$_2$ (scan rate = 100 mV s$^{-1}$) using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte at a glassy carbon working electrode, platinum wire auxiliary electrode, and Ag-AgCl (sat. NaCl) reference electrode of 12a, 12b, 12c, and 12d.

Table 5. Electrochemical data for 12a, 12b, 12c and 12d. $^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$[Complex]</th>
<th>$E_{1/2}(1)$</th>
<th>$E_{1/2}(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>-0.288</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12b</td>
<td>-1.013</td>
<td>-0.930$^b$</td>
<td>-</td>
</tr>
<tr>
<td>12c</td>
<td>-1.008</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12d</td>
<td>-0.825</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ In CH$_2$Cl$_2$ at 298 K (scan rate = 100 mV s$^{-1}$) using 0.1 M NBu$_4$PF$_6$ as supporting electrolyte at a glassy carbon working electrode, platinum wire auxiliary electrode and Ag-AgCl (sat. NaCl) reference electrode. $^b$ Potential for irreversible reduction.
4.3 Iron (III) complexes: Catalytic activity

The reactivity of complexes 12a-d has been explored in the cycloaddition of CO$_2$ to epoxides. As mentioned before, recently the dinuclear iron (III) amino triphenolate complex 7 was found to be an excellent catalyst for the conversion of CO$_2$ and epoxides into cyclic carbonates using an alkylammonium bromide or iodide as co-catalyst. In order to investigate the reactivity of the new complexes and compare their performance, experiments were carried out by using similar reaction conditions previously applied to 7.

The results obtained from the cycloaddition of carbon dioxide (CO$_2$) to propylene oxide are reported in Table 6.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent</th>
<th>7</th>
<th>12a</th>
<th>12b</th>
<th>12c</th>
<th>12d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DCM</td>
<td>n.d.</td>
<td>16</td>
<td>13</td>
<td>82</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>MEK</td>
<td>65</td>
<td>56</td>
<td>72</td>
<td>85</td>
<td>88</td>
</tr>
</tbody>
</table>

Table 6. Yields (%) of cyclic carbonate from propylene oxide obtained using Fe(III) complexes 7 and 12a-d as catalysts and TBAB as co-catalyst.

$^a$Yields (%) calculated via $^1$H NMR with mesitylene as internal standard. Conditions: 2.0 mmol epoxide, 0.01 mmol 12a or 7, 0.02 mmol 12b-d, 0.1 mmol $n$Bu$_4$NBr, 2.0 mmol mesitylene, 5mL of solvent, 1.0 Mpa CO$_2$, (0.2 MPa in the reaction catalysed by 7), 25°C, 18h. MEK = methylethylketone, DCM= dichloromethane.

The reactions were performed in a 25 mL autoclave, charged with methylethyl ketone (MEK) and dichloromethane (DCM) solutions containing the catalyst and co-catalyst, substrate and mesitylene as internal standard. From the data reported in Table 6 it is evident that the mononuclear catalysts 12b-d afford better results than the dinuclear ones. Catalytic performances are better when the reactions are carried out using a coordinating solvent such as MEK. This is particularly true in the case of catalyst 12b (13 vs 72% yields) probably due to the preferential mononuclear nature of the catalyst under these reaction conditions.

In order to investigate the scope of the reaction, the catalytic systems were tested with a series of different substrates, including the less reactive oxetanes Table 7.

Table 7. Cycloaddition of CO$_2$ to differently epoxides and oxetanes using catalysts 12a-d.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>12a (%)$^a$</th>
<th>12b (%)$^a$</th>
<th>12c (%)$^a$</th>
<th>12d (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Oepoxide" /> <img src="image2" alt="Oester" /></td>
<td>12</td>
<td>10</td>
<td>90</td>
<td>67</td>
</tr>
</tbody>
</table>
With styrene oxide (entry 1) the mononuclear complexes are more effective catalysts, especially 12c. With trans-2,3-epoxy butane (entry 2) all catalysts were found to convert stereospecifically the internal epoxide into the corresponding trans cyclic carbonate in very good reactivity and selectivity.

Cyclohexene oxide (entry 3), a very interesting substrate for the production of polycarbonates, afforded the bicyclic carbonate in yields up to 75%.

The reaction with oxetanes, which are particularly challenging substrates due to their low reactivity \(^{34,35}\) were quite successful. In particular with a simple oxetane (entry 4) a six-membered cyclic carbonate was obtained with yields up to 94% (with catalyst 12b). Some reactivity could be also observed with the 3,3-dimethyl oxetane (up to 10%).

Very interestingly, in the case of 12c it was possible to obtain the solid state structure of the complex whereby the tetrahydrofuran ligand is replaced by a trans-2,3-epoxybutane ligand Figure 9, indicating that the substrate is indeed able to bind to the iron(III) center. Thus, it seems that the catalytic activity of these complexes is controlled by their tendency to form dimeric structures, the solvent medium, the reaction temperature and the steric impediment upon coordination of the substrate to the Fe(III) center. In Table 8 are reported selected angles and bonds


Figure 9. X-ray Crystal Structure of 12d (trans-2,3-epoxybutane). H-atoms, co-crystallized solvent molecules and the disorder in the position of the epoxide ligand and the Ph groups of the ligand L₄ are omitted for clarity. Only a partial numbering scheme is provided.

