MANGANESE AND IRON COMPLEXES WITH N-HETEROCYCLIC CARBENE LIGANDS: SYNTHESIS AND CATALYSIS

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Resumo

Esta tese descreve a síntese de novos complexos de manganês e ferro contendo ligantes de carbeno N-heterocíclicos e a sua aplicação em catálise. Em particular, exploramos a atividade catalítica dos novos complexos na oxidação de álcoois e na redução de grupos carbonil.

A tese é composta por seis capítulos, cada um deles abordando aspectos diferentes. O capítulo 1 é introdutório e analisa o estado de arte dos complexos N-heterocíclicos de manganês e ferro em catálise. Em particular, a discussão concentra-se na síntese, caracterização e nas aplicações catalíticas dos complexos N-heterocíclicos de manganês e bis-N-heterocíclicos de ferro. O principal objetivo da tese e os objetivos específicos também são apresentados no capítulo 1.

O capítulo 2 descreve a síntese e caracterização dos complexos fac- [Mn(bis-NHCR)(CO)3Br] (R = Me, Mes) e a sua aplicação na redução eletrocatalítica de CO2 em CO. Além disso, estes complexos foram aplicados como catalisadores para a redução de grupos carbonilo através de reações de hidrosililação. Estes resultados são descritos no Capítulo 3. A síntese e caracterização de uma nova família de complexos de manganês carbonilo contendo ligantes di(1,2,3-triazolidinos) quelantes ou em ponte e a sua aplicação como catalisadores para a oxidação de álcoois em cetonas e aldeídos são apresentados no capítulo 4. O capítulo 5 descreve a preparação de complexos quelantes de carbonos bis-N-heterocíclicos de ferro (II) contendo ligantes piridil. Os complexos [Fe(bis-NHC) (I)2] (L = biperidina, fenantrolina) foram completamente caracterizados e a sua atividade catalítica na oxidação de álcoois foi explorada.

Por fim, são apresentadas as conclusões no capítulo 6.
Manganese and iron complexes with N-Heterocyclic carbene ligands: 
Synthesis and catalysis

Summary

This thesis describes the synthesis of new manganese and iron complexes bearing N-heterocyclic carbene ligands and their application in catalysis. In particular, we have explored the catalytic activity of the new metal complexes in the oxidation of alcohols and in the reduction of carbonyl groups.

The thesis is composed of six chapters, each of them dealing with different aspects. Chapter 1 is introductory and reviews the state-of-the-art of manganese and iron N-heterocyclic carbene complexes in catalysis. In particular, the discussion focus on the synthesis, characterization and catalytic applications of manganese NHC and iron bis-NHC complexes. The main goal of the thesis and the specific objectives are also presented in Chapter 1.

Chapter 2 describes the synthesis and characterization of \( \text{fac-}[\text{Mn}\text{(bis-NHC}^\text{R})(\text{CO})_3\text{Br}]\) (\(R = \text{Me}, \text{Mes}\)) complexes and their application in the electrocatalytic reduction of \(\text{CO}_2\) to \(\text{CO}\). In addition, these complexes have been applied as catalysts for the reduction of carbonyl groups through hydrosilylation reactions. These results are described in Chapter 3. The synthesis and characterization of a new family of carbonyl manganese complexes bearing chelating or bridging mesoionic di(1,2,3-triazolylidene) ligands, and their application as catalysts for the oxidation of alcohols to ketones and aldehydes are presented in Chapter 4. Chapter 5 describes the preparation of chelating bis-N-heterocyclic carbene complexes of iron(II) containing pyridyl ligands. Complexes \([\text{Fe(bis-NHC})\text{L(l)}_2]\) (\(L = \text{bipy}, \text{phen}\)) were fully characterized and their catalytic activity in the oxidation of alcohols was explored.

Lastly, conclusions are drawn in chapter 6.
List of Publications


**List of abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>NHCs</td>
<td>N-Heterocyclic carbenes</td>
</tr>
<tr>
<td>Trz</td>
<td>1,2,3-Triazolylidenes</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl</td>
</tr>
<tr>
<td>t</td>
<td>tert</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic resonance</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofurane</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
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<tr>
<td>i</td>
<td>iso</td>
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<td>Pr</td>
<td>Propyl</td>
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<td>Imidazol</td>
</tr>
<tr>
<td>Bu</td>
<td>Buthyl</td>
</tr>
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<td>TON</td>
<td>Turnover number</td>
</tr>
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<td>Ethyl</td>
</tr>
<tr>
<td>Bn</td>
<td>Benzyl</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electron-spray ionization- mass spectrometry</td>
</tr>
<tr>
<td>NCMe</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental Analysis</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
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1.4. Fe NHC complexes: synthesis and catalytic applications
   1.4.1 Fe bis-NHC complexes
      1.4.1.1 Synthesis and characterisation
      1.4.1.2 Catalytic applications of Fe bis-NHC complexes

1.5. Objectives

1.6. References
1.1 Carbenes

Carbenes are neutral molecules containing a divalent carbon atom. In the ground state, the two nonbonding electrons of the carbon atom can have either antiparallel spins, where the sp\(^2\) orbital is doubly occupied and the p\(_z\) orbital is unoccupied (singlet state) or parallel spins, where the sp\(^2\) and p\(_z\) orbitals are singly occupied (triplet state) (Figure 1.1). The different spin configuration of the carbene, which depends on the relative energy values between sp\(^2\) and p orbitals, and its overlapping with the orbitals of the metal, determines the nature of the metal carbene complex.

![Figure 1.1](image)

**Figure 1.1** Representation of the singlet and triplet state of the carbene.

There are different types of carbenes stabilized by a metal, each of them with very different electronic properties of the M-C bond. They can be classified in three main types:

1.1.1 Fischer type carbenes

These type of carbenes are found in low oxidation state metal centers in combination with singlet carbenes. The M-C bond in Fischer carbenes is based on \(\sigma\)-electron donation from the filled lone pair orbital of the carbene atom to an empty metal d-orbital, and \(\pi\) back bonding of a filled metal d-orbital to the empty p-orbital on carbon (Scheme 1.1). This polarization generates a carbon that is electrophilic in nature; they are stabilized by substituents on the carbene atom such as alkoxy and alkylated amino groups.
1.1.2 Schrock type carbenes

Schrock carbenes, named later by Richard R. Schrock, are characterized by nucleophilic carbene carbon centers. The π electrons are equally distributed between the M-C bond, generating a real double bond. They are typically found with high oxidation state metal centers.[1]

1.1.3 N-Heterocyclic carbenes (NHCs)

NHCs are considered as a type of Fischer carbenes because they form a single metal-carbon bond. However, their particular properties motivate their study separately from other carbenes. NHCs are defined as singlet carbenes in which the divalent carbenic center is connected directly to at least one nitrogen atom in the heterocycle. NHCs were first discovered in 1968 by Ofele[2] and Wanzlick,[3] almost simultaneously. However, the use of NHCs as ligands in organometallic chemistry started 20 years later, when Arduengo isolated for the first time a stable free carbene.[4] The isolation of stable NHCs promoted an intense research in organometallic chemistry.[5] NHCs are electron rich nucleophilic species in which the carbene center benefits from the stabilization associated with both the σ-electron-withdrawing and π-electron donanting character of the nitrogen atoms. Due to their strong σ-electron donating properties, NHC ligands form strong bonds with metal centers, affording metal complexes that are generally resistant to decomposition.[6–9]
NHCs have experienced a remarkable development due to their facile synthesis, their unique properties as ligands, and the application in catalysis of their metal complexes. The catalytic applications include hydrogenations, C–H bond activation, oxidation catalysis, cross-coupling, cyclization, and metathesis reactions among others.\textsuperscript{[10–12]}

1,2,3-Triazolylidenes (Trz) (Figure 1.2) are a subclass of NHCs disclosed by Albrecht and co-workers in 2008.\textsuperscript{[13]} Trz result from the substitution of the C(2)-R unit in imidazolylidenes by nitrogen. These type of NHCs are mesoionic carbenes, dipolar five membered heterocyclic compounds in which both the negative and the positive charge are delocalized. Trz have attracted much interest in the last years due to their facile and versatile synthesis, and their strong \(\sigma\)-electron donanting properties, stronger than classical NHC ligands.

![Figure 1.2 Representation of a 1,2,3-triazolylidene.](image)
1.2 Manganese and iron NHC complexes in catalysis

In recent years, the development of catalysts based on abundant first-row transition metals has become a central topic in catalysis.[14–16] Among 3d metals, manganese and iron are particularly attractive candidates for catalysis owing to their natural abundance and their useful features of being non-toxic and biocompatible metals. In comparison with the spectacular development of catalysis with Fe[17–25], Mn has remained relatively unexploited. However, this area of research has recently emerged as an important field with the discovery of manganese pincer complexes as efficient catalysts for hydrogenation and dehydrogenation reactions.[14,15,25–33,16–19,21–24]

1.3 Manganese N-Heterocyclic carbene complexes

1.3.1 Synthesis and characterization

The majority of the Mn NHC complexes described in the literature contain Mn in the oxidation states +1 and +2. This Section will provide an overview of the Mn NHC complexes described in the literature. It covers from the preparation of the first Mn NHC complex to 2019. Section 1.3.1 comprises several subsections, each dedicated to specific oxidation states of the metal.

1.3.1.1 Manganese(I) NHC complexes

Most of the Mn(I) NHC complexes described in the literature contain carbonyl and/or cyclopentadienyl as co-ligands in their coordination sphere. The first Mn(I) NHC complexes were reported by Lappert and Pye in 1977 (complexes 1 and 2, Figure 1.3).[34] However, both 1 and 2 complexes were obtained in very low yield and were poorly characterized.
In 1989, Aumann and Heinen reported the synthesis of half-sandwich Mn NHC complexes via ketenimine Mn intermediates. The synthetic pathway is depicted in Scheme 1.2. The synthesis starts by preparing the ketenimine metal complex 3 as an intermediate and then a polarized RC=X bond went through a 1,3-addition to form 4.[35] More recently, related half-sandwich complexes have been prepared by Whitessley and co-workers in higher yield by UV irradiation of Cp’Mn(CO)₃ (Cp’ = η⁵-C₅H₄Me) in the presence of the

![Figure 1.3 The first Mn(I) NHC complexes 1 and 2 described by Lappert and Pye.](image)
corresponding free NHC (Figure 1.4). This synthetic pathway allows to obtain the desired compounds in moderate yields (37–51%). Complexes 5–8 have been synthesized and fully characterized in solution and in the solid state. Photochemistry studies of 5–8, through time-resolved infrared spectroscopy in alkane solutions, showed that 5–8 photodissociate CO to generate the monocarbonyl species Cp′Mn(CO)(NHC).[36]

![Cp′Mn(CO)\(_2\)(NHC) complexes 5-8.](image)

Lugan, Sortais, and co-workers, prepared in 2014, related Mn(I) complexes containing different wingtips (complexes 9–14, Figure 1.5) by photoinduced CO substitution in CpMn(CO)\(_3\) in the presence of the appropriate free NHC, which was generated in situ from the corresponding imidazolium salts and potassium tert-butoxide.[37]
Chapter 1: Introduction and Objectives

Two years later, Lugan, Sortais, and co-workers in continuation of their work reported the synthesis of complexes 15 and 16 (Figure 1.6). These complexes were prepared from [CpMn(CO)₃] and N-mesitylimidazole, using a novel synthetic strategy based on the anchoring of an imidazolium moiety to the coordinated Cp ligand, followed by an intramolecular photochemical CO substitution for the pendant NHC moiety generated in situ upon addition of a base. Complexes 15 and 16 were isolated in 73% and 61% yield, respectively, after purification by column chromatography and crystallization. They were fully characterized by spectroscopic methods and single-crystal X-ray diffraction analyses.[38]

Edwards, Hahn and coworkers reported the synthesis of carbene coordinated [11]ane-P₂C^{NHC} macrocycle-substituted transition metal complexes 18-20 (Figure 1.7). Complex 18 was prepared from the reaction of 17 with 1,2-bis(di(o-fluorophenyl)phosphino)benzene in THF. The addition of two equivalents of KO'Bu to 18 led to the

![Figure 1.5 Mn(I) NHC complexes 9-14.](image)

![Figure 1.6 Half-sandwich Mn(I) NHC complexes 15 and 16.](image)
formation of 19. Next, one carbonyl group can be removed from 19 by reaction with Me₃NO, giving 20 as bright red solid in 65% yield. All complexes have been characterized by spectroscopic and analytical methods.\cite{39}

\[ \text{Figure 1.7 Carbene coordinated [11]ane-P}_{2}C^{\text{NHC}} \text{ macrocycle-substituted transition metal complexes 17-20.} \]

Later, Ruiz et al. reported the synthesis of Mn(I) NHC complexes 21 and 22 (Figure 1.8). Complexes 21 and 22 were characterized by spectroscopic and analytical methods; besides this, complex 22 with \( R=2,6\)-difluorophenyl was also characterized by X-ray diffraction methods. The structure of 22 reveals that the different bond lengths within the heterocycle of this complex are, in variable degree, intermediate between single and double bond, reflecting the existence of electronic delocalization in the heterocycle.\cite{40}
In 2007, Smith and co-workers reported the synthesis of a tricarbonyl Mn complex bearing the (tris-NHC)borate ligand PhB(MeIm)₃Mn(CO)₃ (23). Complex 23 was prepared by reacting [MnBr(CO)₃(BuCN)]₂ with the (tris-NHC)borate ligand. IR and cyclic voltammetry measurements of complex 23 established the exceptionally strong donating nature of the tris(carbene)borate ligand."^{[41]} In continuation of their studies, the same authors reported the only Mn mesoionic carbene complex described so far in the literature (complex 24, Figure 1.9)."^{[42]}

**Figure 1.8** NHC-substituted Mn(I) carbene complexes 21 and 22.

**Figure 1.9** Carbonyl tri-NHC Mn(I) complex 24.
Agarwal and co-workers reported the synthesis of the Mn(I) tricarbonyl complexes $25$ and $26$ (Figure 1.10). These complexes were prepared from the reaction of the mixed NHC-pyridyl ligand with Mn(CO)$_5$Br in THF, under argon and in the presence an excess of KO'Bu. Both new species mediated the reduction of CO$_2$ to CO following two-electron electrocatalytic reduction of the Mn(I) center. Their catalytic activities will be discussed in Section 1.3.2.\textsuperscript{[43]}

![Figure 1.10 Mn(I) NHC complexes 25 and 26.](image)

Tricarbonyl Mn(I) complexes bearing a mixed NHC-phosphine ligand have been reported by Sortais and coworkers in 2019. Complex $27$ was readily obtained from the sequential reaction of the corresponding phosphine-imidazolium salt treated with KHMDS and reacted with Mn(CO)$_5$Br (Scheme 1.3). According to IR and NMR spectroscopy, the air stable complex $27$ was formed as a single isomer, presenting a facial arrangement of the three carbonyl ligands as confirmed by the X-ray diffraction studies.\textsuperscript{[44]}

![Scheme 1.3 Synthesis of NHC-phospbine Mn(I) complex 27.](image)
The group of Evgeny A. Pidko, reported also in 2019 the Mn(I) tricarbonyl complexes 28 and 29 (Scheme 1.4). Complexes 28 and 29 were obtained from the reaction of the in situ generated free carbene with Mn(CO)₅Br in THF, in 67% and 89% yield, respectively. Their IR spectra feature three sharp resonances indicative of an octahedral geometry in which the three ligands are bound in a cis-fashion. Their molecular structures have been determined by X-ray diffraction studies, confirming the octahedral geometry.^[45^]

Scheme 1.4 Synthetic procedure for Mn(I) NHCs 28 and 29.

With the goal to obtain new substitution patterns on heterocycles such as oxazoles and imidazoles (30 and 31, Scheme 1.5), the group of Fehlhammer reported multicomponent reactions of Mn(I) complexes. The synthesis of complexes 30 and 31 is depicted in Scheme 1.5.^[46,47^]

Scheme 1.5 Mn(I) oxazole and imidazole complexes 30 and 31 generated by multi-component reactions.
Hahn and coworkers based in the procedure previously described by Liu et al.\cite{48}, reported the synthesis of complex 32 from the reaction of Mn(CO)$_5$Br with the aminophosphineimine ligand ($\text{H}_2\text{N(CH}_2\text{)}_2\text{NQPPh}_3$). The reaction occurred with elimination of triphenylphosphine oxide.\cite{49,50} As we can see in Figure 1.11, the saturated NHC ligand in 32 is not substituted at the NH positions, opening up a variety of substitution patterns by replacing the hydrogen atom of the NHC wingtip with organic residues.

![Figure 1.11 Mn(I) NHC complex 32.](image)

1.3.1.2 Manganese(II) NHC Complexes

In 2001, Cowley, Jones and coworkers reported the synthesis of the first Mn(II) complexes 33-35 (Figure 1.12). These complexes were prepared in good yield (70%) by reaction of the corresponding free carbenes with manganocene in toluene. The X-ray diffraction studies of 34 and 35 showed a distorted tetrahedral geometry, with one of the Cp rings bonded to Mn in an $\eta^1$-fashion, and the second Cp was disordered over two orientations, an $\eta^2$-fashion mode, and an $\eta^1$ and $\eta^2$ intermediate orientation. Magnetic susceptibility measurements indicated that 35 is paramagnetic with two unpaired electrons.\cite{51}
In 2004, Roesky et al., reported the monomeric Mn(II) NHC complexes 36-38 (Figure 1.13), prepared by reaction of MnCl$_2$(THF)$_{1.5}$, MnI$_2$, or Mn(MeCOO)$_2$ with two equivalents of the corresponding free NHC in THF. The solid structures of complexes 36 and 37 revealed a four coordinate central Mn atoms with a distorted tetrahedral geometry. Complex 38 showed a distorted octahedral geometry with the central Mn atom surrounded by four oxygen atoms from the two chelating carboxy groups and two carbene carbon atoms. All complexes were characterized by EPR, as expected complexes 36 and 37 displayed a strong resonance at $g_{\text{eff}} = 4.3$ due to their tetrahedral environment, while complex 38 exhibited a strong band at $g_{\text{eff}} = 2$ and a weaker band at $g_{\text{eff}} = 4.3$ consistent with its symmetric structure and the cis arrangement of the NHC ligands.\[52\]

![Figure 1.13 Monomeric Mn(II) NHC complexes 36-38.](image)

The first Mn complex bearing a bis-NHC pincer ligand (39, Figure 1.14) was reported in 2006 by Danopoulos and co-workers. Complex 39 was isolated from the reaction of MnBr$_2$ with the C–N–C pincer ligand as yellow powder in 93% yield, and was characterized by elemental analysis, magnetic susceptibility, and single-crystal X-ray diffraction. The molecular structure of 39 feature a five-coordinate metal centre in distorted square-pyramidal geometry.\[53\]
In 2009, the group of Chen described two possible syntheses for the preparation of the Mn(II) complex 40 bearing a bis-NHC tetradeinate ligand (Figure 1.15). The first synthesis consisted in the \textit{in situ} formation of the corresponding silver NHC complex, followed by its reaction with Mn metal. An alternative pathway for the synthesis of 40 was the direct reaction of the corresponding imidazolium salt with Mn metal under air.$^{[54]}$

Later, Goicoechea and co-workers reported the Mn(II) complexes bearing anionic N-heterocyclic dicarbene ligands 43-45 (Figure 1.16). The direct reaction of Mn$_3$(Mes)$_6$ with the corresponding imidazolium salt led to the formation of complex 43. Treatment of 43 with KC$_8$,  

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{39.png}
\caption{Mn(II) complex 39 bearing a bis-NHC pincer ligand.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{40.png}
\caption{Mn(II) complex 40 bearing a bis-NHC tetradeinate ligand.}
\end{figure}
resulted in the formation of the Mn(II) bis(carbene) NHC complex 44. Lastly, compound 45 was synthesized by reaction of 44 with AlEt₃. All complexes 43-45 were characterized by single-crystal X-ray diffraction. The bond angles of the structure of 43 are 116.49(6)°, 122.57(7)°, and 120.94(7)°, values very close to the value of 120° expected for a trigonal planar complex. The structure of 44 show a coordination pseudo-tetrahedral, about the Mn(II) metal center, with a weakly bonded THF molecule distorting an otherwise trigonal planar structure. Single crystals of 45 reveal an anionic metal complex where the two dicarbene ligands are coordinated to the metal center in an abnormal fashion, as with 44.[56]

![Figure 1.16 Mn(II) complexes 43-45 with two anionic NHC ligands.](image)

Karsten Meyer et al., in 2014, reported the four-coordinate Mn(II) complexes 46 and 47 (Figure 1.17) containing a bis-NHC mono(phenolate) ligand (BIMPN). These complexes were prepared by reaction of the corresponding proligands with MnCl₂ in an ether/pyridine mixture. In turn, the reaction of 46 with NaN₃ afforded complex 47, which was easily identified by the intense and very characteristic \( \tilde{\nu}(N_3) \) IR vibrational bands (at 2077 and 2056 cm⁻¹). Both Mn(II) compounds are NMR silent. Their UV-vis spectra feature bands with a maxima at 257 and 309 nm of similar intensity that were assigned to a \( \pi-\pi^* \) transition in the phenolate and a charge-transfer (CT) transition, respectively. The molecular structures of 46 and 47
revealed the different steric demand of the ligands. The molecular structure of 46, in which a pyridine molecule is situated next to the Mn–Cl bond, and those of azida complex 47 demonstrated the mixed ligand’s flexibility.\textsuperscript{[57]}

![Figure 1.17 Mn(II) complexes 46 and 47 bearing a (bis-NHC)phenolate ligand.](image)

Tonzetich and co-workers reported in 2015, several Mn(II) complexes (48-54) containing aryl substituted NHCs. The synthesis of these complexes is depicted in Scheme 1.6. Complexes 48-54 were characterized and the solid-state structures and aggregation behavior of Mn chloride complexes containing ‘Pr and ‘Mes ligands are similar to those of the corresponding Fe and Co compounds.\textsuperscript{[58]}
In 2016, the group of Smith prepared the Mn(II) complex 55 (Figure 1.18) in 71% yield, with the aim preparing, from this, a Mn(IV) complex, which will be mentioned later (section 1.3.1.4).[[69]]

**Figure 1.18 Mn(II) complex 55.**

### 1.3.1.3 Manganese(III) NHC Complexes

In 2009, a Mn(III) complex bearing a tetradeutate dicarbene ligand (complex 56, Scheme 1.7) was reported by Jitsukawa. It was prepared through of the reaction of the corresponding imidazolium proligand with Mn(OAc)$_2$·4H$_2$O. The crystal structure of 56 showed a distorted square

![Scheme 1.6 Synthesis Mn(II) Complexes 48-54 Containing NHC Ligands.](image-url)
pyramidal structure, in which two carbene atoms and two aryloxy oxygen atoms of the tetradentate ligand occupied the basal plane. Complex 56 resulted to be air stable, probably due to the rigid structure of the tetradentate NHC ligand which might stabilize the complex.\[60\]

![Scheme 1.7 Mn(III) complex 56 bearing a bis-NHC tetradeic ligand.](image)

Same year, Bellemin-Laponnaz and co-workers reported a square pyramidal Mn(III) complex with a tridentate NHC and an acetylacetonate ligand \((\text{tBu}(OCO))\text{Mn(acac)}) (57). The direct synthesis of the corresponding imidazoliun salt with Mn(acac)\(_3\) allowed to isolate complex 57 in 55% yield.\[61\]

Additionally, two more examples of Mn(III) complexes bearing tri-NHC ligands: \(\{\text{PhB(MeImid)}_3\}_2\text{Mn} \) Cl (58) and \(\{\text{PhB(MeImid)}_3\}_2\text{Mn} \) (CF\(_3\)SO\(_3\))\(_2\) (59) were described by Smith and co-workers in 2013. Complex 58 was prepared in excellent yield by reaction of free carbene with MnBr\(_2\), followed by oxidation with NOSbF\(_6\), in dichloromethane. Treatment of 58 with KOTf led to the mononuclear Mn(III) complex 59. Compound 58 resulted to be air-sensitive, rapidly developing a purple color, indicative of Mn(IV) species, when exposed to air and displayed a paramagnetically shifted \(^1\)H NMR. In addition, complex 59 was characterized by single-crystal X-ray diffraction, revealing a Mn(III) center with a slightly distorted octahedral environment made of two capping (tris-NHC) borate ligands.\[62\]
1.3.1.4 Manganese(IV) and Mn(V) NHC Complexes

Examples of Mn(IV) and Mn(V) complexes are very rare. The first Mn(IV) NHC complex, [PhB(MeImid)$_3$]Mn(OTf)$_2$ (60), was described in 2007 by Smith and coworkers using the tris(carbene)borate PhB(MeImid)$_3$ ligand. Complex 60 resulted from the air oxidation of 23, being later isolated as the triflate salt following metathesis with KOTf. This complex can also be prepared by reaction of 23 with MnBr$_2$, followed by oxidation with AgOTf. The X-ray crystal structure of 60 reveals it to be a rare example of an homoleptic organometallic Mn(IV) complex, displaying a slightly distorted octahedral geometry. The magnetic moment of 60, was calculated using the Evans method, getting the value [$\mu_{\text{eff}} = 3.1(3)\mu_B$], which is in line with the expected $S = 3/2$ spin state.$^{[41]}$ Same author reported the Mn(IV) nitride complex PhB(MesImid)$_3$MnΞN (61), which was prepared from the reaction 55 with NaN$_3$ under UV irradiation.$^{[59]}$

The tris(carbene) ligand TIMEN is also able to stabilize Mn(III,IV,V) complexes. In 2012, Meyer and co-workers prepared several Mn nitride complexes containing the tripodal chelating tris(carbene) ligand framework 62-66. Complex [TIMEN$_{\text{xyl}}$Mn(Cl)]Cl (62) was prepared by the addition of anhydrous Mn(II) chloride to solutions of the tris(carbene) ligand TIMEN$_{\text{xyl}}$ in pyridine. The reaction of 62 with an excess of sodium azide in the presence of NaPF$_6$ led to the formation of [(TIMEN$_{\text{xyl}}$)Mn(N$_3$)]PF$_6$ (63) with 93% yield. When a solution of 63 in acetonitrile was irradiated with UV light, the complex [(TIMEN$_{\text{xyl}}$)Mn(N)]PF$_6$ (64) was formed. Subsequent, reaction of 64 with NOBF$_4$ and NaPF$_6$ in acetonitrile afforded orange solutions of [(TIMEN$_{\text{xyl}}$)Mn(N)](PF$_6$)$_2$ (65) (56 %, yield) with loss of NO. Lastly, the reduced nitride species [(TIMEN$_{\text{xyl}}$)Mn(N)] (66) resulted of the stirring of suspensions of 66 in benzene over potassium graphite. All these complexes were fully characterized. The crystal structure of 63
revealed a four-coordinate Mn(II) center that is located 0.52 Å above the trigonal plane of the three carbene carbon atoms. In complex 64, the four-coordinate Mn(IV) center is located in a trigonal pyramidal ligand environment and resides only 0.42 Å above the trigonal plane of the carbene centers. EPR spectroscopy showed that 63 features a high-spin, $\sigma^6$ Mn(II) species.[63]

1.3.2 Catalytic Applications of Mn NHC complexes

Catalysis with Mn NHC has been poorly studied.[44,64,65] To the best of our knowledge, only seven reports on Mn NHC complexes in catalysis can be found in the literature. In 2009, Jitsukawa and co-workers reported the first application of a Mn NHC complex in catalysis. The Mn(III) complex 56 (Scheme 1.7) bearing a bis-NHC tetradentate ligand was applied in the oxidation of styrene with PhIO.[60] Despite low yield of styrene oxide (38%) was obtained, it was probed that high oxidation Mn(IV) and Mn(V) were generated during the oxygen transfer reactions.

Next catalytic application was reported in 2014 by Agarwal and coworkers, who described the electrocatalytic reduction of CO$_2$ by complexes 25 and 26 presented in Figure 1.10.[43] Both complexes 25 and 26 mediated the electrocatalytic reduction of CO$_2$ to CO following two-electron reduction of the Mn(I) center. The two-electron reduction of these species occurred at a single potential, which contrast with the behavior observed in Mn(2,2-bipyridine)(CO)$_3$Br complexes where a two-electron reduction process occurred in two sequential steps. Interestingly, catalytic current enhancement with complexes 25 and 26 was observed at voltages similar to Mn(2,2-bipyridine)(CO)$_3$Br.[66,67]

In the same year, Lugan and Sortais disclosed the hydrosilylation of aldehydes and ketones under UV irradiation using Mn(I) NHC complexes derived from cymantrene 9-14 (Figure 1.5).[37] The half-
sandwich Mn(I) complex 13 showed excellent activity in the reduction of a variety of aldehydes (Scheme 1.8 A) and ketones (Scheme 1.8 B) using 1.5 equiv. of Ph₂SiH₂ as reducing agent.

![Scheme 1.8 Scope of aldehyde (A) and ketone (B) hydrosilylation catalyzed by Mn(I) NHC complex 13.](image)

Related Mn complexes bearing Cp tethered NHC ligands (complexes 15 and 16, Figure 1.6) displayed lower catalytic activity (Scheme 1.9) than that observed for 13. Interestingly, it was possible to isolate the corresponding silane σ-complexes 67 and 68 (Scheme 1.10), which are proposed to be the primary products of the photochemical CO substitution for diphenylsilane in 15 and 16.[38]

![Scheme 1.9 Catalytic Ketone Hydrosilylation.](image)

![Scheme 1.10 Synthesis of σ²-Silane complexes 67 and 68.](image)
Very recently and already during the writing of my PhD thesis, three new reports appeared in the literature describing catalytic applications with Mn NHC complexes as catalysts.\cite{44,45,68}

Ke\textsuperscript{[68]} et al. reported the selective N-alkylation of anilines with alcohols (\textbf{Scheme 1.11}) using the bis-NHC Mn complex $\text{[Mn(bis-NHC)Br(CO)$_3$]}$ (69) reported by us in 2018, which is described in Chapter 2 of thesis. A large variety of aromatic amines and primary alcohols including biologically relevant motifs were efficiently converted at room temperature into mono N-alkylated amines using complex 69 as catalyst.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme_1_11.png}
\caption{A) N-alkylation of anilines with alcohols and B) N-alkylation with metanol.}
\end{figure}

Experimental and computational studies suggested an outer-sphere mechanism without the dissociation of the CO ligand for the Mn NHC system. The outer-sphere mechanism was also verified by IR spectroscopic study, in which no CO dissociated Mn intermediate was observed during the catalytic cycle. The high activity of Mn NHC in the outer-sphere mechanism, can be the reason of the success of this system at room temperature.

A bidentate Mn complex with NHC bearing an amine donor functionality was reported in 2019 by Pidko\textsuperscript{[45]} and co-workers. Complexes 28 and 29 are highly active catalysts for the transfer hydrogenation of a large variety of ketones, affording quantitative
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reduction of ketones with low catalyst loading (0.0075 mol%) (Scheme 1.12). Interestingly, catalyst deactivation was found to be temperature dependent and became especially prominent at elevated temperatures (70°C). It was proposed that complex 28 operates via the well-established bifunctional protonation/deprotonation mechanism.

Scheme 1.12 Transfer hydrogenation of ketones with 28.

Reduction of ketones through hydrogenation processes has also recently been described using the bidentate NHC-phosphine Mn(I) complex 27 (Scheme 1.3) as catalyst. Complex 27 resulted to be one of the most efficient pre-catalysts for ketone hydrogenation, reaching TON values up to 6200.[44]

1.4 Fe NHC complexes: synthesis and catalytic applications

Development of iron catalysis has experienced spectacular growth in the last decade. The intensive research in this area is well reflected by the number of review articles that have appeared in the literature.[14,17–19,22–25,28,70–72] In the particular field of Fe NHC chemistry, the first catalytic application was described by Grubbs in 2000. They disclosed that Fe(II) halides possessing highly donating imidazolylidene ligands were efficient catalysts for the atom transfer radical polymerization of styrene and methyl methacrylate.[73] Surprisingly, scarce development of this area occurred after that discovery. In fact, in a review published by Nolan in 2009, only 10 publications dealing with catalytic applications of Fe NHCs were reported.[72] Nowadays the situation is rather different, and a number of
groups have largely contributed to the development of this area of research. Several reviews on this topic are available in the literature.[17,19,74–88]

Iron compounds display a broad range of geometric and electronic variations. The oxidation states of Fe NHC compounds range from low-valent to high valent, being Fe(0), Fe(I) and Fe(II) complexes the most common. Regarding the geometry, most reports describe tetrahedral or octahedral coordination at the iron center, however, some trigonal bipyramidal or square planar Fe NHC complexes have also been described. Additionally, three-coordinate Fe NHC complexes are also reported in the literature.

Part of the work of this thesis has focused on the development of catalytic applications using Fe bis-NHC complexes. In this Section, an overview of the chemistry of these type of complexes is described.

1.4.1 Iron bis-NHC complexes

1.4.1.1 Synthesis and characterization

Surprisingly, iron complexes supported by simple bidentate bis(NHC) ligands, which are not part of a multidentate framework are scarce. The first examples appeared in 2007, reported by the group of Kervanic. The dinuclear bis-NHC Fe(I) complexes [{Fe₂(μ-S(CH₂)₃S)-(CO)₅}₂[μ-(IMe-CH₂-IMe)]](70) and [Fe₂{μ-S(CH₂)₃S}(CO)₄{IMe-CH₂-IMe}](71) were prepared by reaction of the corresponding free carbene with [Fe₂{l-S(CH₂)₃S}](CO)₅. This reaction led to formation of the dimer 70 along with the chelated bis-NHC complex 71, which was the major product.[89]

Related Fe complexes [{(μ-SCH₂)₂NBU-f}Fe₂(CO)₅[∗Mes(CH₂)₃I∗Mes]HBr (72) and [{(μ-SCH₂)₂CH₂Fe₂(CO)₅}₂[μ-I∗Mes(CH₂)₃I∗Mes] (73, I∗Mes = 1-(mesityl)imidazol-2-ylidene) were described by Song and co-workers in 2009. They showed that the tether length of the bis-NHC
ligand has a direct implication in the coordination mode, bridging or chelating, of the ligand to the iron center. Long tether lengths (3-C chain) favored the formation of dimetallic complexes bearing bridging bis-NHC complexes.\[^{90}\]

The group of Albrecht reported in 2009 their studies on the coordination of bis-NHC ligands containing a flexible methylene and a rigid phenylene linker to the “CpFe(CO)I” fragment. For both ligands, the bimetallic Fe(II) complexes \( 74-77 \) (Scheme 1.13) containing bridging NHC ligands were obtained. The bridging coordination mode of the dicarbene ligand was unequivocally confirmed by X-ray diffraction studies.\[^{91}\]

![Scheme 1.13 Synthesis of dinuclear Fe(II) complexes 74-77.](image)

Same year, the group of Chen developed a novel procedure for the preparation of Fe NHC complexes using imidazolium salts (Scheme
1.14 A) or the corresponding silver-NHC complexes (Scheme 1.14 B) as carbene sources and Fe powder. Using this simple and practical procedure, the authors described the preparation of the tetradebate Fe complexes 78 and 79 (Scheme 1.14) bearing bis-NHC functionalized with pyridine rings.[92] These complexes represented the first square-planar 14-electron complexes containing NHC ligands.

Scheme 1.14 Synthesis of complexes 78 and 79: via A) from imidazolium salts and Fe power and B) transmetalation with Ag–NHC complex and Fe power.

In 2011, Meyer and co-workers published the Fe complexes bearing chelating bis-carbene ligands 80-93 depicted in Scheme 1.15. A series of new and known bis(imidazolium) chloride and bromide salts bridged by either a methylene group (L9-L19, L21 and L22) or an ethylene group (L20), and bearing different N substituents (Me, Et, Bn, 'Bu, Mes) reacted with [Fe{N(SiMe$_3$)$_2$}]$_2$ to yield the four-coordinate Fe(II) complexes [(L-L)FeX$_2$] (80-93; X = Cl, Br; L-L = chelating bis(imidazolylidene) ligand). When the N-wingtips of the NHC ligand were small (Me, Et) or flexible (Bn), the corresponding dicarbene [(L-L)FeX$_2$] species were formed together with ferrous tetracarbene species [(L-L)$_2$FeX$_2$], which were difficult to separate and could not be isolated in pure form. Complexes [(L-L)$_2$FeX$_2$] (94-96) transformed into [(L-L)$_2$Fe(MeCN)$_2$][FeBr$_4$] (97-99) in acetonitrile when residual FeBr$_2$(THF)$_x$ was present (Scheme 1.16). Complexes [(L-L)FeX$_2$] featured high spin Fe(II) in a distorted tetrahedral environment, while complexes 97-99 presented low spin Fe(II) and distorted octahedral
structures with two acetonitrile ligands in a *cis* configuration.[93]

![Diagram](image1)

**Scheme 1.15** Synthesis of dicarbene Fe(II) dihalide complexes 80-93.

![Diagram](image2)

**Scheme 1.16** Synthesis of tetracarbene Fe(II) complexes 94-99.

Similar results were reported by Evans and Ingleson on chelating (bis-NHC)FeX₂ complexes containing CH₂ or phenyl linkers between the NHC ligands. Complexes 100-102 (**Figure 1.19**) were isolated in 44, 57 and 97 % yield, respectively. All complexes are high-spin in distorted tetrahedral structures, such as observed earlier in Meyer's work for complexes 80-93. The average Fe–C distances of complexes 100-102 (in the range 2.08 to 2.11 Å) consistent with other high spin four-coordinate Fe(II) carbene complexes, including complexes 80-93 (average of around 2.10 Å).[94]
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**Figure 1.19** Fe complexes 100-102 bearing chelating bis-carbene ligands.

Ohki, Tatsumi, Glorius, in 2012 reported the Fe(II) complex 103 with a diamine-bridged bis-NHC, which was prepared from the corresponding imidazolium salt (L23 or L24) and [Fe{N(SiMe$_3$)$_2$}]$_2$ or by reaction of the free carbene (L25) with FeCl$_2$ as shown in Scheme 1.17. The X-ray difraction studies of 103 showed a highly distorted geometry for Fe between octahedral and tetrahedral with weak Fe-N interactions, which is in agreement with a high spin d$^6$ configuration.$^{[95]}$

![Scheme 1.17 Synthesis of complex 103.](image)

Later, the group of Herrmann and Kühn described tetradebate Fe(II) NHC complexes similar to those earlier reported by Chen (Scheme 1.14) with tetradebate NCCN ligands ligated with different alkylene bridges. As shown in Scheme 1.18, the Fe(II) complexes 104-106 were prepared by the reaction of [Fe{N(SiMe$_3$)$_2$}]$_2$ with the appropriate imidazolium hexafluorophosphate salts. These complexes were quantitatively converted in the presence of CO to complexes 107 – 109 (Scheme 1.19).$^{[96]}$ The authors demonstrated that the alkylene bridge connecting the two NHCs has an influence on the coordination
mode of the NCCN ligands. Whereas the methylene- and ethylene-bridged NHC moieties lead to a nearly planar geometry of the NCCN ligand and two trans-positioned acetonitrile ligands, the propylene-bridged complex 106 exhibited a sawhorse-type coordination mode, with two cis-oriented acetonitrile ligands.

Scheme 1.18 Synthesis of complexes 104-106.

Scheme 1.19 Carbonylation of compounds 107-109.

Two years later, the Fe(II) complexes bearing new heteroatom-functionalized methylene-bridged bis-NHC ligands were reported (Scheme 1.20). The complexes 110 and 111 were obtained by
aminolysis of $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2(\text{THF})]$ with furan- and thiophene-functionalized bis(imidazolium) salts L29 and L30 in acetonitrile. The complex 112 was obtained by the crystallization of 110 from acetone.$^{[97]}$

![Scheme 1.20 Synthesis of complexes 110 and 111.](image)

In the same year, Kühn and co-workers prepared complex 113 (Scheme 1.21) with one PMe$_3$ ligand in the axial position that resulted from the addition of PMe$_3$ to a solution of complex 104 (Scheme 1.18) in acetonitrile. With goal of analysing the impact of axially coordinating additives on the electronic structure of 104 (Scheme 1.18), complex 104 was reacted with one equivalent of trimethyl phosphine (Scheme 1.22); substitution of the acetonitrile ligand by trimethyl phosphine was observed.$^{[98]}$

![Scheme 1.21 Synthesis of complex 113 with PMe$_3$ as the axial ligand.](image)
Continuing with their work, in 2015, the same authors prepared complex 119 from complex 104 by addition of tert-butyl isocyanide (CN′Bu) to a solution of 104 in acetonitrile (Scheme 1.23).[99]

Still in 2015, a variety of isocyanide-substituted Fe(II) NHC complexes were reported by Kühn. As shown in Scheme 1.24, complexes 120-123 were prepared from the reaction of the Fe(II) NHC complex 104 with a tetradeactate bis(pyridyl-NHC) ligand. Complexes 124-126 were prepared using the same synthetic procedure.[100]
Scheme 1.24 Synthesis of tri(isocyanide)-substituted complexes 120-123 and mono(isocyanide)-substituted complexes 124-126 starting from 104.

Related tetradeutate Fe(II) complexes, containing NHC-amide hybrid ligands were described by Meyer in 2013. Complex 127 was prepared from the reaction of the amido-imidazolium hexafluorophosphate (L31) with KHMDS and \([\text{Fe}[\text{N(SiMe}_3\text{)}_2]]\) (Scheme 1.25). Complex 127 exhibited a six-coordinated geometry, where one amide arm of each tridentate ligand remains protonated and daniling. Complex 127 undergoes a metal-center oxidation to Fe(II) species, while the NHC/amide hybrid ligands remain innocent, as confirmed by EPR and Mössbauer spectroscopy.\[^{[101]}\]

Scheme 1.25 Synthesis of complex 127 bearing two (bis-NHC)amido ligands.
Unprecedented Fe(0) NHC stabilized $\eta^6$-arene complexes were reported in 2013 by the group of Driess. Complexes 129-131 (Figure 1.20) were prepared by a simple route involving the reduction of 128 in the presence of benzene or toluene. The arene complexes demonstrated to be good precursors for the preparation of Fe(0) NHC complexes. For example, the addition of CO to 131 led to complex 132 by arene elimination.\[102\]

![Figure 1.20 Fe(0) arene complexes 128-132.](image)

Papish and co-workers, in 2013 reported the Fe(II) half-sandwich with the bulky $t$-butyl substituted bis-NHC ligand [CpFe(CO) (CH$_2$(Imid$_{Bu}$)$_2$)][ where Imid$_{Bu}$ = $3$-$t$ert-butyl-$1$H-imidazo$1$-yl-$2$(3H)-ylidene) (133). Complex 133 was prepared from the in situ free NHC generation and coordination to Fe using CpFe(CO)$_2$I in 73% yield. The crystal structure of this complex was studied by X-ray diffraction, revealing a piano-stool geometry with binding of the Cp ring in three coordination sites, the chelating bis NHC ligand in two sites, and the CO ligand.\[103\]

The bis-NHC Fe(II) halide complexes 134-137 depicted in Scheme 1.26 with flexible amine-spacers were published by group of Hazari in
2013. The reaction of the corresponding imidazolium chlorides (L32) with [Fe(N(SiMe$_3$)$_2$)$_2$] afforded complexes 134-137 in high yields (86-93%). Their molecular structures showed a distorted tetrahedral geometry with high spin Fe(II) centers.$^{[104]}$

![Scheme 1.26 Synthesis of complexes 134-137 bearing bis-NHC ligands.](image)

The semirigidity of the biphenyllinked bis-NHC ligand reported by Shi and Deng in 2014, allowed the successful preparation of the Fe(II) diaryl and diallyl complexes: biphenyl- linked bis(benzimidazol-2-ylidene)Fe(II) dichloride (138) and biphenyl- linked bis(benzimidazol-2-ylidene)Fe(II) dihydrocarbyls, denoted as bis(NHC)FeR$_2$ (R = CH$_2$TMS (139), CH$_2$Ph (140), Ph (141), C$_6$H$_3$-3,5-(CF$_3$)$_2$ (142) in good yields (73-98%yield). All complexes were fully characterized and showed a distorted tetrahedral geometries of the Fe(II) centers with high spin.$^{[105]}$

Chen and co-workers, also in 2015, reported the (bis-NHC)borane Fe(II) complex 143 (Scheme 1.27). Complex 143 was obtained by the reaction of the corresponding (bis-NHC)borane (L33) with LDA and (FeCl$_2$)$_{1.5}$THF.$^{[106]}$
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Scheme 1.27 Synthesis of complex 143.

More recently, Kühn reported a novel hydroxyl-functionalized tetradeptate NHC/pyridine hybrid ligand and the Fe(II) complexes 144 and 145 (Figure 1.21). The transmetalation of the corresponding silver bis-NHC complex bearing a pendant hydroxyl group with FeBr$_2$(THF)$_2$ afforded a mixture of the expected mononuclear Fe(II) complex 144 and a dinuclear Fe(II) complex 145. Both complexes were analyzed by ESI-MS, which proved a monomeric structure of 144 and a dinuclear structure of 145. The X-ray diffraction of single crystals of 144 and 145 showed a distorted octahedral coordination geometry.$^{[107]}$

Figure 1.21 Fe bis(NHC) complexes 144 and 145 bearing a pendant hydroxyl group.
### 1.4.1.2 Catalytic applications of Fe bis-NHC complexes

Despite the large number of Fe bis-NHC complexes that have been reported in the literature, few catalytic applications with this type of complexes have been described. In 2014, Herrmann and Kühn described the catalytic activity of Fe(II) complexes bearing tetradeutate NHC–pyridine ligands in the epoxidation of olefins\textsuperscript{108} and in the hydroxylation of toluene and benzene with hydrogen peroxide (H\textsubscript{2}O\textsubscript{2})\textsuperscript{109}. Complex 104 (Scheme 1.18) was found to efficiently catalyze the epoxidation of terminal and cyclic olefins to their corresponding epoxides using H\textsubscript{2}O\textsubscript{2} as oxidant, and without the need of acids or other additives. Alkyl-substituted olefins were epoxidized in high yields, but best yields were obtained for cyclic olefins such as cis-cyclooctene, whereas the aromatic olefins styrene and methyl styrene were less prone to epoxidation\textsuperscript{108}.