Table 8. Selected Bond Lengths (Å) and Angles (deg) in 12d (trans-2,3-epoxybutane).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)-O(1) 1.860(2)</td>
<td>O(1)-Fe(1)-O(2) 116.23(10)</td>
</tr>
<tr>
<td>Fe(1)-O(2) 1.860(2)</td>
<td>O(1)-Fe(1)-O(3) 119.79(10)</td>
</tr>
<tr>
<td>Fe(1)-O(3) 1.880(2)</td>
<td>O(1)-Fe(1)-N(1) 90.66(9)</td>
</tr>
<tr>
<td>Fe(1)-O(4) 2.145(10)</td>
<td>O(1)-Fe(1)-O(4) 119.79(10)</td>
</tr>
<tr>
<td>Fe(1)-N(2) 2.174(2)</td>
<td>O(4)-Fe(1)-N(1) 171.10(30)</td>
</tr>
</tbody>
</table>

4.4 V(V) and Mo(VI) Amino Triphenolate Complexes as catalysts for CO₂ fixation.

4.4.1 Mo(VI) Amino Triphenolate: Catalytic Activity

The reactivity of other amino triphenolate complexes, in particular Mo(VI)/TPA 13 and V(V)/TPA 14, was also investigated.
Beside the finding of new catalysts active in the CO₂ cycloaddition to epoxides, the possibility that complexes such as 13 act as catalysts in the CO₂ addition to epoxides could allow the direct synthesis of cyclic carbonates from olefins via a two consecutive steps: epoxidation and subsequent CO₂ cycloaddition (Scheme 6). Mo(VI) complex 13, in fact, is an active catalyst for the activation of tert-butylhydroperoxide in the epoxidation of olefins.³⁶ (Scheme 6).

Mo(VI) complex 13 has been tested as a catalyst in the CO₂ cycloaddition with a series of terminal and internal epoxides. The experiments were performed under the best conditions obtained for the Fe(III)/TPA catalysts. The reactions were carried out under neat conditions (for liquid epoxides) or using a minimal amount of MEK (for the solid ones). With terminal aliphatic epoxides TBAI was used as co-catalyst while with more hindered substrates (styrene and trans-2,3-epoxybutane) TBAB was employed.²⁶ The results obtained are reported in Table 9.

Table 9. CO₂ cycloadditions with different epoxides in the presence of Mo(VI) 13 as catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>13 (mol%)</th>
<th>Co-catalyst (mol%)</th>
<th>T (°C)</th>
<th>Yield ¹H-NMR (%)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Substrate</th>
<th>Catalyst%</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.5 TBAI (2.5)</td>
<td>45</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1.0 TBAI (2.5)</td>
<td>45</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1.0 --</td>
<td>45</td>
<td>n.r.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>1.0 --</td>
<td>85</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1.0 --</td>
<td>100</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>-- TBAI (2.5)</td>
<td>45</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.0 TBAB (2.5)</td>
<td>45</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.0 TBAB (2.5)</td>
<td>45</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>1.0 TBAB (2.5)</td>
<td>45</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>-- TBAB (2.5)</td>
<td>45</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>1.0 TBAB (2.5)</td>
<td>85</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>-- TBAB (2.5)</td>
<td>85</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Conditions: substrates (1.0 g), catalyst= (0.5 mol%), (1 mol%), TBAB = tert-butyrammonium bromide, TBAI = tert-butyrammonium iodide, 45-85°C, 10 bar initial CO2 pressure in a 30 mL autoclave. * Yields determined by 1H-NMR from the crude reaction mixture.

The results obtained show that Mo(VI) complex 13 is a less effective catalyst than the corresponding Fe(III) and Al(III) complexes. However, in the case of 1,2-epoxyhexane, a terminal epoxide and using TBAI as co-catalyst, reasonably high conversions were obtained (77% yield). This result is quite promising for the future design of a two-step procedure (epoxidation/CO2 cycloaddition) on terminal olefins.

### 4.4.2 V(V) Amino Triphenolate: Catalytic Activity

The reactivity of the V(V) complex 14 has also been investigated. V(V) salophen complexes have been reported to be able to catalyze carbon dioxide addition to epoxides, although the catalytically active species in the process are indeed in-situ formed polyoxometalate species.37 Initially, reactions were performed with 1,2-epoxyhexane and styrene oxide in order to compare these results with the ones obtained with Mo(VI) 13. (Table 10). In this case much better results have been obtained, with yields up to 99%, even upon decreasing the catalyst/co-catalyst loading. In order to investigate the scope of the catalytic system, a variety of differently substituted epoxides were tested. In all cases substrates were transformed into the corresponding carbonates in excellent yields using catalyst loadings as low as 0.5 mol % and TBAI/TBAB as co-catalysts (1.25 mol %) at 45°C under neat conditions.

---

Table 10: CO₂ cycloaddition with a series of terminal epoxides with V(V)/TPA 14 as catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>14 (%)</th>
<th>Co-catalyst (%)</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Conversion ¹H-NMR (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-Bu</td>
<td>1.0</td>
<td>TBAI (2.5)</td>
<td>-</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>n-Bu</td>
<td>0.5</td>
<td>TBAI (1.25)</td>
<td>-</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>1.0</td>
<td>TBAB (2.5)</td>
<td>MEK</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>0.5</td>
<td>TBAB (1.25)</td>
<td>MEK</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>CH₂Cl</td>
<td>0.5</td>
<td>TBAI (1.25)</td>
<td>-</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td>CH₃OH</td>
<td>0.5</td>
<td>TBAI (1.25)</td>
<td>-</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>CH₂OMe</td>
<td>0.5</td>
<td>TBAI (1.25)</td>
<td>-</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8</td>
<td>CH₂OEt</td>
<td>0.5</td>
<td>TBAI (1.25)</td>
<td>-</td>
<td>-</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Conditions: substrates (1.0 g), catalyst= (0.5 mol %), (1 mol%), TBAB= tert-butyrammonium bromide, TBAI= tert-butyrammonium iodide, 45-85°C, 10 bar initial CO₂ pressure in a 30 mL autoclave. <sup>a</sup> Conversion determined by ¹H- NMR from the crude reaction mixture.

The catalytic performance of catalyst 14 has also been tested with internal epoxides, in particular trans-butene and trans-β-methyl styrene oxide. Due to the decreased reactivity reactions were carried out at 85°C with a CO₂ pressure of 10 bar. The results obtained are reported in Table 11.

Table 11: CO₂ cycloadditions to trans-butene and trans-β-methyl styrene oxide catalyzed by V(V)/TPA.

<table>
<thead>
<tr>
<th>R</th>
<th>14 (%)</th>
<th>TBAB (%)</th>
<th>Conversions ¹H-NMR (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yields, %&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>0.5</td>
<td>1.25</td>
<td>98</td>
<td>60</td>
</tr>
<tr>
<td>Ph</td>
<td>0.5</td>
<td>5.0</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>Ph</td>
<td>--</td>
<td>5.0</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

67
<table>
<thead>
<tr>
<th></th>
<th>Me 0.5</th>
<th>1.25</th>
<th>79</th>
<th>79</th>
</tr>
</thead>
</table>

*Conditions:* substrates (1.0 g), catalyst= (0.5 mol %), TBAB= tert-butyl ammonium bromide, 85°C, 10 bar initial CO₂ pressure in a 30 mL autoclave. *Conversions and yields determined by ¹H-NMR from the crude reaction mixture.

Also in this case the catalyst was found to be quite reactive with both substrates. In particular with β-methylstyrene oxide (Table 11, entry 1-2) high conversions and yields were obtained using 0.5 mol% of catalyst and 5 mol% of the co-catalyst. In the presence of less amounts of co-catalyst (Table 11, entry 1) some decomposition of the reagent/product was observed, while the absence of catalyst gave poor conversions and chemical yields (15%, Table 11, entry 3).

However, the results obtained with both Mo(VI) an V(V) amino triphenolate complexes are very promising in order to further investigate the possibility to form cyclic carbonates from olefins in a one-pot synthesis.

### 4.5. Conclusions

In summary, four new Fe(III) amino triphenolate complexes have been synthesized and fully characterized. These complexes have been found to be dinuclear (in the case of 12a) or mononuclear (in the case of 12b, 12c, 12d). The potential to form a dinuclear structure is dependent upon the substituent in the ortho-position of the phenolate moiety. Catalytic testing of the complexes for the cycloaddition of carbon dioxide to oxiranes has shown that the mononuclear form of these iron complexes is significantly more active than the dinuclear species. It has also been shown that by changing the reaction conditions (higher temperatures, using a solvent with coordinating potential and better CO₂-dissolution potential) the dinuclear structure can be disrupted and a more active form of the complex can be obtained. Future prospects include the implementation of these iron complexes in other types of catalytic processes.

Also Mo(VI)/TPA 13 and V(V)/TPA 14 have been found to be active catalysts in the same reaction. In particular the vanadium catalyst 14 was found to be active with terminal and internal epoxides, affording the corresponding cyclic carbonates in high yield under mild reaction conditions.
Chapter 4

4.6 Experimental Part

General Remarks
All manipulations of moisture and/or air sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques. Conventional nitrogen atmosphere glove boxes were used for the preparation of analytical and spectroscopic samples as well as for the weighing and storage of air sensitive compounds. The ligands were prepared by a known literature procedure. All Fe(III) amino triphenolate complexes once prepared, were no longer considered as air/moisture sensitive and were stored on the bench. Tetrahydrofuran and other dry solvents used during the synthesis of the complexes were dried using a Solvent Purification System (SPS), and all other solvent were reagent grade and used without any further purification. All other reagent or starting material and carbon dioxide gas phase (purchased from PRAXAIR) were used as received without any purification.