![Scheme 1.28 Catalytic epoxidation of olefins using H\textsubscript{2}O\textsubscript{2} and complex 104.](image)

The catalytic activity of complex 104 towards the hydroxylation of benzene and toluene with H\textsubscript{2}O\textsubscript{2} was also been investigated (Scheme 1.29). Benzene was hydroxylated with a high selectivity to phenol, whereas the toluene was hydroxylated to cresols with a high selectivity for the ortho- and para-position. The inverse KIE and the high regio- and chemoselectivity suggest that the mechanism of aromatic hydroxylation consisted in an electrophilic attack by an intermediate high valent Fe=O species\textsuperscript{109}.
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Scheme 1.29 Oxidation of benzene to phenol catalysed by complex 104.

Apart from these studies, the catalytic activity of 104 and related Fe complexes 113 and 119 has been investigated for the oxidation of unreactive C-H bonds.

Scheme 1.30 Catalytic oxidation of cyclohexane using complexes 104, 113 and 119 as catalysts.

Complexes 104, 113 and 119 were able to oxidizing cyclohexane with a high selectivity toward cyclohexanol and cyclohexyl hydroperoxide, with the latter being easily reduced to the alcohol by addition of triphenylphosphine. Based on the data obtained for cyclohexane, 119 was chosen as catalyst for studying the scope of the reaction, showing the broad applicability of 119 as C-H oxidation catalyst (Figure 1.22).\[99\]
Figure 1.22 Catalytic C-H bond oxidation using 119 as catalyst.

The catalytic activity of 104 for aldehyde olefination has also been investigated. Complex 104 was applied as catalyst for olefination of benzaldehyde with ethyl diazoacetate (EDA) in the presence of triphenylphosphine. The Fe complex 104 displayed a remarkable catalytic activity affording yields up to 90% with very good selectivity (≥ 94%) of E-olefin\[110\]. Same group, reported the oxidation of the non-activated arene substrates p-xylene and pseudo-cumene using H₂O₂ as the oxidant and 104 as catalyst (Scheme 1.31). Interestingly, p-xylene and pseudo-cumene were efficiently converted to the corresponding phenols and benzoquinones with high selectivity.\[111\]

Scheme 1.31 Reaction products of the catalytic oxidation of p-xylene with 104/H₂O₂.

Apart from the oxidation reactions described with tetradentate bis-NHC Fe(II) complexes, other catalytic applications reported to date with Fe bis-NHC complexes deal with reduction reactions of carbonyl
groups, in particular through hydrosilylation processes. The group of Glorius described in 2012 the use of the bis-NHC Fe(II) complex $\text{103}$ (Scheme 1.17) for the hydrosilylation of acetophenone (Scheme 1.32). Complex $\text{103}$ displayed moderate activity (56–38%) in the reduction of acetophenone with diphenylsilane ($\text{Ph}_2\text{SiH}_2$). When methyllithium was added to generate an iron-methyl species, the catalytic activity increased (95–78%). However, no conversion was observed using triethylsilane as reducing agent in the presence of $\text{103}$ with or without methyllithium.$^{[80]}$

![Scheme 1.32 Reduction of acetophenone via hydrosilylation with $\text{103}$.](image)

In 2014, Driess disclosed the excellent catalytic activity of the Fe(0) Fe($\eta$6-arene)(bis-NHC) complex $\text{131}$ (Figure 1.20) in the reduction of amides to amines with silanes (Scheme 1.33). A number of organic amides bearing different steric and electronic properties were converted into the corresponding amines in good to excellent yields (83–99%) (Scheme 1.33). Interestingly, the results obtained using $\text{131}$ as catalyst were superior in some cases than some modern benchmark systems for other Fe-based amide reduction systems.$^{[102]}$
Finally, the group of Hazari reported in 2013 the activity of a family of well-defined Fe(II) complexes of the general type Fe(bis-NHC)X₂ in homo-coupling of Grignard reagents (Scheme 1.26). All complexes exhibited high activity as pre-catalysts for the homo-coupling of Grignard reagents (Scheme 1.34). The substrate scope studies for aryl-aryl homo-coupling showed good results except when the electron withdrawing CF₃ group is in para position and using a sp hybridized alkynyl substrates in which no reaction was observed.[112]

1.5 Objectives of this work

The main goal of this thesis is the development of new organometallic complexes of Mn and Fe bearing NHC ligands and their application in catalysis. Specifically, we target the synthesis of Mn and Fe complexes bearing bis-NHC ligands and their application in three catalytic processes:

(i) electrocatalytic reduction of CO₂
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(ii) reduction of carbonyl groups with silanes
(iii) oxidation of alcohols

1.6 References

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CHAPTER 2: A HIGHLY ACTIVE N-HETEROCYCLIC CARBENE MANGANESE(I) COMPLEX FOR SELECTIVE ELECTROCATALYTIC CO₂ REDUCTION TO CO

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B.R and J.L.F directed the research. F.F and M.F.P performed all the experiments. J.L.F performed the DFT calculations. J.L.F and F.F. wrote the manuscript with inputs from all the authors. B.R, J.L.F, F.F, and M.F.P discussed the results and revised the manuscript.
2.1. Summary

This chapter reports the first purely organometallic \( \text{fac-[Mn}^\text{I}(CO)_3(bis-MeNHC)Br] } \) complex with unprecedented activity for the selective electrocatalytic reduction of CO\(_2\) to CO, exceeding 100 turnovers with excellent faradaic yields (\( \eta_{CO} \approx 95\% \)) in anhydrous CH\(_3\)CN. Under the same conditions, a maximum turnover frequency (TOF\(_{\text{max}}\)) of 2100 s\(^{-1}\) was measured by cyclic voltammetry, which clearly exceeds the values reported for other manganese-based catalysts. Moreover, the addition of water leads to the highest TOF\(_{\text{max}}\) value (ca. 320000 s\(^{-1}\)) ever reported for a manganese-based catalyst. A Mn\(^\text{I}\) tetracarbonyl intermediate was detected under catalytic conditions for the first time.
2.2. Introduction

The large-scale production of value-added chemicals and fuels from renewable energy and CO₂ as a feedstock would contribute to increasing the sustainability of our society.\cite{1} Despite the increasing number of homogeneous catalysts based on earth-abundant transition metals that are able to reduce CO₂,\cite{2} further catalyst development is needed not only to achieve high catalytic rates, better selectivity for a specific product, and long durability, but also to better understand the operative mechanisms for CO₂ reduction.

Among the different families of molecular catalysts reported to be active for selective electrochemical 2 e⁻ reductions of CO₂ to CO, metal-based porphyrins and polypyridine complexes show promising results in terms of their activity and stability\cite{1-3}. In particular, Mn fac-tricarbonyl derivatives with polypyridyl moieties are able to catalyse the production of CO from CO₂ with high faradaic efficiencies (ηCO) in the presence of Brønsted or Lewis acids (Figure 2.1).\cite{4} However, their further improvement is mainly limited to the functionalization of the bipyridyl\cite{4,5} or pyridyl\cite{6} ligands, whereas reported examples of catalysts with non-pyridyl diimine units are still rare and usually inefficient.\cite{7}

![Figure 2.1](image_url)  
*Figure 2.1* Selected Mn¹ catalysts for electrocatalytic CO₂-to-CO reduction with N^N and N^C ligands reported in the literature and complexes 1 and 2.
In this regard, N-heterocyclic carbenes (NHCs) are attractive for catalysis \[8\] owing to their strong \(\sigma\)-donor and weak \(\pi\)-acceptor properties, which lead to unique stability. However, several NHC-based molecular complexes show low efficiency in CO\(_2\) reduction and low catalyst stability,\[9\] such as tricarbonyl pyridyl-NHC Mn\(^1\) complexes (Figure 2.1).\[10\]

Herein, we explore the electrocatalytic CO\(_2\) reduction properties of the new manganese complex \([\text{Mn}(\text{CO})_3(\text{bis}^{\text{Me}}\text{NHC})\text{Br}]\) (1), bearing the readily available bidentate methylene bis(N-methylimidazolium) ligand \(\text{bis}^{\text{Me}}\text{NHC}\) (Figure 2.1). For comparative reasons, we also evaluated the catalytic properties of the \([\text{Mn}(\text{CO})_3(\text{py}^{\text{Me}}\text{NHC})\text{I}]\) complex (\(\text{py}^{\text{Me}}\text{NHC} = N\)-methyl-\(N\)-2-pyridylimidazolium; 2) under the same reaction conditions.

### 2.3. Results and discussion

#### 2.3.1 Synthesis and characterization of the Mn complex 1

Complex 1 was prepared from a reaction of the \(\text{bis}^{\text{Me}}\text{NHC}\) with \([\text{MnBr}(\text{CO})_5]\) in the presence of KO\(\text{Bu}\) and unambiguously characterized (see the appendices, Figures A2.1-A2.7). According to the IR and \(^{13}\text{C}\) NMR spectra, the Mn\(^1\) centre is facially coordinated by three CO ligands and metalated by the \(\text{bis}^{\text{Me}}\text{NHC}\) ligand, as indicated by the characteristic. \(^{13}\text{C}\) NMR signal for the carbene carbon atom at \(\delta = 189.2\) ppm. Single-crystal X-ray diffraction analysis confirmed the octahedral structure of 1 (Figure 2.2), with Mn-C\(_{\text{carbene}}\) bond lengths of 2.041–2.043(2) Å, in accordance with previously reported complexes.\[8\text{c}\]
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2.3.2 Cyclic voltammetry analysis of 1 and electrocatalytic reduction of CO₂ to CO mediated by 1

Cyclic Voltammetry (CV) analysis of 1 revealed a main reduction event at $E_p = -2.30$ V (all reduction potentials are reported vs. Fc⁺⁰⁻ unless otherwise specified), which is approximately 300 mV cathodically shifted with respect to the corresponding redox wave found for complex 2 ($E_p = -1.97$ V), reflecting the stronger electron-donating properties of the bis-MeNHC ligand. In agreement with FTIR-SEC data (see below) and previous studies,[4,10,11] the observed redox events involve a 2e⁻ reduction of 1 (or 2) to generate a five-coordinate anion, [Mn(CO)₃(bis-MeNHC)]⁻(1⁻) (or [Mn-(CO)₃(py-MeNHC)]⁻, 2⁻), after loss of the axial Br⁻ (or I⁻). An additional minor feature in the CVs of 1 ($E_p = -2.47$ V) merges with the main wave at high scan rates. CVs at different scan rates indicate reductive diffusion-limited processes for 1 (Figures A2.8-A2.10).

Under CO₂ atmosphere, CVs of 1 show a dramatic current increase at the first reduction wave (ca. 35-fold) with an onset potential at approximately -2.12 V and a current plateau at about -2.60 V (Figure 2.3). This is in sharp contrast to the behaviour of 2, which displays only a very small increase in current with a maximum at comparable
reduction potentials (-2.56 V; **Figure 2.3** and **A2.9**). Furthermore, it is worth noting that there are only a few examples of molecular Mn\(^{\text{I}}\) complexes that are able to electrocatalytically activate CO\(_2\) in anhydrous CH\(_3\)CN, and those reported have considerably lower activity than 1.\(^{[6a,11]}\)

**Figure 2.3** Electrochemical behaviour of 1 and 2 (1 mM) in anhydrous 0.1M TBAPF\(_6/\)CH\(_3\)CN electrolyte. CVs under Ar atmosphere (1 and 2: solid and dashed black lines, respectively) and under CO\(_2\)-saturated atmosphere (1: red; 2: blue) at v=0.1 Vs\(^{-1}\). The green dotted line represents the blank electrolyte under CO\(_2\).

For complex 1, the S-shaped catalytic wave, independent of the scan rate, is indicative of a purely kinetic regime for catalytic CO\(_2\) reduction. This behaviour results in a TOF\(_{\text{max}}\) of 2100 s\(^{-1}\) under CO\(_2\) atmosphere in neat CH\(_3\)CN estimated from CV (**Figures A2.11** and **A2.12**).\(^{[12]}\) Notably, the calculated TOF\(_{\text{max}}\) is more than 2000 times higher than the values reported for analogous pyridyl-NHC catalysts under more favourable conditions (CH\(_3\)CN +5% H\(_2\)O),\(^{[10a]}\) and about 50 times higher than the highest CO\(_2\) reduction TOF ever reported for an NHC-containing Mn\(^{\text{I}}\) catalyst.\(^{[10c]}\) Moreover, the TOF\(_{\text{max}}\) value of 1 is of about the same order of magnitude as the ones calculated for common bpy-based Mn\(^{\text{I}}\) complexes (**Table A2.1**).\(^{[6]}\) The linear increase in the
catalytic current with the Mn complex concentration is also consistent with the molecular nature of the catalyst (Figure A2.13).

Controlled potential electrolysis (CPE) of 1 (1 mM) under a constant CO\textsubscript{2} flow (30 mL min\textsuperscript{-1}) in anhydrous CH\textsubscript{3}CN was performed to study its durability and selectivity (Figures A2.14-A2.18). On-line gas chromatography (GC-TCD) analysis of the headspace allowed for quantification of the gaseous products. At an applied potential of -2.32 V, an average electrocatalytic current of about 2.5 mA cm\textsuperscript{-2} and linear variation of charge over time were observed throughout the experiment, leading to catalytic CO production with a high faradaic efficiency ($\eta$\textsubscript{CO}$\approx$92%), without any detectable traces of H\textsubscript{2} (Figure 2.4 A,B).

![Figure 2.4 A) The amount of CO formed during CPE experiments under CO\textsubscript{2} atmosphere with 1 and 3 at E\textsub{appl}=-2.32 V (red) and -2.57 V (blue), respectively. B) Linear correlation between the number of moles of produced CO and the electrons consumed during CPE of 1.](image)

A charge of 50 C passed over 4 h corresponds to a TON\textsubscript{CO} value of 56, without any substantial decrease in catalytic activity. Electrolysis for extended periods of time revealed prolonged catalyst durability, exceeding turnovers of 100 after 8 h with an excellent selectivity to CO. Catalytically active nanoparticles were discarded by the negligible
current observed after a “rinse test” performed after CPE. Remarkably, at a 250 mV more cathodic applied potential ($E_{\text{appl}} = -2.57$ V), the reference compound 2 showed a significantly lower electrocatalytic current (ca. 0.5 mA cm$^{-2}$) than 1 under the same experimental conditions ($CO_2$ in dry CH$_3$CN). Moreover, the average faradaic efficiency of 2 was fairly low (after 3.5 h, $\eta_{CO} \approx 22\%$, TON$_{CO} \approx 2.5$; Figure 2.4 A, A2.19, and A2.20).

### 2.3.3 Mechanistic studies of the catalytic reduction of $CO_2$ to CO

We employed FTIR-SEC to gain insight into the main species involved in the reduction catalysed by 1. Under Ar atmosphere, when the applied potential matched the reduction wave of 1 (ca. -2.30 V), the bands belonging to 1 ($\nu_{CO} = 2007, 1922, 1887$ cm$^{-1}$) started to disappear, giving rise to new CO stretches at 1827, 1731, and 1713 cm$^{-1}$, which can be assigned to the doubly reduced 1$^-$ anion.$^{[4d]}$ This assignment is corroborated by the excellent correlation between the experimental and DFT-calculated IR spectra of 1$^-$. The growth of a broad visible band ($\lambda_{\text{max}} = 527$ nm) in a UV/Vis SEC experiment is in agreement with the formation of 1$^-$ as the main species (Figures A2.22–A2.24 and Table A2.2).$^{[4a,d]}$

Taken together, these results account for the direct conversion of the initial species, 1, into five-coordinate 1$^-$, which is the predominant product formed upon reduction. Importantly, the low-energy nature of the experimental CO stretches of 1$^-$ indicates a strongly localized negative charge on the Mn atom, which is consistent with the redox innocence of the bis-MeNHC ligand. Indeed, comparison of the Kohn–Sham orbitals of 1$^+$ to those of [Mn(CO)$_5$(bis-MeNHC)] (1$^-$) and 1$^-$ shows that the reduction takes place exclusively over the metal centre. The HOMO orbital of 1$^-$, unlike that of 3$^-$, is clearly accessible to engage in a nucleophilic attack (Figure A2.34).
This is reflected by the thermodynamics of the reactions with CO₂, which are exergonic for 1 but endergonic for 3 (Scheme 2.1 and Figures A2.35-A2.41). Moreover, the rate-determining step for the catalytic cycle is the C-O cleavage, with an energy barrier as low as 20.1 kcalmol⁻¹ for 1 and a higher one for 3 (26.8 kcalmol⁻¹), in good agreement with the catalytic activity.

**Scheme 2.1** Proposed mechanism for the reduction of CO₂ to CO by 1. The energies and redox potentials (vs. SHE) given were determined by DFT calculations at the solvent-corrected B3LYP/631+g** level of theory. Mn species experimentally detected by FTIR-SEC are shown in purple.

When a solution of 1 was saturated with CO₂, bands at 1685 and 1646 cm⁻¹, related to free HCO₃⁻/CO₃²⁻, rapidly increased in intensity at the onset potential of the catalytic wave. Sustained CO evolution prevents further monitoring of the reaction. During the reduction, the CO stretches of the initial complex 1 decreased in intensity, with concomitance growth of a new set of low-intensity bands at 2090, 2002, and 1969 cm⁻¹, without any evidence for 1 formation. Differential IR
spectra confirmed the formation of a new species, which was assigned to the tetracarbonyl intermediate \([\text{Mn(CO)}_4(\text{bis-}^{\text{Me}}\text{NHC})]^+\) (1-CO\(^+\)), as corroborated also by the theoretical IR spectrum (Figures A2.23-A2.26). This is the first direct evidence for this type of intermediate under catalytic conditions. An analogous v\(_{\text{CO}}\) pattern has recently been found for a structurally similar complex, which was synthesized under CO atmosphere with a bpy-based Mn\(^{\text{II}}\) catalyst.\(^{[4e]}\)

The addition of a relatively small amount of water (0.09 M) to a CO\(_2\)-saturated solution of 1 significantly boosted the catalytic response, providing a peak-shaped CV with a maximum at -2.61 V (Figure A2.27). Trituration with different aliquots of added water to a CH\(_3\)CN solution of 1 highlighted two distinct regimes. At low water concentrations ([H\(_2\)O] = 0.09–0.56 M), the current tends to increase linearly with [H\(_2\)O], reaching a maximum activity (> 150-fold) for [H\(_2\)O] =0.56 M (Figure 2.5).

![Figure 2.5](image_url)

**Figure 2.5** Linear scan voltammograms (LSVs) of 1 (1 mM) under CO\(_2\) atmosphere in TBAPF\(_6/\)CH\(_3\)CN (0.1M) in the presence of [H\(_2\)O]=0.09 M (blue), 0.19 M (green), 0.37 M (orange), 0.46 M (violet), 0.56 M (brown), 0.74 M (grey), 1.11 M (yellow), 1.67 M (light blue), and 2.59 M (light green) at \(v=0.1 \text{Vs}^{-1}\). Inset: Peak currents under CO\(_2\) in the presence of various [H\(_2\)O] (\(i_p\)) were normalized to the peak current under Ar (\(i_{p,0}\)).
At high scan rates ($v > 50 \ \text{V s}^{-1}$), plateau-shaped catalytic voltammograms were progressively achieved,\textsuperscript{[12]} leading to a $\text{TOF}_{\text{max}}$ value of $3.2 \times 10^5 \ \text{s}^{-1}$ for 1 in wet CH$_3$CN ($[\text{H}_2\text{O}] = 0.56\text{M}$, Figure 2.6).

![Figure 2.6 LSVs of 1 (1 mM) under CO$_2$ atmosphere in TBAPF$_6$/CH$_3$CN (0.1M) in the presence of 0.56M H$_2$O at $v=0.1$ (blue), 0.5 (green), 1 (orange), 2.5 (violet), 5 (brown), 10 (grey), 20 (yellow), 50 (pink), 70 (light blue), or 100 \text{Vs}^{-1} (light green). Insets: Plot of TOF versus $v$ (0.1–100 \text{Vs}^{-1}), highlighting that steady-state conditions are reached at high scan rates ($\text{TOF}_{\text{max}}=3.2 \pm 0.1 \times 10^5 \ \text{s}^{-1}$). In (A) and (B), CVs of 1 recorded under anhydrous conditions under Ar and CO$_2$ atmosphere are shown in black and red, respectively.]

Figure 2.6 LSVs of 1 (1 mM) under CO$_2$ atmosphere in TBAPF$_6$/CH$_3$CN (0.1M) in the presence of 0.56M H$_2$O at $v=0.1$ (blue), 0.5 (green), 1 (orange), 2.5 (violet), 5 (brown), 10 (grey), 20 (yellow), 50 (pink), 70 (light blue), or 100 \text{Vs}^{-1} (light green). Insets: Plot of TOF versus $v$ (0.1–100 \text{Vs}^{-1}), highlighting that steady-state conditions are reached at high scan rates ($\text{TOF}_{\text{max}}=3.2 \pm 0.1 \times 10^5 \ \text{s}^{-1}$). In (A) and (B), CVs of 1 recorded under anhydrous conditions under Ar and CO$_2$ atmosphere are shown in black and red, respectively.

In contrast, the pyridyl-NHC complex 2 displayed only a modest increase in the catalytic current, upon increasing the water content in CH$_3$CN under CO$_2$ atmosphere, in agreement with previous reports.\textsuperscript{[10]} Nevertheless, a further increase in the water concentration rapidly reduced the catalytic current ($[\text{H}_2\text{O}] > 0.56\text{M}$, Figure 2.5). The inhibiting effect of Brønsted acids on Mn$^1$ electrocatalysts has recently been highlighted elsewhere.\textsuperscript{[4e,6a]} No electrocatalytic wave was observed with 1 under Ar atmosphere, over a wider range of H$_2$O/CH$_3$CN mixtures ($[\text{H}_2\text{O}] = 0.09$–2.60\text{M}$), suggesting selective CO$_2$ over H$^+$ reduction (Figure A2.28). In this
regard, CPE (E_{appl} = -2.32 V) of 1 (1 mM) in aqueous CH\textsubscript{3}CN (0.22 M H\textsubscript{2}O) results in quantitative CO production (\eta CO = 98\%) for more than 6 h (Figures A2.31-A2.33), without formation of H\textsubscript{2}. Nevertheless, catalyst deactivation appears to be significantly faster than under anhydrous conditions.

### 2.4. Conclusions

In conclusion we have reported here the first purely organometallic NHC-based tricarbonyl Mn\textsuperscript{I} complex with unprecedented activity for the selective electrocatalytic reduction of CO\textsubscript{2} to CO, exceeding 100 turnovers with excellent faradaic yields (\eta CO\approx 95\%) in anhydrous CH\textsubscript{3}CN. A Mn\textsuperscript{I} tetracarbonyl intermediate was detected under catalytic conditions for the first time. The replacement of a pyridine ring with an NHC unit had a significant effect on the catalytic performance, substantially improving the TOF\textsubscript{max} and selectivity for CO production of well-established C,N-ligand-based Mn systems. Furthermore, the novel bis-NHC catalyst efficiently and selectively converted CO\textsubscript{2} into CO in anhydrous aprotic organic solvents, whereas the majority of classical bpy-based systems are reported to be inactive without an explicit proton source.\textsuperscript{[7a–c,e]} The estimated TOF max for 1 upon addition of moderate amounts of water is several orders of magnitude higher than those commonly reported for Mn complexes containing functionalized polypyridyl motifs under considerably more acidic conditions.\textsuperscript{[7a–e]} Complementary FTIR-SEC measurements and computational data suggest that the strongly nucleophilic character of the Mn atom is likely responsible for the positive ligand effect on catalysis.

We believe that the unique aspects exhibited by this novel family of CO\textsubscript{2} reduction complexes, together with the synthetic viability of ligand
modification, open new perspectives for the design of more efficient molecular catalysts.

2.5. Experimental section

2.5.1 General methods and materials

Synthesis

Synthesis were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents for syntheses were dried according to published methods and distilled before use. Anhydrous CH₃CN (Sigma-Aldrich, 99.8%) stored in a glove-box was used for all the electrochemical experiments. Manipulation of Mn complexes was carried out under reduced light conditions. Tetrabutylammonium hexafluorophosphate (TBAPF₆, Aldrich, ≥ 99.0%) was dried at 100 °C in the oven for 24 h and under vacuum before use. Imidazolium salts 1,1'-methylene-3,3'-di-methylimidazolium dibromide[13] and N-methyl-N'-2-pyridylimidazolium iodide[14] were synthesized according the literature procedures. [MnBr(CO)₅] was purchased from Strem chemicals and used as received. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz. Electrospray mass spectra (ESI-MS) and elemental analyses were provided by our laboratories at ITQB. The quality of the employed Ar and CO₂ was 99.9995 % (5.5).

Electrochemistry

All the electrochemical experiments were carried out with a VSP or PS-50 potentiostat from BioLogic, equipped of the EC-Lab software.

Cyclic Voltammetry (CV)

CV measurements were performed under Ar or CO₂-saturated atmosphere using tetrabutylammonium hexafluorophosphate
(TBAPF$_6$) as supporting electrolyte (0.1 M) in CH$_3$CN. A glassy carbon (GC) working electrode (1 mm or 3 mm diameter) and a Pt wire as a counter electrode were employed in a single-compartment three-electrode setup. An Ag wire immersed in the electrolyte solution was used as a pseudo-reference and separated from the solution by a porous tip. Ferrocene (Fc) was added to the solution as an internal standard and all the potentials are referenced vs. the Fc$^{+/0}$ redox couple.

**Controlled-Potential electrolysis (CPE)**

For CPE experiments, an H-type electrochemical cell was used, in which the counter electrode is a Platinum wire immersed in a bridge tube containing a 0.2 M tetraethylammonium acetate tetrahydrate (99% Sigma -Aldrich) + 0.1 M TBAPF$_6$/CH$_3$CN electrolyte solution and separated from the main (cathodic) compartment by a ceramic frit. As a working electrode we employed a glassy carbon rod (A~1.4 cm$^2$), and a silver wire as a pseudoreference, immersed in a bridge tube containing the same electrolyte solution (0.1 M TBAPF$_6$/CH$_3$CN) and separated from the working solution by a porous tip. The redox potential of the Fc$^{+/0}$ couple was checked in a separate cell prior to and after electrolysis. To ensure saturation with Ar or CO$_2$, a constant gas flow (30 ml min$^{-1}$, fixed with a mass-flow controller, Alicat®) was continuously passed over the solution and on-line analyzed with a gas chromatography every ca. 4 minutes. An Agilent 490 micro gas chromatograph equipped with a thermal conductivity detector and a Molesieve 5Å column was calibrated with diferent H$_2$/He/CO/CH$_4$ mixtures of known composition.

**Spectroelectrochemistry**

Spectroelectrochemical experiments were carried out using an optically transparent thin-layer electrode (OTTLE) cell, equipped with
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a Pt minigrid working and auxiliary electrodes, an Ag microwire pseudo-reference electrode and a CaF₂ window. Thin layer potential sweeps were performed by a SP-50 potentiostat from Bio-Logic. UV/VIS spectra were measured with an Agilent 8453 diode array spectrophotometer (λ=190–1100 nm range). FTIR spectra were recorded on a Nicolet iS50 FT-IR spectrometer.

Computational details

We carried out the molecular modeling using DFT formalism with the Gaussian09 program. Geometry optimizations were performed in the unrestricted spin formalism, with the B3LYP hybrid exchange-correlation functional and the standard 6-31+g(d,f) 6d basis set for all atoms. The solvation effect of CH₃CN was introduced in geometry optimizations and energy through the IEFPCM-SMD polarizable continuum model. Dispersion effects were also included using the Grimme D3 correction. The geometries have been edited with the Gaussian view program. The located stationary points were characterized by analytical frequency calculations at the same level of theory than geometry optimizations.

2.5.2 Synthesis and characterization of 1 and 2

Synthesis and characterization of complex 1

MnBr(CO)₅ (0.35 g, 1.3 mmol) was suspended in THF (25 mL) and potassium tert-butoxide (0.26 g, 2.3 mmol) was first added, followed by slow addition of 1,1′- methylene-3,3′-di-methylimidazolium dibromide (0.34 g, 1 mmol) at 60 °C. The resulting suspension was heated at 60 °C for 16 h under stirring. All volatiles were removed under vacuum and the resulting residue was washed with Et₂O (4 x 20 mL) and dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (100 mL), and the organic extract was dried.
with Na$_2$SO$_4$. The solution was filtered and concentrated to dryness under vacuum to yield a yellow crystalline powder. Yield: 0.25 g (62%).

$^1$H NMR (DMSO-d$_6$, 25 °C) (Figure A2.1): δ 7.56 (s, 2H, CH$_{imid}$), 7.43 s, 2H, CH$_{imid}$), 6.61 (d, 2J$_{H-H}$ = 12 Hz, 1H, NCH$_2$N), 6.01 (d, 2J$_{H-H}$ = 12 Hz, 1H, NCH$_2$N), 3.97 (s, 6H, NCH$_3$).

$^{13}$C($^1$H) NMR (DMSO-d$_6$, 25 °C) (Figure A2.2): δ 220.33 (CO), 206.51 (CO), 189.26 (Mn-C$_{carbene}$), 123.57 (CH$_{imid}$), 121.61 (CH$_{imid}$), 61.53 (NCH$_2$N), 30.65 (NCH$_3$).

IR (KBr) (Figure A2.6): υ (CO) 2004 (s), 1912 (s), 1881 (s) cm$^{-1}$.

HRMS ESI-MS (positive mode) (Figure A2.5): 315.0 [M-Br]$^+$. Anal. Calcd. for C$_{12}$H$_{12}$MnN$_4$O$_3$Br: C, 36.48; H, 3.06; N, 14.18. Found: C, 36.92; H, 3.50; N, 13.89.

**Synthesis and characterization of 2**

MnBr(CO)$_5$ (0.37 g, 1.3 mmol) was suspended in THF (20 mL) and potassium tert-butoxide (0.15 g, 1.3 mmol) was first added, followed by slow addition of and $N$-methyl-$N'$-2-pyridylimidazolium iodide (0.30 g, 1.1 mmol) at 60 °C. The resulting suspension was heated at 60 °C for 16 h under stirring. All volatiles were removed under vacuum and the resulting residue was washed with Et$_2$O (4 x 20 mL) and dissolved in dichloromethane (90 mL). The dichloromethane solution was washed with water (90 mL), and the organic extract was dried with Na$_2$SO$_4$. The solution was filtered and concentrated to dryness under vacuum to yield a yellow crystalline powder. Yield: 0.30 g (67%).

$^1$H NMR (DMSO-d$_6$, 25 °C) (Figure A2.3): δ 8.94 (s, 2H, CH$_{imid}$), 8.48 (s, 1H, CH$_{imid}$), 8.12 (s, 2H, CH$_{Ph}$), 7.73 (s, 2H, CH$_{Ph}$), 7.42 (d, 2J$_{H-H}$ = 1), 4.02 (s, 3H, CH$_3$).

$^{13}$C($^1$H) NMR (DMSO-d$_6$, 25 °C) (Figure A2.4): δ 225.80 (CO), 222.71 (CO), 218.24 (CO), 200.86 (Mn-C$_{carbene}$), 153.61 (CH$_{Mes}$), 152.85
(CH\textsubscript{Mes}), 141.11 (CH\textsubscript{Mes}), 126.91 (CH\textsubscript{Mes}), 122.73 (CH\textsubscript{imid}), 117.03 (CH\textsubscript{imid}), 112.25 (CH\textsubscript{imid}), 37.64 (CH\textsubscript{3}).

IR (KBr) (Figure A2.7): \textit{\nu} (CO) 2009 (s), 1934 (br) cm\textsuperscript{-1}.

Anal. Calcd. For C\textsubscript{12}H\textsubscript{9}MnN\textsubscript{3}O\textsubscript{3}I: C, 33.90; H, 2.13; N, 9.88. Found: C, 34.40; H, 2.57; N, 9.96.

2.6. Acknowledgements
We would like to thank the European Commission (ERCCG-2014–648304, J.L.-F.). Financial support from the ICIQ Foundation and the CELLEX Foundation through the CELLEX-ICIQ high-throughput experimentation platform and the Starting Career Program is gratefully acknowledged. We also thank the CERCA Programme (Generalitat de Catalunya); MINECO is acknowledged for the ICIQ-IPMP program (F.F.) and Severo Ochoa Excellence Accreditation 2014–2018 (SEV-2013-0319). FCT (Portugal) is acknowledged for projects UID/Multi/04551/2013, RECI/BBBBQB/0230/2012 (NMR facilities), grant PD/BD/105994/2014 (M.F.P.), and contract IF/00346/2013 (B.R.). We also thank CARISMA, COST Action CM1205 for networking.

2.7. References
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electro catalytic CO₂ Reduction to CO


Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO


Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electro catalytic CO₂ Reduction to CO


CHAPTER 3: MANGANESE N-HETEROCYCLIC CARBENE COMPLEXES FOR CATALYTIC REDUCTION OF KETONES WITH SILANES

3.1. Summary
3.2. Introduction
3.3. Results and Discussion
   3.3.1 Synthesis and characterization of the Mn bis-NHC complexes 1 and 2
   3.3.2 Hydrosilylation of benzaldehyde and ketones catalyzed by complexes 1–5
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   3.5.1 General methods
   3.5.2 Synthesis and characterization of complexes 1 and 2
   3.5.3 Typical procedure for the hydrosilylation of benzaldehyde and ketones catalyzed by complexes 1–5
3.6. Acknowledgements
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Author Contributions

B.R directed the research. S.F. participated in the synthesis of some of the Mn complexes. M. F. P. performed the synthesis of the Mn complexes and all the catalytic experiments, including the mechanistic studies. F.F. performed the in situ FTIR spectroscopy studies. B.R wrote the manuscript with inputs from all the authors. B.R and M.F.P discussed the results and revised the manuscript.
3.1. Summary

This chapter describes the use of well-defined Mn\textsuperscript{I} carbonyl complexes bearing bis-NHC ligands as catalysts for the reduction of carbonyl groups through hydrosilylation reactions. A wide variety of ketones are selectively reduced to the corresponding alcohols by using phenylsilane, and the cheap and readily abundant polymethylhydrosiloxane (PMHS) in the presence of catalytic amounts of Mn\textsuperscript{I} organometallic complexes. Interestingly, \(\alpha,\beta\)-unsaturated ketones and dialkyl ketones are selectively reduced. Mechanistic studies based on radical scavengers suggest the involvement of radical species in the catalytic reaction.
3.2. Introduction

The last few years have witnessed a remarkable growth of interest in Mn-based catalysis.\textsuperscript{[1,2]} In particular, a number of efficient manganese catalysts have been reported for the reduction of carbonyl compounds through hydrosilylation reactions.\textsuperscript{[2,3]} The hydrosilylation reaction represents a fundamental method for the preparation of silyl ethers, and can be employed as a convenient alternative to hydrogenation when combined with a hydrolysis protocol.\textsuperscript{[4]} So far, the majority of the Mn complexes developed for catalytic reduction of carbonyl groups are coordination compounds bearing N-, O-, and P-ligands;\textsuperscript{[1a,2,3,5–8]} pure organometallic Mn-based catalysts are scarce.\textsuperscript{[1d,f]}

NHCs are a fundamental class of ligands in organometallic chemistry and catalysis. It is well recognized that their use as supporting ligands in transition-metal chemistry can provide metal complexes with enhanced catalytic performances and higher stability.\textsuperscript{[8]} However, until now, catalysis with Mn-NHC has been poorly explored.\textsuperscript{[9]} In particular, in hydrosilylation reactions, the only examples of well-defined Mn-NHC complexes were recently reported by Lugan, Sortais, and co-workers.\textsuperscript{[3g,h]}

In line with our interest in developing the organometallic chemistry and catalysis of 3d metals with NHC ligands,\textsuperscript{[10]} we decided to develop a new family of Mn carbonyl complexes bearing bis-NHCs and explore their potential in catalysis. In a recent work, we demonstrated the high catalytic efficiency of the Mn complex MnBr(CO)\textsubscript{3}(bis-NHC\textsuperscript{Me}) for the electrocatalytic reduction of CO\textsubscript{2} to CO.\textsuperscript{[11]} Here, we report our studies on the reduction of ketones by using Mn(I) compounds bearing bis-NHC, mixed NHC-pyridyl, and bipyridyl ligands, aiming to explore the effect of the introduction of NHCs in the first coordination sphere of the metal.
3.3. Results and Discussion

3.3.1 Synthesis and characterization of the Mn bis-NHC complexes 1 and 2

The synthesis of the Mn bis-NHC complexes \( \text{fac-[Mn(bis-NHC}^\text{R})(\text{CO})_3\text{Br]} \) \([\text{R=Me (1); Mes (2)}]\) was achieved by treatment of \( \text{Mn(CO)}_5\text{Br} \) with the corresponding imidazolium salts in the presence of potassium tert-butoxide (Figure 3.1 and Scheme 3.1).

![Figure 3.1 Manganese NHC complexes 1–5 explored as catalysts in the hydrosilylation of carbonyl groups.](image)

![Scheme 3.1 Synthesis of manganese NHC complexes 1 and 2.](image)

Complexes 1 and 2 are air stable; they can be stored in air for weeks without noticeable decomposition. Complexes \( \text{[Mn(NHC-py)(CO)}_3\text{Br]} \) (3) and \( \text{[Mn(bpy)(CO)}_3\text{Br]} \) (4) were prepared by following the procedure
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

reported in the literature.\textsuperscript{[12,13]} The identity of all complexes was established by analytical and spectroscopic methods. The synthesis and characterization of complex 1, including the X-ray diffraction studies, has been reported in the previous chapter.\textsuperscript{[11]} The $^{13}$C NMR spectrum of 2 (Figure A3.2) compound 2 shows a resonance at 191 ppm, indicative of a Mn-C$_{\text{carbene}}$ bond, confirming that coordination of the NHC has occurred. The IR spectrum of 2 (Figure A3.5) displays characteristic carbonyl stretching bands (at 2007, 1923, and 1887 cm$^{-1}$) for three CO ligands coordinated to Mn in a facial fashion, two carbonyls located trans to the NHC ligands, and the third CO situated trans to the bromide ligand.\textsuperscript{[14]} As expected, complex 2 exhibited lower energy carbonyl bands than those of 3 and 4, consistent with the expected effect of the strong donating NHC ligand versus the mixed pyridyl-NHC and the bipyridyl ligand. In addition, the weaker donating character of the NHC bearing a mesityl wingtip in 2 compared with the methyl group in 1 is reflected in their IR spectra (Figure A2.6) (2004, 1912, and 1881 cm$^{-1}$).

In addition, the cationic complex [Mn(CO)$_3$(bis-NHC$_{\text{Me}}$)(NCMe)][BF$_4$] (5), was prepared by treatment of 1 with one equivalent of AgBF$_4$ in acetonitrile (Scheme 3.2). Complex 5 was isolated as a brown, stable solid, which can be handled in air. The infrared spectrum of 5 (Figure A3.6) shows, as expected, the characteristic pattern of a tricarbonyl complex, displaying the symmetric CO stretching frequency at 2020 cm$^{-1}$, at a higher value than that displayed by the neutral complex 1 (2004 cm$^{-1}$).\textsuperscript{[11]}
3.3.2 Hydrosilylation of benzaldehyde and ketones catalyzed by complexes 1–5

The hydrosilylation of benzaldehyde was selected as a benchmark reaction for an initial screening of the Mn$^1$ catalysts 1–4 by using phenylsilane as reducing agent. Initially, reactions were performed in benzene at 80°C by using 1 mol % of catalyst. Conversion of benzaldehyde to the corresponding silyl ether was monitored by $^1$H NMR spectroscopy. When the reaction was completed, hydrolysis with aqueous NaOH (2M) solutions, followed by extraction with dichloromethane allowed the isolation of the corresponding alcohols. Results are summarized in Table 3.1. Excellent aldehyde conversions were achieved for complexes 1–3 bearing NHC ligands (entries 2, 4, 6, Table 3.1). Interestingly, the presence of the strong donating NHC ligands improves the catalytic efficiency (1–3 versus 4). Complex 4, bearing a bipyridyl ligand, resulted in the least active catalyst, affording a moderate yield of benzyl alcohol (53 %) after 24 h (entry 8, Table 3.1). Complexes 1–3 displayed comparable activity, achieving high yields of benzyl alcohol in 16 h; although a slight decrease in activity in the series 1$>$2$>$3 was observed after 6 h of reaction (entries 1, 3, 5, 7, Table 3.1). These results suggest that increasing the donor properties of the chelating $C_{\text{NHC}}$,$C_{\text{NHC}}$/$C_{\text{NHC}}$,$N_{\text{byp}}$ fragment in [LMn(CO)$_3$Br] (L= bisNHC, NHC-py) complexes, makes the Mn$^1$ center more electron
rich, facilitating the activation of silane. A blank experiment in the absence of a Mn complex under identical conditions did not yield any detectable conversion of benzaldehyde (entry 9, Table 3.1).

Table 3.1 Hydrosilylation of benzaldehyde catalyzed by complexes 1–4. [a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>t [h]</th>
<th>Yield [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>6</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>16</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>6</td>
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</tr>
<tr>
<td>4</td>
<td></td>
<td>16</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>6</td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>16</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>6</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>24</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>24</td>
<td>0</td>
</tr>
</tbody>
</table>

[a] All reactions were performed with 1 mmol of benzaldehyde and 1.2 mmol of phenylsilane by using 1 mol % of catalysts 1–4 at 80°C in benzene (0.4 mL). [b] Yields were determined by ¹H NMR spectroscopy by using n-tetradecane as an internal standard after basic hydrolysis.

Encouraged by the efficiency of complex 1 in the hydrosilylation of benzaldehyde, we decided to investigate its catalytic activity in the reduction of acetophenone and evaluate the effect of the solvent on the catalysis. Full conversion of acetophenone was observed when using 1 and PhSiH₃ in benzene after 20 h at 80°C (entry 1, Table 3.2). Interestingly, the reaction proceeded similarly in THF and neat conditions (entries 2 and 3, Table 3.2), but a dramatic increase in the reaction rate was observed when the reaction was performed in acetonitrile, affording quantitative yield in 5 h. Attempts to reduce the temperature of the reaction and catalyst loading resulted in a decrease in the yield of 1-phenylethanol (53 % yield at 60°C, and 37 % yield when using 0.5 mol % of 1 in 5 h).
Interestingly, complex 5 displayed higher catalytic activity than 1 in the hydrosilylation of acetophenone when using phenylsilane as a reducing agent. As illustrated in Table 3.3, under similar conditions, quantitative conversion of acetophenone was obtained after 1 h, whereas 5 h were needed for complex 1 to reach full conversion (entries 1 and 2).

The scope of the reaction was explored by using complexes 1 and 5. All ketone substrates were converted within 1–5 h when using 5, whereas 1 needed slightly longer reaction times (2–8 h), depending on the substrates. Both catalysts 1 and 5 tolerated fluoro, chloro, and bromo functionalities (entries 3–10, Table 3.3), in contrast with other Mn-based catalysts, reported to be inactive in the presence of chloro- and bromo-substituents.\[^{[3g]}\] For the \( p \)-iodo-benzaldehyde, reductive dehalogenation occurred and formation of 1-phenyethanol was detected by NMR spectroscopy. Ketones bearing electron-donating substituents such as methoxy and methyl groups in the \( para \) position were fully reduced and the corresponding alcohols obtained in high yields (entries 15–18, Table 3.3). Reduction of 4-nitro-acetophenone was also selective, achieving a good yield of the corresponding alcohol after 3–4 h. Interestingly, both 1 and 5 were capable of reducing

### Table 3.2 Hydrosilylation of acetophenone catalyzed by 1.\[^{[a]}\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>( t ) [h]</th>
<th>Yield [%][^{[b]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>benzene</td>
<td>20</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>20</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>neat</td>
<td>24</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>acetonitrile</td>
<td>5</td>
<td>99</td>
</tr>
</tbody>
</table>

\[^{[a]}\] All reactions were performed with 1 mmol of acetophenone and 1.2 mmol of phenylsilane by using 1 mol % of catalyst 1 at 80°C in 0.4 mL of solvent. \[^{[b]}\] Yields were determined by \(^1\text{H}\) NMR spectroscopy by using \( n \)-tetradecane as an internal standard after basic hydrolysis.
aliphatic ketones, cyclic and linear, including the selective reduction of 
trans-4-phenyl-3-buten-2-one (entries 19–28, Table 3.3). All yields 
were consistently very good to excellent, ranging between 72 and 99 
% isolated yields. Unfortunately, our catalytic system was inactive 
towards the reduction of esters under similar reaction conditions.

Table 3.3 Hydrosilylation of ketones catalyzed by 1 and 5 with PhSiH₃.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>t [h]</th>
<th>Yield [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>1</td>
<td>5</td>
<td>97 (92)</td>
</tr>
<tr>
<td>2</td>
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<td>5</td>
<td>1</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1</td>
<td>5</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>5</td>
<td>1</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1</td>
<td>3</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>5</td>
<td>2</td>
<td>97 (93)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1</td>
<td>2</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>5</td>
<td>2</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>1</td>
<td>8</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>5</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>1</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>5</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>1</td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>5</td>
<td>3</td>
<td>83</td>
</tr>
</tbody>
</table>
### Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

| 15 | ![Structure](structure15.png) | 1 | 4 | 93 |
| 16 | ![Structure](structure16.png) | 5 | 3 | 95 |
| 17 | ![Structure](structure17.png) | 1 | 6 | 72 |
| 18 | ![Structure](structure18.png) | 5 | 3 | 86 |
| 19 | ![Structure](structure19.png) | 1 | 5 | 72 |
| 20 | ![Structure](structure20.png) | 5 | 4 | 92 (85) |
| 21 | ![Structure](structure21.png) | 1 | 8 | 91 |
| 22 | ![Structure](structure22.png) | 5 | 5 | 93 (93) |
| 23 | ![Structure](structure23.png) | 1 | 5 | 94 |
| 24 | ![Structure](structure24.png) | 5 | 2 | 99 |
| 25 | ![Structure](structure25.png) | 1 | 8 | 93 |
| 26 | ![Structure](structure26.png) | 5 | 5 | 91 (88) |
| 27 | ![Structure](structure27.png) | 1 | 8 | 89 |
| 28 | ![Structure](structure28.png) | 5 | 4 | 93 |

[a] All reactions were performed with 1.0 mmol of substrate and 1.2 mmol of PhSiH$_3$ in acetonitrile (0.4 mL) at 80$^\circ$C and with 1 mol % of catalyst.

[b] Yields were determined by $^1$H NMR spectroscopy by using $n$-tetradecane as an internal standard after basic hydrolysis. Isolated yields are indicated in parenthesis.