The NMR spectra have been recorded on Bruker AV 400 (\(^1\text{H}: 300.13\) MHz; \(^{13}\text{C}: 75.5\) MHz) spectrometer. Chemical shift (\(\delta\)) have been reported in parts per million (ppm) relative to the residual undeuterated solvent as an internal reference (CDCl\(_3\): 7.26 ppm for \(^1\text{H}\) NMR and 77.0 ppm for \(^{13}\text{C}\) NMR; CD\(_3\)OD: 4.84 ppm for \(^1\text{H}\) NMR and 49.05 ppm for \(^{13}\text{C}\) NMR). The following abbreviations have been used to describe the multiplicities of the NMR signals: s (singlet), d (doublet), t (triplet), dd (double doublet), dt (double triplet), br (broad) and m (multiplet). The \(^{13}\text{C}\) NMR spectra were all proton decoupled.

X-Ray Crystallography
The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions immersed in perfluoropoly ether as protecting oil for manipulation. Data collection measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4 K CCD area detector, an FR591rotating anode with MoK\(\alpha\) radiation, Montel mirrors, and a Kryoflex low temperature device (\(T = -173\) °C). Full-sphere data collection was used with \(\omega\) and \(\phi\) scans. Programs used: data collection Apex2V2011.3 (Bruker-Nonius 2008), data reduction Saint+ Version 7.60 A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008). For structure solution SHELXTLVersion 6.10 (Sheldrick, 2000)36 was used (Table 12). Structure refinement: SHELXTL-97-UNIX version.

Table 12: X-ray structure data collection and refinement parameters for all reported structures 12a, 12b, 12c and 12d.
<table>
<thead>
<tr>
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<th>12a</th>
<th>12b</th>
<th>12c</th>
<th>12d</th>
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<td>C₃₃H₄₆FeNO₅</td>
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<td>100(2)</td>
<td>100(2)</td>
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<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
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<td><strong>a (Å)</strong></td>
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<td><strong>b (Å)</strong></td>
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<td>10.9051(6)</td>
<td>10.9015(11)</td>
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<td><strong>c (Å)</strong></td>
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<td>11.2722(6)</td>
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<td><strong>µ (mm⁻¹)</strong></td>
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<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
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<td>5817/ 4/ 382</td>
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<td>1.041</td>
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<td>R¹ = 0.0359, wR² = 0.0944</td>
<td>R¹ = 0.0833, wR² = 0.2054</td>
<td>R¹ = 0.0979, wR² = 0.2416</td>
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<tr>
<td><strong>R indices (all data)</strong></td>
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<td>R¹ = 0.0402, wR² = 0.0970</td>
<td>R¹ = 0.1002, wR² = 0.2144</td>
<td>R¹ = 0.1453, wR² = 0.2524</td>
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<td><strong>Largest diff. peak and hole (e.Å⁻³)</strong></td>
<td>0.833 and -0.889</td>
<td>0.822 and -0.257</td>
<td>1.267 and -0.671</td>
<td>1.161 and -1.170</td>
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</table>

Table 12 X-ray structure data collection and refinement parameters for all reported structures

---

### 12d (Py) | 12d (trans-2,3-epoxybutane)

<table>
<thead>
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<th>12d (Py)</th>
<th>12d (trans-2,3-epoxybutane)</th>
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<tr>
<td><strong>Formula</strong></td>
<td>C₄₅H₃₄FeNO₄</td>
<td>C₄₃H₃₄FeNO₄</td>
</tr>
<tr>
<td><strong>Fₚ (g·mol⁻¹)</strong></td>
<td>695.59</td>
<td>688.59</td>
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<tr>
<td><strong>T (K)</strong></td>
<td>100(2)</td>
<td>100(2)</td>
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<tr>
<td><strong>λ (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<tr>
<td><strong>Space group</strong></td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
</tr>
</tbody>
</table>
Cyclic Voltammetry

Cyclic voltammetric measurements were carried out with a Princeton Applied Research PARSTAT 2273 electrochemical analyzer. A three electrode assembly, comprising a glassy carbon working electrode, a platinum wire auxiliary electrode, and Ag/AgCl (sat. NaCl) reference electrode was used. The experimental data were obtained under an argon atmosphere in dichloromethane solvent using NBu₄PF₆ as supporting electrolyte.

FT-IR measurements were carried out on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm⁻¹.

UV-vis measurements were carried out on a Shimadzu UV-1800 spectrophotometer.

UV-Vis Titration Procedure with propylene oxide: A 1.0x10⁻⁴M toluene solutions of 12a, 12b, 12c and 12d were prepared and the UV-Vis spectrum recorded using a quartz cell with a 1 cm path length. An 0.40 M solution of propylene oxide containing the Fe complex (at 1.0x10⁻⁴M) was prepared and added in 50 mL aliquots to 2.0 mL of the solution of the Fe complex, with spectra being recorded after each addition.
UV-Vis Titration Procedure with pyridine. A 1.0 x10^{-4}M toluene solutions of 12a and 12d were prepared and the UV-Vis spectrum recorded using a quartz cell with a 1 cm path length. An 0.40 M solution of pyridine containing the Fe complex (12a or 12d) (at 1.0 x10^{-4}M) was prepared and added in 50 mL aliquots to 2.0 mL of the solution of the Fe complex, with spectra being recorded after each addition.