To determine the highest attainable turnover frequencies (TOFs) and turnover numbers (TONs) for 5-catalyzed ketone hydrosilylation, the catalyst loading was reduced to 0.1 mol %, reaching a TOF number of 320 h$^{-1}$ (calculated at 90 min of reaction, kinetic profile in Figure 3.2), and a TON of 1000 (in acetonitrile at 80$^\circ$C). The TON value is comparable to those obtained by the scarce Mn-NHC complexes known to catalyze this reaction (TON up to 960 reported in the literature).
for \([\text{CpMn(CO)}_2(\text{NHC})])^{[9h]}\) but is lower than the best performing Mn catalysts reported in the literature (TOF of up to 76 800 h\(^{-1}\) reported by Trovitch and co-workers).\(^{[2]}\)

![Figure 3.2 Kinetic profile of the reduction of acetophenone (1 mmol) with PhSiH\(_3\) (1.2 mmol) in the presence of catalyst 5 (0.1 mol\%) in acetonitrile at 80 °C.](image)

We have also explored the applicability of the method by using other silanes, such as Ph\(_2\)SiH\(_2\) and Ph\(_3\)SiH. Both silanes afforded the reduction of acetophenone in good yields, 94% and 89%, respectively, in 8 h in the presence of catalyst 5. Gratifyingly, we observed that hydrosilylation could be performed by using the cheap and readily available PMHS as a reducing agent. When the reactions were done with PMHS, catalyst 1 displayed higher activity than 5 (80% versus 64% yield of 1-phenylethanol in 8 h, when using 1 and 5, respectively), achieving moderate to good yields and selectivities for the reduction of a wide variety of substrates, including both aromatic and aliphatic ketones. Results are summarized in Table 3.4.
**Table 3.4** Hydrosilylation of ketones catalyzed by 1 with PMHS.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Yield [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Substrate 1" /></td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Substrate 2" /></td>
<td>88 (82)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Substrate 3" /></td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Substrate 4" /></td>
<td>65 (58)</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Substrate 5" /></td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Substrate 6" /></td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Substrate 7" /></td>
<td>75 (72)</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Substrate 8" /></td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9.png" alt="Substrate 9" /></td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10.png" alt="Substrate 10" /></td>
<td>69</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11.png" alt="Substrate 11" /></td>
<td>65</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Reaction conditions: 1 mol% of 1, 10 mol% of PMHS, toluene, 80°C, 30 min.

\(^{[b]}\) Yields are given for both the hydrosilylation product and the original substrate.
Prompted by the observation that acetonitrile accelerates the hydrosilylation reaction rate, we decided to investigate the influence of radical traps on the catalytic rates. The catalytic reduction of acetophenone with PhSiH$_3$ (1.2 equiv) when using 5 (1 mol%) was performed in the presence of a variety of spin-traps. Interestingly, the presence of Ph$_2$NH, CBrCl$_3$, and 2,2,6,6-tetramethylpiperidin N-oxide (TEMPO) radical scavengers of oxygen, carbon, and silyl, respectively, strongly inhibited the reaction. As shown in Table 3.5, hydrosilylation of acetophenone in the presence of 1 mol% of Ph$_2$NH, CBrCl$_3$, and TEMPO afforded only 11, 14, and 26% conversion in 1 h, respectively, whereas in the absence of radical scavengers, full conversion was obtained (entries 1, 4, 7, 10, Table 3.5). However, the reaction resumed and reached quantitative conversions after 8 h when TEMPO and Ph$_2$NH were present, and it afforded 44% conversion in the presence of CBrCl$_3$. These observations indicated the involvement of radical species as intermediates in the catalytic reaction.

<table>
<thead>
<tr>
<th>12</th>
<th><img src="" alt="Chemical Structure" /></th>
<th>91 (88)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td><img src="" alt="Chemical Structure" /></td>
<td>63</td>
</tr>
<tr>
<td>14</td>
<td><img src="" alt="Chemical Structure" /></td>
<td>64 (58)</td>
</tr>
</tbody>
</table>

[a] All reactions were performed with 1.0 mmol of substrate and 1.2 mmol of PhSiH$_3$ by using 1 mol% of 1 in acetonitrile at 80°C for 8 h. [b] Yields were determined by $^1$H NMR spectroscopy by using n-tetradecane as an internal standard after basic hydrolysis. Isolated yields are indicated in parenthesis.

### 3.3.3 Mechanistic studies

Prompted by the observation that acetonitrile accelerates the hydrosilylation reaction rate, we decided to investigate the influence of radical traps on the catalytic rates. The catalytic reduction of acetophenone with PhSiH$_3$ (1.2 equiv) when using 5 (1 mol%) was performed in the presence of a variety of spin-traps. Interestingly, the presence of Ph$_2$NH, CBrCl$_3$, and 2,2,6,6-tetramethylpiperidin N-oxide (TEMPO) radical scavengers of oxygen, carbon, and silyl, respectively, strongly inhibited the reaction. As shown in Table 3.5, hydrosilylation of acetophenone in the presence of 1 mol% of Ph$_2$NH, CBrCl$_3$, and TEMPO afforded only 11, 14, and 26% conversion in 1 h, respectively, whereas in the absence of radical scavengers, full conversion was obtained (entries 1, 4, 7, 10, Table 3.5). However, the reaction resumed and reached quantitative conversions after 8 h when TEMPO and Ph$_2$NH were present, and it afforded 44% conversion in the presence of CBrCl$_3$. These observations indicated the involvement of radical species as intermediates in the catalytic reaction.
In addition to the spin-trap experiments, cyclopropyl phenyl ketone was employed as a mechanistic probe of intermediate radical species involvement. In fact, formation of the cyclopropyl ring-opening products would indicate a radical mechanism, allowing us to differentiate between heterolytic and homolytic pathways for reduction.\textsuperscript{[16]} If cyclopropyl phenyl ketone is reduced by the hydride transfer mechanism, it yields phenylcyclopropylcarbonol \textbf{A} (Scheme 3.3), whereas the homolytic pathway, based on the formation of a ketyl intermediate, would provide the open-chain phenyl propyl ketones \textbf{B} and \textbf{C} as final products (Scheme 3.3).

\begin{table}[h]
\centering
\caption{Effect of addition of spin-traps in the hydrosilylation of acetophenone catalyzed by 5.\textsuperscript{[a]}}
\begin{tabular}{lll}
\hline
Entry & Spin-trap & t [h] & Yield [%]\textsuperscript{[b]} \\
\hline
1 & & 1 & 11 \\
2 & \textbf{Ph}_2\textbf{NH} & 3 & 30 \\
3 & & 8 & >99 \\
4 & & 1 & 14 \\
5 & \textbf{CBrCl}_3 & 3 & 28 \\
6 & & 24 & 44 \\
7 & & 1 & 26 \\
8 & \textbf{TEMPO} & 3 & 64 \\
9 & & 8 & 93 \\
10 & ____ & 1 & >99 \\
\hline
\end{tabular}
\begin{flushleft}
\textsuperscript{[a]} All reactions were performed with 1 mmol of acetophenone and 1.2 mmol of phenylsilane by using 1 mol\% of catalyst 5, and 1 mol\% of radical scavenger at 80\textdegree C in acetonitrile (0.4 mL). \textsuperscript{[b]} Yields were determined by \textsuperscript{1}H NMR spectroscopy by using \textit{n}-tetradecane as an internal standard after basic hydrolysis.
\end{flushleft}
\end{table}
In our studies with complex 5, the hydrosilylation reaction of cyclopropyl phenyl ketone afforded, after hydrolysis, a complex mixture in which the ringopening product β-ethyl styrene (C) and cyclopropyl phenyl methanol (A) were detected in a C/A ratio of 1:2.8 (Figure 3.3). The presence of C, unequivocally indicates the involvement of a radical pathway. Our findings differ from the Mn-based catalysts reported in the literature, in which the classical Ojima-like mechanism has been proposed to be operative.\textsuperscript{[3a,d,e]} Trovitch and colleagues elegantly proved that the concurrent modified Ojima and Mn–H insertion mechanisms were responsible for catalysis with a Mn\textsuperscript{0} catalyst.\textsuperscript{[3a,d]} Identification of Mn–H species was also achieved by Lugan, Sortais, and co-workers with CpMn(NHC)(CO)\textsubscript{2} systems.\textsuperscript{[3g,h]} In contrast, a radical transfer mechanism has been proposed by Trovitch and co-workers with a Mn complex bearing a redox-active ligand.\textsuperscript{[3]}
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Figure 3.3 $^1$H NMR spectrum of the reduction of cyclopropyl phenyl ketone (1 mmol) with PhSiH$_3$ (1.2 mmol) in the presence of catalyst 5 (0.1 mol%) in acetonitrile at 80 °C.

Further experiments were performed to get an insight into the mode of activation of the Mn-NHC catalyst. The stoichiometric reaction of 5 and acetophenone in a molar ratio 1:1 did not display any observable change, neither by NMR nor by UV/Vis spectroscopy. Treatment of complex 5 with two equivalents of PhSiH$_3$ in acetonitrile at 80°C over 2 h, produced a rapid color change from brownish to grey. As shown in the Figure 3.4, formation of a new Mn complex featuring a $^1$H NMR signal at -6.8 ppm was detected. The signal at -6.8 ppm could be indicative of the formation of Mn–H or Mn(η$_2$-H-SiH$_2$Ph) species.$^{[3g,h]}$ In an attempt to characterize Mn–H species, the reaction of 5 with LiEt$_3$BH$_4$ was performed without success.
Finally, the stoichiometric reaction of 5 with phenylsilane in THF was monitored in a high-pressure sealed reactor by FTIR spectroscopy. The temperature of the reactor was controlled externally with a thermocouple and progressively increased. At room temperature (20°C), the typical CO stretches of 5 at 2025, 1935, 1925 cm⁻¹ are observed in the spectrum, together with the $\nu_{\text{Si-H}}$ band at 2158 cm⁻¹ and a new set of signals (2007, 1925, 1879 cm⁻¹), most likely corresponding to a new carbonyl Mn species. Increasing the temperature favors the formation of the new species at the expense of 5 being predominant at 80°C. The new compound showed the typical pattern of a facial tricarbonyl compound without loss of any CO ligand. This finding contrasts with CpMn(NHC)(CO)₂ compounds, in which dissociation of a CO ligand precedes activation of silane.\[^{3g,h}\]
3.4. Conclusions

We have reported Mn\(^{1}\) NHC complexes for the effective catalytic reduction of ketones groups by using silanes as reducing agents, including polymethylhydrosiloxane, which is an inexpensive, easy to handle, and environmentally friendly byproduct of the silicone industry. Interestingly, the Mn NHC complexes are air stable and catalytic experiments are performed under atmospheric air. The reduction reaction is compatible with aromatic and aliphatic ketones bearing a wide variety of functional groups. We have demonstrated that the presence of NHC ligands in the coordination sphere of Mn produces an enhancement of the catalyst performance. It is expected that the enormous flexibility of NHC ligands will allow a significant optimization of these promising catalysts. Ongoing studies in our group are focusing on the synthesis of Mn NHC compounds with improved catalytic efficiencies, and further development of the methodology to other applications.

3.5. Experimental Section

3.5.1 General methods

The synthesis of Mn complexes was performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were purified from appropriate drying agents and distilled under nitrogen. Deuterated solvents were degassed and stored over molecular sieves. The imidazolium salt 1,1’-methylene-3,3’-di-mesitylimidazolium dibromide\(^{[17]}\) and the Mn complexes [Mn(bpy)(CO)\(_3\)Br]\(^{[13]}\) [Mn(NHC-py)(CO)\(_3\)Br]\(^{[12]}\) and [Mn(bisNHC\(_{Me}\))(CO)\(_3\)Br]\(^{[11]}\) were synthesized according to the methods described in the literature. All other reagents were purchased from commercial suppliers and used without further purification. \(^1\)H and \(^{13}\)C NMR spectra were recorded with a Bruker Avance III 400 MHz. Assignment of resonances was made from HMQC
and HMBC experiments. Electrospray mass spectra (ESI-MS) were recorded with a Micromass Quatro LC instrument; nitrogen was employed as a drying and nebulizing gas. Elemental analyses were performed in our laboratories at ITQB.

3.5.2 Synthesis and characterization of complexes 2 and 5

Preparation and characterization of 2

Solid MnBr(CO)$_5$ (0.19 g, 0.7 mmol) was suspended in THF (15 mL) and potassium tert-butoxide (0.14 g, 1.2 mmol) was added first, followed by addition of 1,1’-methylene-3,3'-di-mesitylimidazolium dibromide (0.30 g, 0.55 mmol) at 60°C. The resulting suspension was heated at 60°C for 16 h under stirring. All volatiles were removed under vacuum and the resulting residue was washed with Et$_2$O (4x15 mL) and dissolved in dichloromethane (80 mL). The dichloromethane solution was washed with water (80 mL) and the organic extract was dried with Na$_2$SO$_4$. The solution was filtered and concentrated to dryness under vacuum to yield a yellow crystalline powder. Yield: 0.15 g (45% yield).

$^1$H NMR ([D$_6$]DMSO, 25°C) (Figure A.3.1): $\delta$= 7.83 (s, 2H, CH$_{imid}$), 7.36 (s, 2H, CH$_{imid}$), 7.01 (s, 2H, CH$_{Ph}$), 6.96 (s, 2H, CH$_{Ph}$), 6.78 (d, $\text{J}_{H-H}$=12 Hz, 1H, NCH$_2$N), 6.43 (d, $\text{J}_{H-H}$=12 Hz, 1H, NCH$_2$N), 2.28 (s, 6H, CH$_3$), 2.07 (s, 6H, CH$_3$), 1.82 ppm (s, 6H, CH$_3$).

$^{13}$C NMR ([D$_6$]DMSO, 25°C) (Figure A.3.2): $\delta$=223.99 (CO), 217.91 (CO), 191.63 (Mn-C$_{carbene}$), 138.32 (C$_{ipso}$), 136.64 (C$_{ipso}$), 136.00 (C$_{ipso}$), 135.16 (C$_{ipso}$), 128.69 (C$_{Ph}$), 128.50 (C$_{Ph}$), 123.33 (CH$_{imid}$), 123.04 (CH$_{imid}$), 61.79 (NCH$_2$N), 20.64 (CH$_3$), 18.03 (CH$_3$), 17.46 ppm (CH$_3$).

IR(KBr) (Figure A3.5): $\tilde{\nu}$(CO)=2007 (s), 1923 (s), 1887 cm$^{-1}$ (s).

In addition, the data relatively on mass spectroscopy and elemental analysis, to complete the characterization of complex 2. HRMS ESI-
MS (positive mode): 523 [M-Br]+; Elemental analysis calcd (%) for C_{28}H_{28}MnBrN_{4}O_{3}Br: C 55.73, H 4.68, N 9.28; found: C 55.40, H 4.61, N 8.90.

**Preparation and characterization of 5**

AgBF_{4} (0.14 g, 0.73 mmol) was added to a solution of 1 (0.26 g, 0.66 mmol) in NCMe (15 mL), and the reaction mixture was stirred at room temperature overnight. The solution was filtered, and the filtrate was concentrated to dryness under vacuum. The residue was washed with diethyl ether and dried under vacuum to afford 0.20 g (72% yield) of crystalline brown solid.

^{1}H NMR (CD_{3}CN, 250°C) (**Figure A3.3**): δ=7.41 (s, 2H, CH_{imid}), 7.21 (s, 2H, CH_{imid}), 6.11 (d, 2J_{H-H}=12 Hz, 1H, NCH_{2}N), 6.01 (d, 2J_{H-H}=12 Hz, 1H, NCH_{2}N), 3.93 ppm (s, 6H, NCH_{3}).

^{13}C NMR (CD_{3}CN, 250°C) (**Figure A3.4**): δ=220.99 (CO), 218.29 (CO), 188.28 (Mn-C_{carbene}), 124.93 (CH_{imid}), 123.13 (CH_{imid}), 63.07 (NCH_{2}N), 38.37 ppm (NCH_{3}).

IR (KBr) (**Figure A3.6**): δ (CO)=2020 (s), 1928 cm^{-1} (s).

HRMS ESI-MS (positive mode) (**Figure A3.7**): 356.0 [M-BF_{4}]^{+} and 315.0 [M-NCMe-BF_{4}]^{+}.

Elemental analysis calcd (%) for C_{14}H_{15}MnN_{5}O_{2}: C 37.95, H 3.41, N 15.81; found: C 37.81, H 3.21, N 15.90.

**3.5.3 Typical procedure for the hydrosilylation of benzaldehyde and ketones catalyzed by complexes 1–5**

An open-air flask was charged with catalyst (1 mol%) and solvent (0.4 mL). Then, silane (1.2 equiv) and the corresponding substrate (1 mmol) were added. The reaction mixture was stirred and heated at 80°C. The progress of the reactions was monitored by taking aliquots of the reaction mixtures and subjecting them to ^{1}H NMR spectroscopy.
in chloroform-d. Conversion was determined by $^1$H NMR spectroscopy by using $n$-tetradecane as an internal standard. At the end of the reaction, MeOH (1 mL) and 2M NaOH (10 mL) were added consecutively under vigorous stirring. The reaction mixture was stirred overnight at room temperature and was extracted with dichloromethane (3x10 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under vacuum to afford the isolated product. For some representative samples, the final products were isolated by following same experimental procedure (reactions were performed in the absence of internal standard), dried, and weight to calculate the isolated yields.

3.6. Acknowledgements

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3.7. References

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CHAPTER 4: (DI)TRIAZOLYLIDENE MANGANESE COMPLEXES IN CATALYTIC OXIDATION OF ALCOHOLS

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4.3. Results and Discussion
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Author Contributions
B.R directed the research. M.F.P performed all the experimental work including the synthesis of ligands, Mn complexes, characterization of the complexes and catalytic essays. M.O and A.V. performed the voltammetry studies and the *in situ* IR. G.G.-B., M.O and A.V. sent some samples of ligands for initial screening. B.R wrote the manuscript with inputs from all the authors. B.R, M.A and M.F.P discussed the results and revised the manuscript.
4.1. Summary

This Chapter describes the synthesis of a new family of carbonyl manganese complexes bearing chelating or bridging mesoionic di(1,2,3-triazolylidene) ligands, and their application as catalysts for the oxidation of alcohols to ketones and aldehydes. All complexes have been fully characterized including the X-ray diffraction study of a bimetallic Mn(0) complex. This unprecedented bimetallic complex displayed high yield and selectivity in the catalytic oxidation of secondary alcohols and benzyl alcohol with tert-butyl hydroperoxide (TBHP) under mild conditions.
4.2. Introduction

Mn complexes have emerged in the last few years as excellent catalysts for numerous transformations.[1] The vast natural abundance of Mn—it is the third most abundant metal in Earth’s crust—together with its low price and non-toxicity render it a particularly attractive alternative to expensive noble metals in catalysis. Moreover, Mn offers facile access to multiple oxidation states, and it can accommodate up to seven ligands in its first coordination sphere, hence providing a large window of reactivity. Recent work of Beller,[2] Kempe,[3] Milstein,[4] Kirchner,[5] Trovitch,[1h,6] Turculet,[7] and other groups[8] have demonstrated the great potential of Mn complexes in hydrogenation, hydrosilylation, and hydrogen transfer processes. Mn catalysed oxidation reactions have mainly focussed on alkene epoxidation and bio-inspired C–H functionalisations with coordination compounds featuring nitrogen- and oxygen-based ligands.[9,1b] More recently, alcohol dehydrogenation has been demonstrated with Mn-based catalysts, though the carbonyl products were either directly trapped for oxidative coupling reactions,[2–8] or further oxidized. Only very few Mn complexes are known to catalyse the oxidation of alcohols,[10,11] and the selective formation of aldehydes is still a challenge.[11c]

We hypothesized that selective alcohol oxidation with Mn may be imparted by mesoionic 1,2,3-triazolylidene (trz) ligands, a subclass of NHCs,[12] which offer attractive opportunities for oxidation catalysis. They can act as electron reservoirs in redox transformations,[13] and additionally, their strong σ-donor capability may facilitate the stabilisation of high oxidation states in transition metals. In comparison with noble metals, the synthesis of 1,2,3-triazolylidene complexes of first-row transition metals and their application in catalysis have been scarcely studied.[14,15] Noteworthy is the application of well-defined triazolylidene copper complexes in catalytic [3 + 2] cycloaddition
between azides and alkynes. The only other examples in base-metal catalysis with trz ligands are limited to the electrocatalytic production of hydrogen mediated by a trz Co complex, and the recent examples reported by some of us using Fe and Ni complexes in hydrosilylation and C–C bond formation reactions.

In Chapters 2 and 3, we described the activity of fac-[Mn(bis-NHCR)(CO)₃Br] (R = methyl, mesityl) complexes in the selective electrocatalytic reduction of CO₂ to CO and in the reduction of aldehydes and ketones through hydrosilylation reactions. One of the most interesting features of this new type of complexes is their air and moisture stability, which allows catalytic experiments to be performed in an open flask. Encouraged by these results, we decided to investigate the coordination chemistry of di(1,2,3-triazolylidenes) to Mn and evaluate their performance in catalysis.

4.3. Results and Discussion

4.3.1 Synthesis and characterization of Mn complexes 2 and 3

The monometallic Mn(I) complex [Mn(CO)₃(ditrz)Br] (2) containing a bidentate chelating di(triazolylidene) ligand was prepared in 48% yield from ditriazolium triflate salt 1a₁₂d which was subjected to anion exchange for bromide followed by treatment with Mn(CO)₅Br in the presence of 2 equiv. of KOtBu (Scheme 4.1). Surprisingly, when the same reaction protocol was applied to the ditriazolium triflate salt 1b₁₂e bearing an ethyl group on N1 rather than the mesityl group as in 1a, the bimetallic Mn(0) complex [Mn₂(CO)(μ-di-trz)] (3) with the two metal centers bridged by the di(triazolylidene) ligand was isolated from the reaction in 52% yield with indication of concomitant bromine formation. Both complexes 2 and 3 are air- and moisture-stable at ambient temperature and were fully characterised using NMR and FTIR.
spectroscopy, elemental analysis, and in the case of 3 by X-ray crystallography.

**Scheme 4.1** Synthesis of manganese complexes 2 and 3 (Mes = 2,4,6-trimethylphenyl; Et = ethyl).

The molecular structure of complex 3 (Figure 4.1) features two formally zero-valent Mn centers in a slightly distorted octahedral geometry with a Mn–Mn bond length of 2.9389(4) Å, comparable to the distance observed in Mn₁₂(CO)₁₀\(^{[21]}\) and consistent with the presence of a formal single bond required to account for the favored 18-electron configuration of both Mn centers. The Mn–Ctrz bond length in 3 is 2.044(15) Å, comparable to that observed in tris(trz)borate-Mn(CO)₃ the only example of a triazolylidene Mn complex reported in the literature.\(^{[15]}\)
The spectroscopic features of 3 are consistent with the crystallographically determined structure. The (di) triazolylidene ligand displays a single set of resonances, as expected for a highly symmetric complex, with a resonance at 4.15 ppm for the N–CH₃ protons and a set of resonances for the ethyl wingtip group at 4.77 and 1.63 ppm (Figure A4.4). The Mn–C_{trz} resonance is observed at 181.2 ppm in the ^{13}C NMR spectrum (Figure A4.5). The carbonyl ligands in 3 give rise to three strong IR bands at 1971, 1912 and 1881 cm⁻¹ and a relatively weak band at 2035 cm⁻¹, (Figure A4.6) in accordance with reported data for C₂-symmetric tetracarbonyl dimers of Mn.²² In contrast, the IR spectrum of 2 (Figure A4.3) showed the expected pattern for a fac tricarbonyl species with three bands corresponding to the CO stretching frequencies at 2005, 1918, and 1884 cm⁻¹, at lower wavelengths than those reported for the imidazole-2-ylidene analogue fac-[Mn(bis-NHC_{Mes})(CO)₃Br] (2007, 1923, and 1887 cm⁻¹) (Figure A3.5), indicating stronger donor properties of the triazolylidene vs. imidazole-2-ylidene ligand.⁸c The carbonic carbon of the Mn(I) complex 2 resonates at lower field than that in the Mn(0) complex 3 (δ_C

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**Figure 4.1** X-ray crystal structure of 3. Hydrogen atoms are omitted for clarity; selected bond lengths: Mn1–Mn1a 2.9389(4) Å, Mn1–C1 2.0440(15) Å.
196.3 vs. 181.2 ppm, (Figure A4.5) as expected for a higher metal oxidation state.

**4.3.2 Catalytic activity in the oxidation of alcohols**

The new complexes 2 and 3 were evaluated as catalyst precursors for the oxidation of selected alcohols with TBHP as oxidant. First, the reaction conditions were optimised using 1-phenylethanol as a model substrate and complex 3 as catalyst (Table 4.1). Initially, the reaction was carried out in MeCN at 80°C with a catalyst loading of 1 mol% and using TBHP in slight excess (1: 1.5 ratio of substrate/oxidant). Under these conditions 3 induced quantitative conversion of 1-phenylethanol to acetophenone in 2 h (Table 4.1, entry 1).

**Table 4.1 Oxidation of 1-phenylethanol with complex 3**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>t (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>80</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>60</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>MeCN</td>
<td>40</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>MeCN</td>
<td>25</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>25</td>
<td>24</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>CH₂Cl₂</td>
<td>40</td>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>CH₂Cl₂</td>
<td>40</td>
<td>24</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8</td>
<td>CHCl₃</td>
<td>40</td>
<td>2</td>
<td>55</td>
</tr>
<tr>
<td>9</td>
<td>CHCl₃</td>
<td>40</td>
<td>24</td>
<td>&gt;99</td>
</tr>
<tr>
<td>10</td>
<td>Neat</td>
<td>40</td>
<td>2</td>
<td>61</td>
</tr>
<tr>
<td>11</td>
<td>Neat</td>
<td>40</td>
<td>8</td>
<td>&gt;99</td>
</tr>
<tr>
<td>12</td>
<td>MeCN</td>
<td>40</td>
<td>24</td>
<td>45</td>
</tr>
<tr>
<td>13</td>
<td>MeCN</td>
<td>40</td>
<td>48</td>
<td>45</td>
</tr>
</tbody>
</table>

Reaction conditions: 1-phenylethanol (0.5 mmol), catalyst 3 (1 mol%), TBHP (0.75 mmol), mesitylene (0.5 mmol), solvent (0.4 mL).
As illustrated in the Figure 4.2, similar conversion rates were obtained when the reaction temperature was gradually decreased to 60°C and 40°C (entries 2, 3, Table 4.1). At 25°C the reaction is slower, achieving 82% yield in 24 h (entries 4, 5, Table 4.1).

As we can see by kinetic profiles in the Figure 4.3, lower catalytic activity was observed when MeCN was replaced by CH₂Cl₂ or CHCl₃, or when the oxidation was run under neat conditions (entries 6–11, Table 4.1).
Figure 4.3 Kinetic profiles of complex 3 in the oxidation of 1-phenylethanol with TBHP at 40 °C in different solvents. Reaction conditions: 1-Phenylethanol (0.5 mmol), 3 (1 mol%), TBHP (0.75 mmol), solvent (0.4 mL) at 40 °C; conversions determined by $^1$H NMR spectroscopy.

The Figure 4.4 show decreasing the catalyst loading to 0.5 mol% led to a marked drop in activity, irrespective whether the catalyst quantity is reduced or the substrate/oxidant concentration is increased (45% conversion within 24–48 h; entries 12 and 13, Table 4.1).

Figure 4.4 Kinetic profiles of complex 3 in the oxidation of 1-phenylethanol with TBHP at 40 °C in acetonitrile using different catalyst loadings. Black trace: 1-phenylethanol (1 mmol), TBHP (1.5 mmol), 3 (0.01 mmol; 1 mol%); Blue trace: 1-phenylethanol (1 mmol), TBHP (1.5 mmol), 3 (0.005 mmol; 0.5 mol%); Red
trace: 1-phenylethanol (2 mmol), TBHP (3.0 mmol), 3 (0.01 mmol; 0.5 mol%); conversions determined by $^1$H NMR spectroscopy.

Longer reaction times are needed (6 h) to achieve completion of the reaction when the amount of TBHP is reduced to 1 equivalent (Figure 4.5).

![Figure 4.5](image)

**Figure 4.5** Kinetic profiles of complex 3 in the oxidation of 1-phenylethanol at 40 °C in acetonitrile with TBHP. Black trace: 1-phenylethanol (1 mmol), TBHP (1.5 mmol), 3 (1 mol%); Red trace: 1-phenylethanol (1 mmol), TBHP (1 mmol), 3 (1 mol%); conversions determined by $^1$H NMR spectroscopy.

When the sacrificial oxidant was changed from TBHP to aqueous H$_2$O$_2$ (1.5 equiv.), only 27% of acetophenone was produced after 24 h, suggesting a critical role of the oxidant. To assess the impact of the triazolylidene ligand, we compared the catalytic performance of complexes 2 and 3 to that of the related bis-imidazolylidene complex $\text{fac-}[\text{Mn(CO)}_3(\text{bis-NHC}^\text{Me})\text{Br}]$ (4),$^{[20]}$ and to Mn$_2$(CO)$_{10}$ (5) under optimised reaction conditions (MeCN, 40 °C, 1 mol% catalyst; Figure 4.6). The pertinent time-conversion profiles indicate that complex 3 is considerably more active than the other Mn compounds.
The selective conversion of 1-phenylethanol to acetophenone was completed in 2 h with a turnover frequency TOF$_{\text{ini}}$ = 72 h$^{-1}$ (measured at 15 min of reaction, TOF$_{50}$ at 50% conversion is 56 h$^{-1}$), while complexes 2 and 4 featured three times lower activity (TOF$_{\text{ini}}$ < 24 h$^{-1}$) and reached a mere 22% and 16% yield, respectively, in the time span that complex 3 accomplished quantitative conversion (2h). No induction period was observed, indicating that the catalytically active species is formed rapidly upon addition of the oxidant to the reaction medium. Interestingly, the introduction of the trz ligand in the coordination sphere of the Mn(0) center has a markedly positive effect.
and enhanced the catalytic activity compared to the carbene-free dimer Mn$_2$(CO)$_{10}$ (cf. activity of complex 3 vs. 5).

To explore the scope of 3 as catalyst, we studied the oxidation of a variety of alcohols with TBHP under the optimized conditions (1 mol% catalyst, MeCN, 40 °C; Table 4.2). Secondary aromatic as well as both cyclic and linear aliphatic alcohols were efficiently oxidised to the corresponding ketones with good to moderate yields (72–99%, Table 4.2). Benzyl alcohol was selectively oxidised to benzaldehyde (84%, Table 4.2) in high yield and very good selectivity with only minor overoxidation (<7%) to the corresponding acid. However, primary aliphatic alcohols such as 2-phenylethanol are not oxidised under the same reaction conditions.

**Table 4.2 Oxidation of alcohols with complex 3**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>t (h)</th>
<th>Yield $^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Phenylethanol</td>
<td>Acetophenone</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexanol</td>
<td>Cyclohexanone</td>
<td>8</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>1,2,3,4-Tetrahydro-1 naphthol</td>
<td>1-Tetralone</td>
<td>8</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>1-Phenyl-1-propanol</td>
<td>Propiophenone</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>2-Hexanol</td>
<td>2-Hexanone</td>
<td>24</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>1-Cyclopropylethanol</td>
<td>Cyclopropyl methyl ketone</td>
<td>24</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Benzyl alcohol</td>
<td>Benzaldehyde</td>
<td>8</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8</td>
<td>2-Phenylethanol</td>
<td>------</td>
<td>24</td>
<td>55</td>
</tr>
</tbody>
</table>

$a$ Reaction conditions: alcohol (0.5 mmol), catalyst 3 (1 mol%), TBHP (0.75 mmol), mesitylene (0.5 mmol), acetonitrile (0.4 mL) at 40 °C. $^b$ Yields determined by $^1$H NMR spectroscopy using mesitylene as internal standard. In parenthesis are isolated yields. $^c$ Conversion calculated by GC using n-tetradecane as internal standard. $^d$ Reaction performed with 2 mol% of 3.
As far as we know, this work represents the first example of oxidation of alcohols catalysed by trz complexes of first-row transition metals,\textsuperscript{[12c]} and the most active Mn-based catalyst for oxidation of alcohols with TBHP under mild conditions (\textbf{Tables A4.1 and A4.2}).\textsuperscript{[10,11]} Oxidation of selected secondary benzyl alcohols with TBHP has been successfully achieved by related trz ruthenium complexes containing a pyridyl or picolyl functionality. However, these catalytic systems were inactive towards aliphatic secondary alcohols and primary benzyl alcohols were overoxidised.\textsuperscript{[13,23]} Iron(II) complexes bearing NHC and bipyridyl ligands efficiently catalyse the oxidation of 1-phenylethanol with TBHP, however longer reaction times, higher temperature, and higher catalyst loadings were needed to achieve quantitative conversion.\textsuperscript{[24]}

To probe the longevity of complex 3 and its potential for reuse, multiple fresh batches of substrate (1-phenylethanol) and oxidant were sequentially added to the reaction mixture. The catalyst was reused for up to 6 cycles without any loss of selectivity and quantitative yields of acetophenone were observed after each run, providing an accumulated turnover number TON = 600. While this productivity implies a high catalyst robustness, activity gradually erodes and the time to reach completion increases with every addition of fresh substrate from 2 h in the first cycle up to 24 h for the sixth cycle (\textbf{Figure 4.7}).
Figure 4.7 Reuse of catalyst 3. Time-conversion profile for the oxidation of 1-phenylethanol catalyzed by 3 when adding new charges of substrate (1 mmol) and TBHP (1.5 mmol) after each cycle. Reaction performed with 3 (1 mol%), acetonitrile (0.4 mL) at 40 °C; conversions determined by $^1$H NMR spectroscopy.

4.3.3 Electrochemical analysis of complexes 2-5

Electrochemical analysis of complexes 2–5 offers some hints for the high catalytic activity of complex 3 in alcohol oxidation. Complexes 2–4 (Figure 4.8) all show quasi-reversible oxidation at high scan rate and an EC mechanism at lower scan rate. As illustrated in Figure 4.8, the Mn(I) complexes 2 and 4 are reversibly oxidised at similar potential ($E_{1/2} = +0.30$ and +0.39 V, respectively), the Mn(0) system is much easier to oxidise with $E_{1/2} = −0.02$ V (all potentials vs. Fc/Fc$^+$ in MeCN).
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**Figure 4.8** Overlaid CV plots of 0.5 mM solutions of complexes 2 (left) at 50 to 1000 mV s\(^{-1}\) and 4 (right) at different scan rates in 0.1 M [NBu₄]PF₆ in MeCN.

As we can see in the **Figure 4.9**, complex 5 features an irreversible oxidation at \(E_{pa} = +0.94\) V.

**Figure 4.9** Overlaid CV plots of 0.5 mM solutions of complex 5 in 0.1 M [NBu₄]PF₆ in MeCN indicates an irreversible oxidation which depends on the scan rate with \(E_{pa} = +0.967\) V (500 mV s\(^{-1}\)), +0.938 V (100 mV s\(^{-1}\)), and +0.921 V (25 mV s\(^{-1}\)), respectively (ferrocene as internal reference).

Relatively of complex 3, their facile oxidation (**Figure 4.10**) may therefore be critical for fast turnover.
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4.3.4 Mechanistic insights into the catalytic reaction

Mechanistic insights have been obtained by poisoning experiments and in operando spectroscopy. Catalyst homogeneity was assessed by the mercury drop test experiment to distinguish between homogeneous and heterogeneous catalysts, since mercury leads to the amalgamation of the surface of a heterogeneous catalyst.\textsuperscript{[25]} Performing the oxidation of 1-phenylethanol with 3 (1 mol\%) in the presence of a large excess of Hg(0) (>1000 equiv.) did not affect the conversion. As illustrated in Figure 4.11, similar conversion profiles were obtained for catalytic runs in the presence and absence of mercury, indicating that the catalytic species derived from complex 3 remains homogeneous.

**Figure 4.10** Overlaid CV plots of 0.5 mM solutions of complex 3 at different scan rates in 0.1 M [NBu\textsubscript{4}]PF\textsubscript{6} in MeCN providing \(E_{1/2} = -0.02\) V vs Fc\textsuperscript{+/−}. 
**Figure 4.11** Time-conversion profile (¹H NMR monitoring) for the oxidation of 1-phenylethanol catalyzed by 3 with TBHP in the presence of Hg (>1000 eqv.); all conversions determined by ¹H NMR spectroscopy.

Black trace: typical procedure under standard conditions using 1-phenylethanol (0.5 mmol), TBHP (0.75 mmol), complex 3 (1 mol%).

Red trace: typical procedure with Hg added at the onset of the reaction. Elemental mercury (>1 g, >5 mmol) was added to complex 3 (2.77 mg, 0.005 mmol, 1 mol%) and 1-phenylethanol (0.06 mL, 0.5 mmol). Then, TBHP (0.15 mL, 5.0–6.0 M in decane, 0.75 mmol) and acetonitrile (0.4 mL) were added and the reaction mixture was heated to 40 °C.

Blue trace: typical procedure with Hg added at 30% conversion. 1-phenylethanol (0.06 mL, 0.5 mmol), TBHP (0.15 mL, 5.0–6.0 M in decane, 0.75 mmol), and complex 3 (2.77 mg, 0.005 mmol) were dissolved in acetonitrile (0.4 mL) and the reaction mixture was heated to 40 °C. After 30 min, Hg (>1 g, >5 mmol) was added and stirring of the reaction at 40 °C was continued.

As we can see in the **Figure 4.12** and **Figure 4.13**, reaction monitoring in operando by IR spectroscopy reveals an increase of the characteristic carbonyl intensity at 1688 cm⁻¹ of the acetophenone product, which correlates with conversions determined from ¹H NMR samples (Table 4.3).
Figure 4.12 Superimposed IR spectra of the catalytic reaction using complex 3 at 40 °C. IR spectra recorded at time 0 (purple), 30 min (black), 1 h (red), 2 h (blue), 3 h (brown), 16 h (green) and 24 h (orange). The IR band at 1686 cm⁻¹ corresponds to acetophenone as the product of alcohol oxidation is detected already after 30 min and keeps increasing over the course of the reaction. Conditions: Complex 3 (12 mg, 0.02 mmol), 1-phenylethanol (260 µL, 2.16 mmol), TBHP (650 µL, 3.24 mmol) and mesitylene (300 µL, 2.16 mmol) in MeCN (1 mL) were mixed. Mesitylene was added as internal standard. The reaction mixture was heated at 40 °C and monitored by time resolved online MCT FT-IR spectroscopy.
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**Table 4.3** Conversions determined by IR and NMR spectroscopy for 1-phenylethanol oxidation catalyzed by complex 3.

<table>
<thead>
<tr>
<th>time (h)</th>
<th>conv. IR (%)</th>
<th>conv. NMR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>1</td>
<td>32</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>42</td>
<td>43</td>
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<td>3</td>
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<td>49</td>
</tr>
<tr>
<td>16</td>
<td>64</td>
<td>68</td>
</tr>
<tr>
<td>24</td>
<td>69</td>
<td>74</td>
</tr>
</tbody>
</table>
As illustrated in the Figure 4.14, a substoichiometric run (complex 3/phenylethanol/ TBHP 1: 4: 4) reveals a rapid loss of the characteristic CO bands of complex 3 at 1971, 1912 and 1881 cm\(^{-1}\), which supports Mn oxidation with concomitant loss of CO as a critical step for catalyst activation (cf. electrochemistry).

![Figure 4.14 Superimposed IR spectra of the stoichiometric reaction using complex 3 at 40 °C. IR spectra recorded at time 0 (green), 20 min (turquoise), 40 min (grey), 80 min (orange), 4 h (purple), 18 h (blue) and 24 h (red line). Conditions: Complex 3 (12 mg, 0.02 mmol), 1-phenylethanol (11 µL, 0.08 mmol), TBHP (17 µL, 0.08 mmol) and mesitylene (12 µL, 0.08 mmol) in MeCN (1 mL) were mixed. Mesitylene was added as internal standard.](image)

The three IR bands for complex 3 at 1969, 1943 and 1883 cm\(^{-1}\) in MeCN rapidly deplete under stoichiometric conditions (1:4:4; complex: alcohol: TBHP) and eventually fully disappear. At the same time, three new IR bands appear at 1671, 1640 and 1534 cm\(^{-1}\) presumably from the active species that are shifted ca. 300 cm\(^{-1}\) for the first two bands and 350 cm\(^{-1}\) for the last band of the starting complex 3. The new three IR bands steadily increase in intensity for the first 2 h. Then, the
intensity remains constant for approximately 3 h and starts to decrease after this time (Figure 4.14).

**4.4. Conclusions**

In conclusion, we have described the synthesis of new Mn(0) and Mn(I) complexes containing 1,2,3-triazolylidene ligands and their application in oxidation of alcohols to synthetically versatile carbonyl compounds. The catalytic process is remarkably selective and suppresses overoxidation, and is applicable to a variety of alcohols under mild conditions (40°C). Further investigation of the application of the organometallic Mn complexes in catalysis, and in elucidating the reaction mechanism is currently underway in our laboratories.

**4.5. Experimental Section**

**4.5.1 General considerations**

The synthesis of complexes 2 and 3 was performed under a nitrogen atmosphere using standard Schlenk techniques, and solvents were purified from appropriate drying agents and distilled under nitrogen. Deuterated solvents were degassed and stored over molecular sieves. The ditriazolium triflate salts 1a,1b ditriazolium bromide salts of 1a and 1b, and the Mn complex 4 were synthesized according to the methods described in the literature. All other reagents were purchased from commercial suppliers and used without further purification. MnBr(CO)$_5$ was purchased from Strem chemicals and used as received. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Avance III 400 MHz. Electrospray mass spectra (ESI-MS) were recorded with a Micromass Quatro LC instrument; nitrogen was employed as a drying and nebulizing gas. Elemental analyses were performed in the laboratories at ITQB.
4.5.2 Synthesis and characterization of complexes 2 and 3

Preparation of (di-trz)MnBr(CO)_3 (2)

The ditriazolium triflate salt 1a (0.60 g, 0.86 mmol) was dissolved in a minimum amount of dry acetone and treated with tetra(n-butyl) ammonium bromide (0.58 g, 1.8 mmol). After stirring for few minutes, the ditriazolium bromide salt precipitated. It was isolated by filtration, washed with acetone, dried under vacuum and weighed (0.40 g, 0.71 mmol, 83% yield). Solid MnBr(CO)_5 (0.25 g, 0.90 mmol) was suspended in THF (15 mL) and potassium tert-butoxide (0.18 g, 1.6 mmol) was added first, followed by addition of the corresponding ditriazolium bromide (0.40 g, 0.71 mmol) at 60 °C. The resulting suspension was heated at 60 °C for 16 h under stirring. All volatiles were removed under vacuum and the resulting residue was washed with toluene (4 x 15 mL) and dissolved in dichloromethane (80 mL). The dichloromethane solution was washed with water (80 mL), and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow-orange powder. Yield: 0.20 g, 45%.

^1H NMR (DMSO-d_6, 25 °C) (Figure A4.1) : δ 7.11, 7.09 (2 x s, 2H, Ar-C_6H_5), 4.71 (s, 6H, NCH_3), 2.33 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 2.02 (s, 6H, CH_3).

^13C NMR (DMSO-d_6, 25 °C) (Figure A4.2): δ 220.40 (CO), 196.28 (C_{trz-Mn}), 141.22 (C_{Ph}), 139.71 (C_{trz-C_{trz}}), 135.82 (C_{Ph}), 134.96 (C_{Ph}), 134.40 (C_{Ph}), 128.96 (C_{Ph}), 128.54 (C_{Ph}), 38.7 (NCH_3) 20.76 (CH_3), 18.01 (CH_3), 16.68 (CH_3), one CO not resolved.

IR (KBr) (Figure A4.3): u(CO) 2004, 1918, 1884 cm^{-1}.

Anal. Calcd. For C_{27}H_{28}Mn_{6}O_{3}Br.C_{2}H_{2}Cl_{2}: C, 47.73; H, 4.29; N, 11.93. Found: C, 47.50; H, 4.84; N, 12.21.
**Preparation of (μ-di-trz)Mn2(CO)8 (3)**

The ditriazolium triflate salt 1b (0.43 g, 0.83 mmol) was dissolved in a minimum amount of dry acetone and treated with tetra(n-butyl) ammonium bromide (0.56 g, 1.7 mmol). After stirring for few minutes, the ditriazolium bromide salt precipitated. It was isolated by filtration, washed with acetone, dried under vacuum and weighed (0.24 g, 0.63 mmol, 76% yield). Solid MnBr(CO)5 (0.22 g, 0.80 mmol) was suspended in THF (15 mL) and potassium tert-butoxide (0.16 g, 1.4 mmol) was added first, followed by addition of the corresponding ditriazolium bromide (0.24 g, 0.63 mmol) at 60 °C. The resulting suspension was heated at 60 °C for 16 h under stirring. All volatiles were removed under vacuum and the resulting residue was washed with toluene (4 x 15 mL) and dissolved in dichloromethane (80 mL). The dichloromethane solution was washed with water (80 mL), and the organic extract was dried with Na2SO4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow-orange powder. Yield: 0.18 g, 52%.

\[ ^1\text{H NMR (DMSO-d$_6$, 25 °C) (Figure A4.4): } \delta \text{ 4.77 (m, 4H, NCH$_2$CH$_3$), 4.15 (s, 6H, NCH$_3$), 1.63 (t, 6H, NCH$_2$CH$_3$).} \]

\[ ^{13}\text{C NMR (DMSO-d$_6$, 25 °C) (Figure A4.5): } \delta \text{ 231.26 (CO), 229.32 (CO), 225.36 (CO), 223.27 (CO), 181.15 (C$_{\text{trz-Mn}}$), 138.03 (C$_{\text{trz-Mn}}$), 48.88 (NCH$_2$CH$_3$), 38.56 (NCH$_3$), 15.38 (NCH$_2$CH$_3$).} \]

\[ \text{IR (KBr) (Figure A4.6): } \upsilon(\text{CO}) \text{ 2035, 1971, 1912, 1881 cm}^{-1}. \]

\[ \text{Anal. Calcd. for C}_{18}\text{H}_{16}\text{Mn}_2\text{N}_6\text{O}_8: C, 38.99; H, 2.91; N, 15.16. Found: C, 38.40; H, 3.27; N, 15.30.} \]

**4.5.3 Catalytic procedures**

**Typical procedure for catalytic alcohol oxidation**

A flask was charged in open air with catalyst (1 mol%) and substrate (0.5 mmol). Then, TBHP (5.0–6.0 M in decane, 0.75 mmol) and
acetonitrile (0.4 mL) were added. The progress of the reaction was monitored by taking aliquots of the reaction mixtures and subjecting them to $^1$H NMR analysis in CDCl$_3$. The yield was determined by $^1$H NMR spectroscopy using mesitylene as an internal standard. In some cases, the yield was determined by GC. The corresponding products were extracted in dichloromethane, filtered and the residue dried under vacuum. The products were identified by comparison of their NMR (Figures A4.7-A4.12) spectral data to the literature.