**Synthesis Fe(III) amino triphenolate complexes 12a-d.**

General synthetic procedure for all complexes 12a-d is the following. To a suspension of sodium hydride (75.2 mg, 3.13 mmol) in tetrahydrofuran (10 mL) was slowly added a solution of 11a (350 mg, 1.04 mmol) in tetrahydrofuran (10 mL). The mixture was stirred for 18 h and after this time it was added to a solution of anhydrous iron(III) chloride (167.7 mg, 1.04 mmol) in tetrahydrofuran (10 mL). The mixture was stirred for a further 4 h and then filtered through a path of Celite, followed by removal of the solvent to yield a brown residue, which was subsequently dissolved in dichloromethane, filtered and the solvent then removed to yield a brown powder.

12a Yield: 397 mg (88%). Anal. Calcd for C_{42}H_{36}Fe_{2}N_{2}O_{6}: C, 64.97; H, 4.67; N, 3.61. Found: C, 64.92; H, 4.61; N, 3.38. MALDI (+)−MS (pyrene): for C_{21}H_{18}FeNO_{3} m/z = 388 [M]^+ (calcd. 388), for 777 C_{42}H_{36}Fe_{2}N_{2}O_{6} [2M+H]^+ (calcd 777). UV−vis (CH_{2}Cl_{2}, 0.1 mM, 25 °C, ε = L·mol^{-1}·cm^{-1}): 314 nm (ε = 7970), 358 nm (ε = 5290, sh), 430 nm (ε = 3510). Magnetic moment (298 K) μ_{eff} = 4.14 μB.

12b This compound was prepared in an analogous manner to that described above for 12a. Yield: 231 mg (89%). Anal. Calcd for C_{24}H_{24}FeNO_{3}: C, 66.99; H, 5.62; N, 3.26. Found: C, 67.21; H, 5.82; N, 3.02. MALDI I(+)−MS (pyrene): m/z = 430 [M]^+ (calcd. 430). UV−vis (CH_{2}Cl_{2}, 0.1 mM, 25 °C, ε = L·mol^{-1}·cm^{-1}): 329 (ε = 4065), 416 (ε = 3625). Magnetic moment (298 K) μ_{eff} = 6.74 μB.

12c (THF) This compound was prepared in an analogous manner to that described above for 12a Yield: 408 mg (90%). Anal. Calcd for C_{37}H_{50}FeNO_{4}: C, 70.69; H, 8.02; N, 2.23. Found: C, 70.60; H, 8.34; N, 2.12. MALDI(+)−MS (dithranol): m/z = 557 [M+H−THF]^+ (calcd. 557).UV−vis (CH_{2}Cl_{2}, 0.2 mM, 25 °C, ε = L·mol−1·cm−1): 329 nm (ε = 3570), 410 nm (ε = 3135). Magnetic moment (298 K) μ_{eff} = 5.49 μB.
12d (THF) This compound was prepared in an analogous manner to that described above for 12a
Yield: 266 mg (61%). Anal. Calcd for C_{43}H_{38}FeNO_{4}: C, 75.00; H, 5.56; N, 2.03. Found: C, 74.75;
H, 5.80; N, 2.12. MALDI (+)–MS (pyrene): m/z = 616 [M–THF]+ (calcd. 616). UV–vis (CH_{2}Cl_{2},
0.2 mM, 25 °C, ε = L·mol\(^{-1}\) cm\(^{-1}\)): 357 nm (ε = 5460), 426 nm (ε = 5045). Magnetic moment (298
K) μ\(_{\text{eff}}\) = 5.53 μB.

X-Ray Crystallography.

Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of
tetrahydrofuran solutions of 12b, 12c, and 12d or in the case of 12a, crystals were obtained from a
concentrated toluene solution after three weeks. The structure obtained for 12c contains a molecule
of water instead of the expected molecule of tetrahydrofuran as the co-ligand and is denoted as 12c.
The crystals of 12d (Py) were grown by slow evaporation of a concentrated solution of the complex
in tetrahydrofuran/pyridine (50:1).

Catalytic Experiments.

In a typical catalytic experiment the oxirane (2.0 mmol), tetra-butyl-ammonium bromide (TBAB)
(32.6 mg, 0.1 mmol), the respective iron(III) amino triphenolate complex (0.01 mmol of complex
12a or 12b, and 0.02 mmol 12c or 12d and mesitylene (278 μL, 2.0 mmol) were dissolved in the
respective solvent (5 mL). The reaction mixture was then transferred to a stainless steel autoclave
and three cycles of pressurization and depressurization with carbon dioxide were applied (pCO\(_{2}\) =
0.5 MPa). The final pressure was then adjusted to 1.0 MPa, and the reaction was left stirring at the
required temperature for 18 h. After this time, the yield was calculated using the \(^1\text{H} \)NMR spectrum
(d\(_{6}\)-DMSO or CDCl\(_{3}\)) of an aliquot of the reaction mixture and mesitylene as the internal standard.

Product Characterization

All organic products from the catalysis experiments were characterized by \(^1\text{H}-\text{NMR} \) and IR
spectroscopy and the spectra were compared with the data reported in literature. For these see
characterization. For each cyclic carbonate compounds references are provided.
4-methyl-1,3-dioxolan-2-one (Table 6, 4a) 38

Yield calculated by $^1$HNMR using mesitylene as internal standard. (400 MHz, CDCl$_3$): $\delta$ m 4.94-4.86 (m, 1H), 4.58 (t, $J$=8.0 Hz, 1H), 4.01 (t, $J$=8.8 Hz, 1H), 1.45 (d, $J$= 6.0 Hz, 3H).
IR Neat: 1751cm$^{-1}$.

4-phenyl-1,3-dioxolan-2-one (Table 7, Entry 1) 39

Yield calculated by $^1$HNMR using mesitylene as internal standard are reported in Table 7 (400MHz, CDCl$_3$): $\delta$
7.35–7.44 (m, 5H), 5.86 (t, $J$= 8.0 Hz, 1H), 4.80 (t, $J$= 8.4 Hz, 1H), 4.34 (t, $J$= 8.4 Hz, 1H).
IR Neat: 1788 cm$^{-1}$.

(4R, 5R)-4,5-dimethyl-1,3-dioxolan-2-one (Table 7, entry2) 39

Yields for each complex are reported in Table 7.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.39 – 4.27 (m, 2H), 1.45 (d, $J$ = 5.9 Hz, 6H).
IR Neat: 1796 cm$^{-1}$ (C=O).

4, 5-tetramethylene-1, 3-dioxolan-2-one (Table 7, Entry 3) 40

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.78 – 4.59 (m, 2H), 2.02 – 1.79 (m, 4H), 1.69 – 1.52 (m, 2H), 1.51 – 1.24 (m, 2H). IR Neat: 776 cm$^{-1}$ (C=O).

1,3-dioxan-2-one (Table 7, Entry 4). Yield for each complex are given in table 3. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.53 – 4.35 (m, 4H), 2.27 – 2.08 (m, 2H). IR Neat: 1728 cm$^{-1}$ (C=O).

5,5-dimethyl-1,3-dioxan-2-one (Table 7, Entry 5). Yield for each complex are given in table 3. $^1$H NMR (300 MHz, CDCl$_3$) δ 4.06 (s, 4H), 1.10 (s, 6H). IR Neat: 1736 cm$^{-1}$ (C=O).

The synthesis of tiphenolamine ligands 11c is reported in literature. The synthesis of Mo(VI) amino triphenolate complex 13c and 14d is reported in literature and fully characterized. The general procedure for 13c is the following. Milled MoO$_2$Cl$_2$ (200 mg, 1 mmol) and the ligand precursor 2d (503 mg, 1 mmol) were mixed with toluene (50 mL) and the stirred suspension was heated to reflux for 18 h. The resulting intense purple solution was filtered through a short pad of silica and evaporated to afford complex 3-Cl as a violet solid; yield: 500 mg (80%).

$^1$H NMR (300 MHz, CDCl$_3$): δ=7.40 (dd, J=7.8, 1H, and 1.4 Hz, ArH), 7.34 (dd J=7.8, 2H, and 1.8 Hz, ArH), 7.15 (dd, J=9.2, 3H, and 1.4 Hz, ArH), 6.98 (m, 3H, ArH), 3.99 ( d, 2H, J=11.5, NCH$_2$), 3.6 (d, J=21.1 Hz, 2H, NCH$_2$), 3.49 (s, 2H, NCH$_2$),1.59 (s, 9 H), 1.47 (s, 18H); ESI-MS: m/z=672.2 (M$^+$Na$^+$), 650.2 (M$^+$ H$^+$), 614.3 (M-Cl).

General procedure for the synthesis of cyclic carbonate reported in Table 9, 10 and 11.

In a typical CO$_2$ cycloaddition reaction, a 30 mL autoclave was charged with the epoxide, Mo(VI) amino triphenolate complex 13c and co-catalyst TBAB or TBAI (and if necessary 0.5 mL of methyl ethyl ketone (MEK) in the cases where the substrate/cyclic carbonate product is a solid). The reaction was stirred for 18 h at the required temperature, after which time the reaction was cooled and an aliquot of the reaction mixture analyzed by $^1$H NMR spectroscopy in order to calculate the conversion and compared with those reported in literature.

Same procedure was followed for cyclic organic carbonate reported in Table 11 catalyzed by 14c.