### 4.5.4 Electrochemical analysis of complexes 2–5

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out using a Metrohm Autolab Model PGSTAT101 potentiostat employing a three electrodes cell under an argon atmosphere. A platinum electrode with 7.0 mm$^2$ surface area was used as the working electrode. The reference electrode was Ag/AgCl; the counter electrode was Pt wire. [NBu$_4$]PF$_6$ (0.1 M) in dry MeCN was used as supporting electrolyte. All voltammograms are referenced to ferrocene/ferrocenium (Fc/Fc$^+$) using either Fc or [Ru(bpy)$_3$]$^{2+}$ as internal standard (2 mg standard added after each measurement). The oxidation potential of [Ru(bpy)$_3$](PF$_6$)$_2$ vs Fc/Fc$^+$ was determined in MeCN to use this complex as an internal standard when Fc was not suitable, providing $E_{1/2} = +0.89$ V vs Fc$^+/Fc$ (Figure A4.13). Data pertaining to complex 2 are shown in Figures A4.14–A4.17 and Table A4.3; to complex 3 in Figures A4.25–A4.27 and Table A4.4 and to complex 4 in Figures A4.18 and A4.19 and Table A4.5.
4.5.5 In operando IR analysis of alcohol oxidation

Time-resolved online MCT FT-IR spectra were recorded on a ReactIR 15 Instrument (Mettler Toledo) equipped with a diamond probe (DiComp, optical range of 3000–650 cm⁻¹). For online monitoring, the diamond probe was introduced into a glass tube (100 mm height, 12 mm diameter) containing the reaction mixture and spectra were recorded at specific times. Complex 3, 1-phenylethanol, TBHP, mesitylene and acetophenone were recorded separately in MeCN at 40 °C to simulate catalytic reaction conditions (Figures A4.21–A4.25).

4.5.6 Crystallographic details of complex 3

Crystals of 3 were grown by slow diffusion of Et₂O into a solution of the complex in CH₂Cl₂. A suitable crystal was mounted in air at ambient conditions. All measurements were made on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å) and Al filtered. The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of reflections in the range 2.4° < θ < 27.7°. A total of 657 frames were collected using ω scans, with 5+5 seconds exposure time, a rotation angle of 1.0° per frame, a crystal-detector distance of 65.0 mm, at T = 123(2) K. Data reduction was performed using the CrysAlisPro program. The intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied. The structure was solved by direct methods using SHELXT, which revealed the positions of all non-hydrogen atoms of the title compound. The non-hydrogen atoms were refined anisotropically. All H-atoms were placed in geometrically calculated positions and refined using a
riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent atom (1.5Ueq for methyl groups). Refinement of the structure was carried out on \( F^2 \) using full-matrix leastsquares procedures, which minimized the function \( \Sigma w(F_0^2 - F_c^2)^2 \). The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the SHELXL-2014/74 program. Further crystallographic details are compiled in Table A4.6. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number 1895142. Selected bond lengths and angles are compiled in Table A4.7.

4.6. Acknowledgements

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4.7. References


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Chapter 4: (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols


CHAPTER 5: CHELATING BIS-N-HETEROCYCLIC CARBENE
COMPLEXES OF IRON(II) CONTAINING BIPYRIDYL LIGANDS AS
CATALYST PRECURSORS FOR OXIDATION OF ALCOHOLS

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5.2. Introduction
5.3. Results and Discussion
  5.3.1 Synthesis and characterization of Fe complexes 1 and 2
  5.3.2 Catalytic activity in the oxidation of alcohols
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  5.5.3 Typical procedure for the oxidation of alcohols
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5.7. References

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Author Contributions

B.R and A.M.M directed the research. B.P.C performed preliminary essays and M.F.P performed all the experiments including the synthesis, characterization of the iron complexes and catalytic essays. S.B performed the X-Ray studies. B.R wrote the manuscript with inputs from all the authors. B.R, A.M.M and M.F.P discussed the results and revised the manuscript.
5.1. Summary

This chapter describes the preparation of chelating bis-N-heterocyclic carbene (bis-NHC) complexes of Fe(II) containing pyridyl ligands prepared by reaction of [FeCl₂L] [L = bipy (1), phen (2)] with [LiN(SiMe₃)₂] and a bisimidazolium salt. Their catalytic activity in the oxidation of alcohols is described. The [Fe(bis-NHC)L(I)₂] complexes were active pre-catalysts in the oxidation of 1-phenylethanol with tert-butyl hydroperoxide (TBHP) in neat conditions, affording a quantitative yield of acetophenone in 4.5 h. The catalyst could be reused up to six cycles giving a turnover number (TON) of 1500. Various secondary alcohols, both aromatic and aliphatic were selectivity oxidised to the corresponding ketones in excellent yields. Compound 1 is stable in acetonitrile solution for ca. 4 h, although after 16 h, it evolves to a mixture of [Fe(bis-NHC)(bipy)₂]I₂ (3), [Fe(bipy)₃]²⁻ and bis-imidazolium salt. The molecular structure of 3 has been determined by X-ray diffraction studies.
5.2. Introduction

As discussed in Chapter 1, the low price, high abundance and nontoxicity of iron, along with the great popularity of NHC ligands in catalysis have triggered a growing interest in the development of iron-NHC chemistry. Several iron complexes supported by chelating bis-NHC have been reported in the literature, as described in the section 1.4.1 of Chapter 1, but their use as catalysts is still rather rare. Therefore, we became interested in exploring complexes containing the “Fe-bis-NHC” fragment combined with 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands, aiming to explore their reactivity in oxidation reactions. Phenanthroline and bipyridine are classical ligands that play an important role in coordination chemistry. Their related transition metal complexes often show interesting properties that can be applied in catalysis, artificial photosynthesis, molecular electronics, and metallosupramolecular chemistry, among others. Iron complexes bearing NHCs and polypyridines which are independently bound to the metal center are very rare. The first heteroleptic tetrakis(NHC) Fe(II) complex containing a mesoionic bis(1,2,3-triazol-5-ylidene) and a bipyridine ligand was recently described by Sundström. In contrast, Fe–NHCs containing polypyridine ligands as a part of multidentate frameworks have been intensively studied in the last few years. Recently, Herrmann and Kühn reported exciting results describing the catalytic activity of Fe(II) complexes bearing tetradentate NHC-pyridine ligands in the epoxidation of olefins, and in hydroxylation of toluene and benzene with H₂O₂. Based on these precedents, and on our own experience on the preparation of Fe–NHC based complexes, we now report the synthesis of a series of chelating bis-NHC Fe(II) pyridyl complexes and their application as catalysts for the oxidation of alcohols.
5.3. Results and Discussion

5.3.1 Synthesis and characterization of Fe complexes 1 and 2

The iron bis-NHC complex \([\text{Fe(bis-NHC)(bipy)I}_2]\) (1) (NHC = 1,1’-methylene-3,3’-di-benzylimidazole-2-ylidene) was prepared as shown in Scheme 5.1, by the reaction of \([\text{FeCl}_2(\text{bipy})]\) with two equivalents of \([\text{LiN(SiMe}_3)_2]\) followed by addition of 1,1’-methylene-3,3’-di-benzylimidazolium diiodide in THF. This procedure is based on the method disclosed by Danopoulos for the preparation of Fe bis-NHCs.[8]

Complex 1 precipitated from the reaction as a deep purple crystalline solid. The analogous phenanthroline complex \([\text{Fe(bis-NHC)(phen)I}_2]\) (2) was prepared using \([\text{FeCl}_2(\text{phen})]\) by following a similar synthetic procedure.

![Scheme 5.1 Synthesis of iron complexes 1 and 2.](image)

The identity of complexes 1 and 2 was established by elemental analysis and ESI-mass spectroscopy. As illustrated in Figures A5.8 (ESI mass spectrum of 1 recorded in acetonitrile), displayed a prominent signal at m/z 666.9 assignable to the monocationic Fe species \([\text{Fe(bis-NHC)(bipy))}]^+\). A lower intensity signal at m/z 270.0 was attributed to the dicationic species \([\text{Fe(bis-NHC)(bipy))}]^{2+}\). The ESI-MS spectrum of complex 2 (Figure A5.9) displayed an intense signal at m/z 691.0 due to the cation \([\text{Fe(bis-NHC)(phen))}]^+\). Consistent with their paramagnetic nature, the \(^1\)H NMR spectra of 1 and 2 displayed broad signals, so structural information could not be obtained.
Both compounds 1 and 2 were insoluble in non-polar solvents such as hexane and toluene, and also in THF, yet soluble in polar solvents. They were air and moisture stable in the solid state and were stored for weeks under air without noticeable decomposition.

5.3.2 Catalytic activity in the oxidation of alcohols

In order to assess the reactivity of 1 toward oxidation reactions, we explored its catalytic activity in the oxidation of alcohols. First we tested 1 in the oxidation of 1-phenylethanol in the presence TBHP as oxidant in a 1:1.5 molar ratio (substrate vs oxidant). The reaction was carried out in the absence of solvent at 80 °C, with a catalyst loading of 2 mol%, which afforded a quantitative yield of acetophenone in 4.5 h (Table 5.1, entry 1). The study of the reaction profile showed conversions already at very early reaction times (5 min, 12% yield), thus indicating that the active species formed rapidly upon addition of TBHP.

Interestingly, the reaction mixture remained active upon 6 consecutive additions of substrate and oxidant, reaching quantitative conversion to the ketone after 4.5 h. An accumulated TON of 1500 was achieved. Using the same conditions, a series of aromatic and aliphatic secondary alcohols were oxidised to the corresponding ketones in excellent yields (Table 5.1, entries 6-9). Moderate production of hexanaldehyde was obtained in the oxidation of 1-hexanol (61%, Table 5.1, entry 10), while mixtures of several compounds were obtained when primary benzyl alcohols were used. Catalyst 1 was inactive when the reaction was performed using H₂O₂ as oxidant instead of TBHP (Table 5.1, entry 11). The phenanthroline Fe complex 2 displayed similar catalytic activity compared to 1, indicating that substitution of bipyridine by phenanthroline was irrelevant to the performance of the catalyst.
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Encouraged by these results, we explored the reactivity of 1 under oxidative conditions in different solvents. When the reaction was carried out in THF or toluene, low yields were obtained, probably due to the insolubility of the catalyst (Table 5.1, entries 2 and 3). In contrast, quantitative conversion of 1-phenylethanol to acetophenone was observed when polar solvents (acetonitrile or water) were used (Table 5.1, entries 4 and 5).

Table 5.1 Oxidation of alcohols with TBHP using 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant/solvent</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Yield b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBHP/neat</td>
<td>1-Phenyethanol</td>
<td>4.5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>TBHP/THF</td>
<td>1-Phenyethanol</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>TBHP/toluene</td>
<td>1-Phenyethanol</td>
<td>8</td>
<td>51</td>
</tr>
<tr>
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<td>TBHP/MeCN</td>
<td>1-Phenyethanol</td>
<td>4.5</td>
<td>&gt;99</td>
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<td>1-Phenyethanol</td>
<td>4.5</td>
<td>&gt;99</td>
</tr>
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<td>TBHP/neat</td>
<td>Cyclohexanol</td>
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<tr>
<td>8</td>
<td>TBHP/neat</td>
<td>Tetrahydro-1-naphthol</td>
<td>8</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>TBHP/neat</td>
<td>1-Phenyl-1-propanol</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>TBHP/neat</td>
<td>1-Hexanol</td>
<td>9</td>
<td>61</td>
</tr>
<tr>
<td>11</td>
<td>H2O2/neat</td>
<td>1-Phenyethanol</td>
<td>24</td>
<td>0</td>
</tr>
</tbody>
</table>

a Reaction conditions: substrate (0.5 mmol), catalyst 1 (2 mol%), TBHP (0.75 mmol), 80 °C. b Yield determined by 1H NMR using diphenylmethane as an internal standard.
5.3.3 Mechanistic insights into the catalytic reaction

In order to get a mechanistic insight into the catalytic reaction, we performed the stoichiometric reaction of 1 with TBHP in the presence of one equivalent of 1-phenylethanol in acetonitrile. The reaction mixture was heated at 80 °C for 30 min, and the resulting acetonitrile solution was filtered and subjected to ESI-MS analysis, (Figure A5.10) showing a significant signal at m/z 270 (z = 2), due to [Fe(bis-NHC)(bipy)]^{2+}. This experiment strongly suggests that the NHC ligand remains bound to the iron center under the oxidative conditions used for the catalytic reactions.^[9]

The stability of 1 in acetonitrile was explored by ESI-MS spectroscopy. In a typical experiment 1 was dissolved in acetonitrile, and then solution was stirred for 2 or 4 hours before the ESI-MS spectra were taken. The mass spectra displayed the same pattern as those recorded with freshly prepared solutions, showing the diagnostic signal at 666.9 assigned to the iron cation [Fe(bis-NHC)(bipy)]^{+}. This result is strongly indicating that 1 is stable in acetonitrile solutions for at least a few hours. After 16 h in MeCN, the colour of the solution changed from the initial deep purple to purplish red. The ^1H NMR spectrum (in CD₃N) (Figure A5.51) became well-resolved and suggested the formation of a diamagnetic product mixture. The observed resonances were attributed to [Fe(bis-NHC)(bipy)]₂ (3) and [Fe(bipy)]³²⁺, along with small quantities of bis-imidazolium salt (in a proportion of 46.5 %, 40.8 %, and 12.4 %, respectively).

The identity of complex 3 was confirmed by single crystal X-ray diffraction (vide infra). The complex [Fe(bipy)]^{2+} and the bis-imidazolium salt were identified by comparing their spectra with the ones taken from pure samples. As a diagnostic of the presence of the NHC ligand bound to the metal, the ^{13}C NMR spectrum of 3 (Figure A5.4) shows a signal at 189 ppm, which is a clear indication of the
presence of a carbene carbon. Similar evolution of 1 was observed in water and methanol. The NMR spectra of 1 in D$_2$O and MeOD recorded after 16 h displayed the same NMR pattern as in the acetonitrile solution.

The molecular structure of 3 is displayed in Figure 5.1. The cation displays a slightly distorted octahedral geometry defined by the carbon atoms of the bis-NHC ligand (C1 and C12) and the nitrogen atoms of the two bipy ligands (N5, N6, N7 and N8). The equatorial plane is defined by N5, N6, N8 and C12 while the axial positions are occupied by C1 and N7. The angles between the mutually trans ligands range between 171.8(1)° and 175.1(2)°. The Fe1–C1 (1.976(4) Å) and Fe1–C12 bond lengths (1.965(4) Å) are within the range observed for other dicationic bis-NHC iron complexes (1.818 Å < Fe–C$_{\text{NHC}}$ < 2.007 Å). The Fe–N$_{\text{bipy}}$ distances are also in agreement with commonly reported values.

In light of these results, we decided to explore the catalytic activity of acetonitrile solutions of 1 after being incubated for 16 h. Then, TBHP and 1-phenylethanol were added and heated at 80 °C for 4.5 h. Under
these conditions, 40% yield of acetophenone was obtained. We also evaluated the catalytic activity of a series of iron salts. As shown in Table 5.1, FeCl$_2$, FeCl$_3$, FeCl$_2$(bipy), and [Fe(bipy)$_3$]Cl$_2$ catalysed the reaction to a much lower extent (<45 %) than 1. These results strongly support that complex 1 is a pre-catalyst in the catalytic oxidation reaction, thus indicating a beneficial role of the NHC in the coordination sphere of the metal. No catalytic reaction occurred in the absence of a catalyst (Table 5.2, entry7).

**Table 5.2 Oxidation of 1-phenylethanol using Fe species**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Yield$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><a href="1">Fe(bis-NHC)(bipy)$_2$</a></td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Fe(bipy)Cl$_2$</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>[Fe(bipy)$_3$]Cl$_2$</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>FeCl$_2$</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>FeCl$_3$</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>[Bis-NHC]$_2$</td>
<td>0</td>
</tr>
<tr>
<td>7$^c$</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: alcohol (0.5 mmol), catalyst (2 mol%), TBHP (0.75 mmol), MeCN (0.4 mL), 80 °C, 4.5 h. $^b$ Yield determined by $^1$H NMR using diphenylmethane as an internal standard. $^c$ The blank reaction has been performed under neat conditions and in MeCN (0.4 mL).

Finally, we have performed spin trap experiments, which showed that radicals such as $^t$BuOO$^\cdot$ or $^t$BuO$^\cdot$ could be involved in this reaction. When the catalytic oxidation of 1-phenylethanol with TBHP in acetonitrile was performed in the presence of an oxygen-radical trap, such as Ph$_2$NH, the yield of acetophenone was reduced to 5%,
indicating that the oxidation reaction proceeds via a radical mechanism involving oxygen-centered radicals. In contrast, the presence of CBrCl₃, a carbon-radical trap did not affect the catalytic reaction.

5.4. Conclusions

In summary, we prepared two Fe(II) bis-NHC complexes bearing bipyridyl and phenanthroline ligands in good yields. These complexes were used in the oxidation of alcohols with TBHP. The reaction can be performed in the absence of a solvent, and the active species can be reused over 6 cycles without a measurable loss of activity. The catalytic reaction can also be performed in polar solvents such as acetonitrile and water, affording a quantitative yield of the corresponding ketones. Compound 1 is stable in acetonitrile solution for at least 4 h, although after 16 h it evolves to a mixture of [Fe(bis-NHC)(bipy)₂] I₂ (3), [Fe(bipy)₃]²⁺ and bis-imidazolium salt. The molecular structure of 3 has been determined by X-ray diffraction studies.

This work represents the first example of an Fe(II)–NHC complex catalysing the oxidation of alcohols with TBHP.

5.5. Experimental section

5.5.1 General methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, and the solvents were purified from appropriate drying agents. Deuterated solvents were degassed and stored over molecular sieves. FeCl₂(bipy), FeCl₂(phen), and 1,1′-methylene-3,3′-di-benzylimidazolium diiodide were synthesised according to the method described in the literature. All other reagents were purchased from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz. Assignment of resonances was made from HMQC
and HMBC experiments. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as a drying and nebulising gas. Elemental analyses were performed in our ITQB laboratory services.

**X-ray crystallography**

Crystals suitable for single-crystal X-ray analysis were obtained for complex 3 by slow diffusion of Et₂O in acetonitrile solution of 1. The data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem openflow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS. The structures were solved and refined using direct methods with program SIR2004 using WINGX-Version 2014. SHELXL system of programs. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealised positions and allowed to refine riding on the parent carbon atom. The molecular diagrams were drawn with ORTEP-3 for Windows included in the software package. For crystallographic experimental data and structure refinement parameters see Table A5.1. CCDC 1455061 contains the supplementary crystallographic data for this paper.

5.5.2 Synthesis and characterization of Fe complexes 1 and 2

**General procedure for the synthesis of complexes 1 and 2**

Two equivalents of [LiN(SiMe₃)₂] were added to a suspension of [FeCl₂L] (L = bipy, phen) (1 equiv.) in toluene at 0 °C, and the mixture was stirred overnight at room temperature. The toluene solution was evaporated and all the volatiles were removed under vacuum to yield
a green residue, which was redissolved in THF (10 mL). Solid 1,1’-methylene-3,3’-di-benzylimidazolium diiodide (1 equiv.) was added at once to the THF solution, and the reaction mixture was stirred for 16 h at room temperature. A deep purple crystalline solid insoluble in THF was isolated by filtration, washed several times with THF and Et₂O to yield the pure product.

**Preparation and characterisation of [Fe(bis-NHC)(bipy)I₂]** (1)

Following the general procedure, [LiN(SiMe₃)₂] (150 mg, 0.90 mmol), [FeCl₂(bipy)] (127 mg, 0.45 mmol) and 1,1’methylene-3,3’-di-benzylimidazolium diiodide (475 mg, 0.81 mmol) afforded 1 (520 mg, 0.65 mmol, 80%) as a deep purple solid.

Anal. Calc for C₃₁H₂₈N₆FeI₂ (794.25): C, 46.88; H, 3.55; N, 10.58. Found: C, 47.10; H, 3.86; N, 10.27.

MS (ESI-TOF) in acetonitril (Figure A5.8): m/z [M]+ calcd for [C₃₁H₂₈N₆FeI⁺], 667, found: 666.9; [C₃₁H₂₈N₆Fe]²⁺, 270, found: 270; [C₄₂H₄₀N₈Fe]⁺.

**Preparation and characterisation of [Fe(bis-NHC)(phen)I₂]** (2).

Following the general procedure, [LiN(SiMe₃)₂] (119 mg, 0.71 mmol), [FeCl₂(phen)] (109 mg, 0.36 mmol), and 1,1’methylene-3,3’-di-benzylimidazolium diiodide (377 mg, 0.65 mmol) afforded 2 (275 mg, 0.34 mmol, 52%) as a deep purple solid.

Anal. Calc for C₃₃H₂₈N₆FeI₂ (818.27): C, 48.44; H, 3.45; N, 10.27. Found: C, 48.30; H, 3.77; N, 9.87.

MS (ESI-TOF) in acetonitrile (Figure A5.9): m/z [M]+ calcd for [C₃₃H₂₈N₆FeI⁺], 691, found: 691.0.
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

**Characterisation of [Fe(bis-NHC)(bipy)₂]I₂ (3)**

Crystals of complex 3 were obtained by slow diffusion of Et₂O into a MeCN solution of 1.

^1^H NMR (298 K, 400 MHz, CD₃CN) (**Figure A5.3**): δ = 8.26 (d, 2H, ^3^J_{HH} = 8.1 Hz, H_bipy), 8.18 (d, 2H, ^3^J_{HH} = 8.0 Hz, H_bipy), 8.08 (d, 2H, ^3^J_{HH} = 8.0 Hz, H_bipy), 7.97 (t, 2H, ^3^J_{HH} = 7.8 Hz, H_bipy), 7.78 (br, 2H, H_PPh), 7.48–7.43 (m, 2H, H_bipy), 7.43–7.38 (m, 2H, H_bipy), 7.20–7.15 (m, 2H, H_bipy), 7.13–7.07 (m, 4H, H_PPh), 7.07–7.02 (m, 4H, H_PPh), 6.71 (t, 2H, ^3^J_{HH} = 6.5 Hz, H_bipy), 6.31 (s ap., 2H, H_imid), 6.29 (s ap., 2H, H_imid), 6.27 (s, 2H, NCH₂N), 4.50 (d, 2H, ^2^J_{HH} = 16.9 Hz, NCH₂Ph), 4.22 (d, 2H, ^2^J_{HH} = 16.9 Hz, NCH₂Ph).