4-butyl-1,3-dioxolan-2-one (Table 9, Entry 1). Conversion into the corresponding cyclic carbonate are reported in table 6.

\[\delta 4.79 – 4.62 (m, 1H), 4.52 (dd, J= 8.1 and 8.1 Hz, 1H), 4.06 (dd, J = 8.1, 7.3 Hz, 1H), 1.90 – 1.58 (m, 2H), 1.53– 1.25 (m, 4H), 0.92 (t, J =7.0 Hz, 3H).\]

4-(chloromethyl)-1,3-dioxolan-2-one (Table 10, Entry 5)\(^{43}\)

\[\delta 5.09 – 4.81 (m, 1H), 4.59 (dd, J = 8.5 and 8.5 Hz, 1H), 4.41 (dd, J = 8.5, 5.8 Hz, 1H), 3.91 – 3.53 (m, 2H). IR Neat: 1778 cm\(^{-1}\) (C=O).\]

4-(hydroxymethyl)-1,3-dioxolan-2-one (Table 10, Entry 6)\(^{44}\)

\[\delta 4.87 – 4.78 (m, 1H), 4.55 (dd, J = 8.4 and 8.4 Hz, 1H), 4.48 (dd, J = 8.4 and 6.6 Hz, 1H), 4.01 (dd, J = 12.8, J = 3.0 Hz, 1H), 3.73 (dd, J = 12.8, J = 3.5 Hz, 1H), 2.86 (br s, 1H). IR Neat: 1788 cm\(^{-1}\) (C=O).\]

4-(methoxymethyl)-1,3-dioxolan-2-one (Table 10 Entry 7)\(^{26,28,38}\)

\[\delta 4.88 – 4.77 (m, 1H), 4.51 (dd, J = 8.3 and 8.3 Hz, 1H), 4.38 (dd, J = 8.3 and 5.9 Hz, 1H), 3.66 (dd, J = 11.0, J = 3.9 Hz, 1H), 3.58 (dd, J = 11.0, J = 3.8 Hz, 1H), 3.44 (s, 3H).\]

Allylglycidil ether 1,3-dioxolan-2one (Table 10 Entry 8)\(^{28}\)


$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 – 7.42 (m, 3H), 7.41 – 7.33 (m, 2H), 5.16 (d, $J$ = 8.0 Hz, 1H), 4.75 – 4.53 (m, 1H), 1.58 (d, 3J $HH$ = 6.2 Hz, 3H). IR Neat:1797 cm$^{-1}$ (C=O). HR MS (ESI+): calcd. $m/z$ 179.0708 [M$^+$ H]$^+$; found: 179.0696.

(Table 11). Conversion into the corresponding cyclic carbonate are reported in Table 11.

![Structural diagram of (4R,5R)-4-methyl-5-phenyl-1,3-dioxolan-2-one (Table 11, Entry 1).](image)
Summary

This Ph.D thesis describes a novel synthesis of analogues of amino triphenolate ligands and the use of Fe(III) and V(V) amino triphenolate complexes as catalysts for renewable carbon feedstocks transformation into valuable compounds.

In general, in Chapter 1 an overview of synthetic approaches of triphenolamines are reported, followed by explanation of their coordination chemistry in particular with two metals, which are the subject of this thesis work, vanadium and iron. Finally the catalytic reactivity of both V(V) and Fe(III) complexes is reported. In particular the activity of V(V) amino triphenolate complexes is related to their capability to act as Lewis Acid, stabilizing the active species under turn-over conditions in oxygen transfer reaction such as sulfoxidation and halogenation of trimethoxybenzene in the presence of an oxidant. The reactivity of iron(III) amino triphenolate complexes as catalyst for the cycloaddition of carbon dioxide to epoxides for the synthesis of cyclic carbonate is reported.

Having established that amino triphenolate ligands and in particular the substituents in ortho positions to the phenoxy moieties play an important role in order to control the environment of the metal, modulate the electronic and steric properties around the metal centre and therefore control their catalytic properties, in Chapter 2, a novel synthetic methodologies for the synthesis of their analogues amino trithiophenolate ligands is reported. The synthetic methodology allows the synthesis of ortho-substituted trithiophenolamines with very satisfactory yields via a three step procedure starting form commercially available aldehydes. This approach led to the possibility, for the first time, to access this important class of ligands in a systematic way using either commercially or readily available building blocks.

In Chapter 3 a novel reactivity of V(V) amino triphenolate complex is described. More in detail, V(V)/TPA complex has been found to be a very effective catalyst for the aerobic oxidative C-C cleavage of tertiary and secondary vicinal diols. These studies were carried out in order to develop catalysts capable of controlled oxidative degradation of more challenging substrates, such as lignin models to demonstrate the feasibility of producing fine chemicals from a renewable carbon feedstock. The mild reaction conditions and high yields achieved for 1,2-diols and an ethereal derivative make this catalyst not only competitive to those previously reported but also good candidate for lignin model compounds transformation.
Finally, in Chapter 4 four new Fe(III) amino triphenolate complexes have been synthesized and fully characterized. These complexes have been found to be dinuclear or mononuclear. The potential to form a dinuclear structure is dependent upon the substituent in the \textit{ortho}-position of the phenolate moiety. Catalytic testing of the complexes for the cycloaddition of carbon dioxide to oxiranes has shown that the mononuclear form of these iron complexes is significantly more active than the dinuclear species. It has also been shown that by changing the reaction conditions (higher temperatures, using a solvent with coordinating potential and better CO$_2$-dissolution potential) the dinuclear structure can be disrupted and a more active form of the complex can be obtained. Moreover, Mo(VI) and V(V) amino triphenolate have been found to be active catalysts in the same reaction. In particular the vanadium catalyst was found to be active with terminal and internal epoxides, affording the corresponding cyclic carbonates in high yield under mild reaction conditions.

In summary, this thesis work had the aim to identify new opportunities in homogeneous catalysis by using alternative carbon feedstocks for the production of small molecules.
Riassunto

Questa tesi di dottorato riporta una nuova sintesi degli analoghi dei leganti trifenolamminici e l’impiego dei complessi trifenolamminici di Fe(III) e V(V) come catalizzatori per la trasformazione di fonti di carbonio rinnovabili per la produzione di composti organici.

In generale nel Capitolo 1 vengono riportate le strategie sintetiche impiegate per l’ottenimento delle trifenolammine, seguita dalla spiegazione della loro chimica di coordinazione, in particolare con due metalli quali il ferro e il vanadio, oggetto di studio del lavoro di dottorato. Più in dettaglio vengono altresì riportate le reattività di questi complessi in catalisi. Per quanto riguarda il complesso di V(V), la sua reattività è legata alla sua capacità di fungere come Acido di Lewis, stabilizzando le specie attive in reazioni di ossidazione come per esempio nelle sulfossidazioni e alogenazioni in presenza di un opportuno ossidante.

Per quanto riguarda invece i complessi di Fe(III) con le trifenolammine viene riportata la loro reattività come catalizzatori nella addizione della CO₂ agli epossidi per la sintesi di carbonati ciclici. I leganti triphenolamminici e in particolare i sostituenti in orto al gruppo fenolico giocano un ruolo importante nel modulare le proprietà steriche ed elettroniche così come dell’intorno chimico del metallo a cui si vanno a complessare. Questo si traduce nella possibilità di modulare anche la loro attività catalitica. In virtù di quanto detto, nel secondo Capitolo 2 si è illustrato una nuova metodologia per la sintesi di leganti amino tritiofenolati, analoghi delle triphenolamine. La sintesi di questi leganti avviene solo in tre passaggi sintetici, partendo da substrati come i derivativi del aldeide salicilica, passando poi per la protezione del gruppo ossidrilico con un tiocarbammato il quale permette poi il successivo riarrangiamento, chiamato di Myazaki-Newmann-Kwart, consentendo così di avere la funzionalità tiofenolica. La sintesi procede con la successiva amminazione riduttiva per avere lo scheletro triaminico, seguita dal passaggio finale della deprotezione del gruppo carbammico ottenendo così il legante finale. Questo approccio di sintesi ha consentito per la prima volta ad avere leganti orto sostituiti, amino tritiofenolici in buone rese partendo da prodotti commercialmente disponibili.

Nel Capitolo 3 invece il lavoro è proseguito nello studio di una nuova reattività data da complessi amino trifenolati di V(V). In dettaglio in questa parte ha riguardato la loro attività come catalizzatori nelle reazioni di scissione di legami carbonio-carbonio di dioli e preliminarmente nella scissione di composti β-idrossi eteri. Il complesso di V(V) si e rivelato essere moto attivo e in condizioni di reazioni blande. Questi studi sono stati effettuati al fine di poter sviluppare catalizzatori capaci di degradare, in condizioni controllate di ossidazione, substrati come la lignina.
la quale è considerata essere, insieme alla cellulosa, una fonte di carbonio rinnovabile, difficile però da poter utilizzarla come tale.

Nella parte finale di questo lavoro viene riportato lo studio, sintesi, caratterizzazione e reattività di quattro complessi amino trifenolici di Fe(III). Questi complessi allo stato solido, a seconda del sostituente in orto al gruppo fenolico, hanno dimostrato essere mononucleari o binucleari. La loro attività poi è stata testata nella cicloaddizione della CO₂ a differenti epossidi e ossirani per la sintesi di carbonati ciclici. Test catalitici hanno dimostrato come la forma mononucleare del complesso è molto più reattiva di quella dinucleare. Inoltre è stato dimostrato come cambiando le condizioni di reazione, temperature alte o usando solventi con potenzialità coordinative e di dissoluzione per la CO₂, la forma dinucleare può essere aperta, permettendo in questo modo al substrato di coordinarsi e di avere una buona reattività. Nella seconda parte del Capitolo 4 si è riportato l’attività di altri due complessi trifenolamminici rispettivamente di Mo(VI) e V(V) i quali sono stati testati come catalizzatori per la stessa reattività. Entrambi i catalizzatori hanno dimostrato avere buona reattività nell’attivazione dell’anidride carbonica. In particolare il complesso di V(V) ha dimostrato avere ottima reattività, ottenendo carbonati ciclici a cinque termini, sia partendo da epossidi terminali o interni.

In sintesi, questa tesi di dottorato ha avuto come obiettivo l’identificazione di nuove opportunità in catalisi omogenea sfruttando fonti di carbonio rinnovabili ed alternative per la produzione di piccole molecole organiche.