^1^C NMR (298 K, 400 MHz, CD₃CN) (**Figure A5.4**): δ = 189.8 (Fe–CNHC), 161.0 (C_ipso, bipy), 158.8 (CH, bipy), 158.3 (C_ipso, bipy), 155.3 (CH, bipy), 152.0 (CH, bipy), 139.7 (CH, bipy), 138.3 (CH, bipy), 137.6 (CH, Ph), 137.5 (C_ipso, Ph), 129.2 128.1, 127.1, 126.8 (CH, Ph), 126.4 (CH, bipy), 126.2 (C_ipso, Ph), 125.9 (CH, imid), 125.8 (CH, Ph), 124.6, 124.0 (CH, bipy), 63.2 (NCH₂N), 53.0 (CH₂Ph).

5.5.3 Typical procedure for the oxidation of alcohols

An open-air flask was charged with a catalyst and alcohol (0.5 mmol). Then, TBHP (5.0–6.0 M in decane, 0.75 mmol) was added. The progress of the reactions was monitored by taking aliquots of the reaction mixtures and subjecting them to ^1^H NMR in chloroform-d₃, indicating the presence of the corresponding ketones and unreacted alcohols. The yield was determined by ^1^H NMR using diphenylmethane as an internal standard. The corresponding ketones were extracted in dichloromethane, and identified by comparison of their NMR spectral data to the literature. [20]
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II)
containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

5.6. Acknowledgements

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5.7. References


Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols


Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols


Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols


CHAPTER 6: CONCLUSIONS AND OUTLOOK
Conclusions and Outlook

The use of Mn NHC complexes in catalysis is an area that has been poorly investigated. For this reason, the main goal of this thesis was the development of new Mn-NHC complexes and their application in catalysis.

Specifically, we have demonstrated that purely organometallic NHC-based tricarbonyl Mn(I) complexes are highly efficient catalysts for the selective electrocatalytic reduction of CO₂ to CO, exceeding 100 turnovers with excellent faradaic yields (ηCO ≈95%) in anhydrous acetonitrile. These findings contrast with those reported for classical bpy-based manganese systems, which resulted to be inactive without an explicit proton source. Moreover, the addition of water leads to the highest TOF max value (ca. 320000 s⁻¹) ever reported for a manganese-based catalyst. Complementary FTIR_SEC measurements and computational data, allow us to propose a mechanism for the reduction of CO₂, which includes the participation of a Mn(I) tetracarbonyl intermediate that was detected under catalytic conditions for the first time. It was proved that the strongly nucleophilic character of the Mn atom was responsible for the positive ligand effect on catalysis.

These new Mn NHC complexes were also applied in the reduction of carbonyl groups through hydrosilylation reactions. They displayed excellent catalytic activity in the reduction of a wide variety ketones, using silanes as reducing agents, including polymethylhydrosiloxane, which is an inexpensive, easy to handle, and environmentally friendly byproduct of the silicone industry. Interestingly, the Mn NHC complexes are air stable and catalytic experiments were performed under atmospheric air. We have demonstrated that the presence of NHC ligands in the coordination sphere of Mn produces an enhancement of the catalyst performance. In situ monitoring of the
Chapter 6: Conclusions and Outlook

reaction allow us the detection of the active species, a facial tricarbonyl compound without loss of any CO ligand. In addition, $^1$H NMR experiments showed the formation of a Mn complex featuring a signal at -6.8 ppm, which could be indicative of the formation of manganese hydride species.

Next, we dedicate our studies to the synthesis of an entirely new family of carbonyl manganese complexes containing 1,2,3-triazolylidene ligands. We have described the synthesis of new Mn(0) and Mn(I) complexes with bridging or chelating di(1,2,3-triazolylidene) ligands. All complexes were fully characterized, including the X-ray diffraction study of a bimetallic Mn(0) complex. This unprecedented bimetallic complex displayed high yield and selectivity in the catalytic oxidation of secondary alcohols and benzyl alcohol with TBHP under mild conditions.

Finally, the last part of my thesis was dedicated to develop a new family of Fe(II) NHC complexes containing pyridyl systems. The Fe bis-NHC complex [Fe(bis-NHC)(bipy)$_2$] is stable in acetonitrile for at least 4 h. However after 16 h, it evolves to a mixture of [Fe(bis-NHC)(bipy)$_2$]$_2$ and [Fe(bipy)$_3$]. Similar decomposition of [Fe(bis-NHC)(bipy)$_2$] was observed in other solvents such as methanol and water. Interestingly, [Fe(bis-NHC)(bipy)$_2$] complexes were active pre-catalysts in the oxidation of 1-phenylethanol with TBHP in neat conditions. Nevertheless, the lack of stability of these Fe(II) complexes in solution prevented their further investigation in catalysis.

In summary, we have contributed to expand the area of catalytic reductions and oxidations using Mn and Fe NHC complexes as catalysts. We believe that our work may inspire future studies in the field of catalysis with abundant first-row transition metals. Currently, ongoing studies in our group are focusing on exploring the catalytic activity of Mn NHC complexes in the reduction of other carbonyl groups.
such as esters and carboxamides. In addition, the synthesis of Mn NHC compounds with improved catalytic efficiencies is underway.
APPENDICES
CHAPTER 2: A HIGHLY ACTIVE N-HETEROCYCLIC CARBENE MANGANESE(I) COMPLEX FOR SELECTIVE ELECTROCATALYTIC CO₂ REDUCTION TO CO

A2.1 TOF_{max} calculation from CV data
A2.2 Characterization data for complexes 1-2 (\textsuperscript{1}H-\textsuperscript{13}C NMR, ESI-MS TOF, IR (KBr))
A2.3 Electrochemistry/ electrocatalysis/ Spectroelectrochemistry
A2.4 Computational details
A2.5 References
A2.1 TOF\textsubscript{max} calculation from CV data

The values reported in the main text for the TOF\textsubscript{max} of complex 1 under CO\textsubscript{2}-saturated atmosphere in anhydrous and aqueous CH\textsubscript{3}CN (0.56 M H\textsubscript{2}O) are obtained from CV data by using the equations 1–7. We consider a pseudo-first order kinetics for the catalytic process since there is a large excess of substrate in comparison to the catalyst during CV experiments. Therefore, the observed catalytic current plateau under CO\textsubscript{2} can be described by the eq. 1:

\[ i_{\text{cat}} = n_{\text{cat}}F A C_{\text{cat}}^0 \sqrt{(D k_{\text{cat}}[C O_2])^y} \]  

(1)

\[ \text{TOF}_{\text{max}} = k_{\text{cat}}[C O_2]^y \]  

(2)

where \( n_{\text{cat}} \) is the number of electrons required for the catalytic CO\textsubscript{2}-to-CO reaction (\( n_{\text{cat}}=2 \)), \( F \) is Faraday’s constant, \( A \) is the surface area of the working electrode, \( C_{\text{cat}}^0 \) is the catalyst concentration in the bulk solution, \( D \) is the diffusion coefficient for the catalytically-active species, \( k_{\text{cat}} \) is the rate constant of the overall catalytic reaction, \([C O_2]\) is the concentration of the substrate in the electrolyte and \( y \) is the order of the latter in the catalytic process. The normalization of the catalytic current (\( i_{\text{cat}} \)) to the peak current obtained for the uncatalyzed process in the absence of substrate (\( i_{p} \), eq. 3) leads to a practical relationship between the TOF\textsubscript{max} and the ratio \( i_{\text{cat}}/i_{p} \) (eqs. 4-5):

\[ i_{p} = 0.4463 n_{p}^2 F A C_{\text{cat}}^0 \sqrt{F \frac{RT}{v}} \]  

(3)

\[ \frac{i_{\text{cat}}}{i_{p}} = \frac{n_{\text{cat}}}{n_{p}} \frac{1}{0.4463} \frac{RT}{Fv} \frac{\text{TOF}_{\text{max}}}{T} \]  

(4)

\[ \text{TOF}_{\text{max}} = 0.1992 \frac{n_{p}^3}{n_{\text{cat}}^2 RT} \left( \frac{i_{\text{cat}}}{i_{p}} \right)^2 \]  

(5)

where \( n_{p} \) is the number of electrons transferred in the non-catalytic process (\( n_{p}=2 \) for 1), \( R \) is the universal gas constant, \( T \) is temperature.
and $\nu$ is the scan rate of the potential sweep. Accordingly to eq. 4, the access to $TOF_{\text{max}}$ can be obtained by the slope of the linear plot between $i_{\text{cat}}/i_p$ and the function $\nu^{-1/2}$:

$$slope = \frac{n_{\text{cat}}}{n_p^{3/2}} \frac{1}{0.4463} \sqrt{\frac{RT}{F}} TOF_{\text{max}}$$

(6)

$$TOF_{\text{max}} = 0.199 (slope)^2 \frac{n_p^3}{n_{\text{cat}}^2} \frac{F}{RT}$$

(7)

The use of eq. 1 requires steady-state catalytic conditions, represented by a scan rate-independent plateau current. As it can be seen by the Figures A2.11 and 2.3, a “pure kinetic” regime is observed at high scan rates for 1. Thus, the scan rate-independent $TOF_{\text{max}}$ values for the electrocatalytic process under CO$_2$ in anhydrous CH$_3$CN and in the presence of 0.56 M H$_2$O is evaluated in the ranges $\nu$=0.1–1.0 V s$^{-1}$ (Figures A2.11 and A2.12) and $\nu$=50–100 V s$^{-1}$ (Figure 2.3), respectively. As a result it is observed an $i_{\text{cat}}/i_p$ that linearly vary over $\nu^{-1/2}$. Moreover, it is worth mentioning that $i_{\text{cat}}$ and $i_p$ refer to solutions with the same electrolyte composition.
Table A2.1 Electro catalytic CO$_2$-to-CO reduction TOF values reported in the literature for selected Mn(I)-based molecular catalysts containing bipyridyl and pyridyl-NHC ligands.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$i_{cat}/i_p$</th>
<th>$\text{TOF}_{\text{max}}$ (s$^{-1}$)</th>
<th>Exp. Conditions</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(CO)$_3$(bpy)Br]</td>
<td>–</td>
<td>0.89 [a]</td>
<td>CH$_3$CN + 5% H$_2$O</td>
<td>[A]</td>
</tr>
<tr>
<td>[Mn(CO)$_3$(bpy-t-Bu)Br]</td>
<td>25</td>
<td>120</td>
<td>CH$_3$CN + 3.1 M H$_2$O</td>
<td>[B]</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>340</td>
<td>CH$_3$CN + 1.4 M TFE</td>
<td></td>
</tr>
<tr>
<td>[Mn(CO)$_3$(dhbpy)Br]</td>
<td>–</td>
<td>1.4 [b]</td>
<td>Dry CH$_3$CN</td>
<td>[C]</td>
</tr>
<tr>
<td><a href="OTf">Mn(CO)$_3$(mesbpy)(CH$_3$CN)</a></td>
<td>20 [c]</td>
<td>700 [c]</td>
<td>CH$_3$CN + 3.5 M H$_2$O</td>
<td>[D]</td>
</tr>
<tr>
<td></td>
<td>50 [c]</td>
<td>5000 [c]</td>
<td>CH$_3$CN + 1.4 M TFE</td>
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</tr>
<tr>
<td><a href="OTf">Mn(CO)$_3$((MeO)$_2$Ph)$_2$bpy)(CH$_3$CN)</a></td>
<td>5.9 [d]</td>
<td>258 [e]</td>
<td>CH$_3$CN + 6.33 M H$_2$O</td>
<td>[E]</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>&lt;1 [f]</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>12.6 [g]</td>
<td>1257 [e]</td>
<td>CH$_3$CN + 1.37 M PhOH</td>
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<td></td>
<td>–</td>
<td>138 [f]</td>
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<tr>
<td>[Mn(CO)$_3$(Me-Im-Py)Br]</td>
<td>1.9 [h]</td>
<td>0.07 [h]</td>
<td>CH$_3$CN + 5% H$_2$O</td>
<td>[F]</td>
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<td>[Mn(CO)$_3$(Et-Im-Py)Br]</td>
<td>2.1 [c]</td>
<td>0.86 [c]</td>
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<td>[Mn(CO)$_3$(Et-Im-Py)(SCN)]</td>
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<td>[Mn(CO)$_3$(Et-Im-Py)(CN)]</td>
<td>1.4 [c]</td>
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<tr>
<td>[Mn(CO)$_3$(Et-BIm-Py)(CN)]</td>
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<td>0.28 [c]</td>
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<tr>
<td>[Mn(CO)$_3$(Et-BIm-Pyrim)Br]</td>
<td>5.2 [c]</td>
<td>42 [c]</td>
<td>CH$_3$CN + 5% H$_2$O</td>
<td>[H]</td>
</tr>
</tbody>
</table>
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

A2.2 Characterization data for complexes 1-2 (¹H-¹³C NMR, ESI-MS TOF, IR (KBr))

Figure A2.1 ¹H NMR in DMSO-d₆ of manganese complex 1.

Figure A2.2 ¹³C(¹H) NMR in DMSO-d₆ of manganese complex 1.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

Figure A2.3 ¹H NMR in DMSO-d₆ of manganese complex 2.

Figure A2.4 ¹³C(¹H) NMR in DMSO-d₆ of manganese complex 2.
Figure A2.5 MS (ESI-TOF) in methanol of 1.

Figure A2.6 IR (KBr) of manganese complex 1.
Figure A2.7 IR (KBr) of manganese complex 2.

A2.3 Electrochemistry/electrocatalysis/Spectroelectrochemistry

Figure A2.8 CV of 1 (1 mM) in 0.1 M TBAPF$_6$/MeCN under Ar at v = 0.1 V s$^{-1}$. 

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**Figure A2.9** CVs of 3 (1 mM) in 0.1 M TBAPF$_6$/MeCN under Ar (black curve) and under CO$_2$- saturated atmosphere (red curve). Scan rate $v = 0.1$ V s$^{-1}$.

**Figure A2.10** Up: CVs of 1 (1 mM) in 0.1 M TBAPF$_6$/MeCN under Ar at different scan rates: $v=0.1$ (black), 0.2, 0.3, 0.5, 0.8, 1, 1.5, 2, 2.5, 3.5 (blue), 10 (red) V s$^{-1}$. Bottom: Plot of the reductive peak current ($i_p$) as a function of the square root of the scan rate ($v^{1/2}$).
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Figure A2.11 CVs of 1 (1 mM) in 0.1 M TBAPF$_6$/MeCN under CO$_2$-saturated conditions at different scan rates (v): v= 0.05 (blue), 0.1 (violet), 0.2 (orange), 0.3 (red), 0.5 (green), 0.8 (grey), 1 (brown) V s$^{-1}$.

Figure A2.12 Plot of the catalytic plateau current normalized for the current peak under Ar ($i_{cat}/i_p$) vs. the function $v^{-1/2}$. Scan rates: $v = 0.1–1.0$ V s$^{-1}$. From the slope of the plot, a TOF$_{max}$ = 2.1 ± 0.1 × 10$^3$ s$^{-1}$ is calculated.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO$_2$ Reduction to CO

**Figure A2.13** CVs of various amounts of 1 in 0.1 M TBAPF$_6$/MeCN under CO$_2$-saturated conditions at $v = 0.1$ V s$^{-1}$. Catalyst loading: [cat] = 0.20 (green), 0.37 (orange), 0.53 (grey), 0.67 (yellow), 0.81 (blue), 0.93 (red) mM. Linear plot of catalytic current density ($j$) vs. catalyst concentration.

**Figure A2.14** Current (blue) and charge (red) passed over electrolysis time during CPE of 1 (1 mM) in 0.1 M TBAPF$_6$/MeCN under CO$_2$ at $E_{appl} = -2.32$ V.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

Figure A2.15 Variation of Faradaic efficiency for CO production (η_{CO}) over electrolysis time during CPE of 1 (1 mM) in 0.1 M TBAPF₆/MeCN under CO₂ at E_{appl} = –2.32 V.

Figure A2.16 Catalytic CO production over time during CPE of 1 (1 mM) in 0.1 M TBAPF₆/MeCN under CO₂ at E_{appl} = –2.37 V.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

Figure A2.17 CPE of 1 (1 mM) in 0.1 M TBAPF₆/MeCN under CO₂ at $E_{\text{appl}} = -2.37$ V. Linear correlation between the moles of CO evolved during the reaction and the moles of electrons consumed. The value for $\eta_{CO}$ (∗100) is obtained by multiplying the slope of the linear plot for 3 ($\eta_{CO} = 97\%$).

Figure A2.18 “Rinse test” experiment. The red curve describes the charge passed during CPE of 1 (1 mM) in 0.1 M TBAPF₆/MeCN under CO₂ at $E_{\text{appl}} = -2.32$ V. After electrolysis, the working electrode (a GC rod) was rapidly replaced from the 1 solution and immersed into a fresh CO₂-saturated 0.1 M TBAPF₆/MeCN blank electrolyte. Indeed, another CPE performed at $E_{\text{appl}} = -2.32$ V revealed a negligible charge (blue curve) in comparison with the one achieved in the presence of the catalyst 1 (red).
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO$_2$ Reduction to CO

**Figure A2.19** Current (blue) and charge (red) passed over electrolysis time during CPE of 3 (1 mM) in 0.1 M TBAPF$_6$/MeCN under CO$_2$ at $E_{appl} = -2.57$ V.

**Figure A2.20** CPE of 3 (1 mM) in 0.1 M TBAPF$_6$/MeCN under CO$_2$ at $E_{appl} = -2.57$ V. Left: Catalytic CO production over time. Right: Variation of Faradaic efficiency for CO production ($\eta_{CO}$) over electrolysis time.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

Figure A2.21 FTIR spectra of 1 (~4 mM) in 0.2 M TBAPF₆/CH₃CN recorded under Ar at different times (Δt = t₃ − t₁ approximately 30 minutes). A slow solvolysis equilibrium between the neutral starting species 1 (νCO = 2007, 1922 and 1887 cm⁻¹) and [Mn(CO)₃(bis-MeNHC)(CH₃CN)]⁺ (1- CH₃CN⁺, νCO = 2025, 1935(sh) and 1925 cm⁻¹) takes place at resting potential.

Figure A2.22 FTIR-SEC changes observed during reduction (at ca. −2.30 V) of 1 (~4 mM) in 0.2 M TBAPF₆/MeCN under Ar. Black and red curves describe the starting and the final spectra, whereas blue line refers to an intermediate spectrum.
Table A2.2 Experimental and DFT calculated FTIR spectra of the proposed species for 1.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\nu_{\text{CO}}$ (cm$^{-1}$)</th>
<th>Experimental</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mn(CO)}_3(L1)\text{Br}]$ (1)</td>
<td>2007, 1922, 1887</td>
<td>2005, 1927, 1893</td>
<td></td>
</tr>
<tr>
<td>$[\text{Mn(CO)}_3(L1)(\text{CH}_3\text{CN})]^+$(1 -CH$_3$CN$^+$)</td>
<td>2025, 1935(sh), 1925</td>
<td>2024, 1938, 1928</td>
<td></td>
</tr>
<tr>
<td>$[\text{Mn(CO)}_3(L1)]^-$ (1$^-$)</td>
<td>1827, 1731, 1713</td>
<td>1823, 1731, 1707, 1695</td>
<td></td>
</tr>
</tbody>
</table>

Linear correlation between Experimental and theoretical IR data. Scaling factor employed for the theoretical IR data was 0.9775.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO$_2$ Reduction to CO

**Figure A2.23** DFT calculated FTIR spectra (vCO) of the main intermediate species observed during IR-SEC experiments. The experimental values of the CO stretches are represented by vertical lines for each species.

**Figure A2.24** UV-Vis spectroelectrochemical changes observed during reduction of 1 under Ar in a 0.2 M TBAPF$_6$/MeCN solution. Black and red curves describe the starting and the final spectra, whereas blue lines refer to selected intermediate spectra.
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**Figure A2.25** As recorded FTIR-SEC spectra of 1 (~4 mM) in a CO$_2$-saturated 0.2 M TBAPF$_6$/CH$_3$CN solution at the foot of the catalytic wave. Black and red curves describe the starting and the final spectra, whereas blue lines refer to selected intermediate spectra.

**Figure A2.26** Differential FTIR-SEC spectra of 1 (~4 mM) in a CO$_2$-saturated 0.2 M TBAPF$_6$/CH$_3$CN solution at the foot of the catalytic wave. Black and red curves describe the starting and the final spectra, whereas blue lines refer to selected intermediate spectra. Difference spectra vs. OCP (open circuit potential).
Figure A2.27 CVs of 1 (1 mM) in 0.1 M TBAPF$_6$/MeCN under Ar (black), under CO$_2$-saturated atmosphere (red) and under CO$_2$ saturation in wet (0.09 M H$_2$O) MeCN (blue). Scan rate $v = 0.1$ V s$^{-1}$.

Figure A2.28 CVs of 1 (1 mM) in 0.1 M TBAPF$_6$/MeCN under Ar in the absence (black) and in the presence of various amounts of H$_2$O: 0.09 M (violet), 0.19 M (green), 0.28 M (orange), 0.37 M (light blue), 0.56 M (pink), 0.74 M (grey), 1.67 M (blue), 2.60 M (brown). Scan rate $v = 0.1$ V s$^{-1}$. 
Figure A2.29 CVs of 2 (1 mM) in 0.1 M TBAPF$_6$/CH$_3$CN under Ar in the absence (black) and in the presence of added 5% H$_2$O (green), as well as under CO$_2$-saturated atmosphere in the absence (red) and in the presence of added 5% H$_2$O (blue). Scan rate $v = 0.1$ V s$^{-1}$.

Figure A2.30 CVs of 2 (1 mM) in 0.1 M TBAPF$_6$/CH$_3$CN under Ar (black) and under CO$_2$ (red) without the addition of an explicit proton source, and under CO$_2$ upon the addition of various amounts of H$_2$O: 0.18 M (blue), 0.28 M (brown), 0.55 M (orange), 1.09 M (grey), 1.88 M (green). Scan rate $v = 0.1$ V s$^{-1}$. 
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

Figure A2.31 Current (blue) and charge (red) passed over electrolysis time during CPE of a 0.1 M TBAPF₆/MeCN solution of 1 (1 mM) containing 0.22M H₂O under CO₂ at \( E_{\text{appl}} = -2.32 \) V.

Figure A2.32 CPE of a 0.1 M TBAPF₆/MeCN solution of 1 (1 mM) containing 0.22M H₂O under CO₂ at \( E_{\text{appl}} = -2.32 \) V. Linear correlation between the moles of CO evolved during the reaction and the moles of electrons consumed. The value for \( \eta_{\text{CO}} (\times 100) \) is obtained by multiplying the slope of the linear plot for 3 (\( \eta_{\text{CO}} = 98\% \)).
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO\textsubscript{2} Reduction to CO

Figure A2.33 Catalytic CO production over time during CPE of a 0.1 M TBAPF\textsubscript{6}/CH\textsubscript{3}CN solution of 1 (1 mM) containing 0.22 M H\textsubscript{2}O under CO\textsubscript{2} at E\textsubscript{appl} = −2.32 V.

Table A2.3 Crystal data and structure refinement for 1.

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<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
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<td>Empirical formula</td>
<td>C12 H12 Br0.90 Mn N4 O3</td>
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<tr>
<td>Formula weight</td>
<td>387.11</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.6714(3) Å</td>
</tr>
<tr>
<td></td>
<td>b = 17.9400(4) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90°</td>
</tr>
<tr>
<td></td>
<td>β = 93.498(3)°</td>
</tr>
</tbody>
</table>
## Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
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<tr>
<td>c = 10.3393(3) Å</td>
<td>Y = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1420.31(8) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.810 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.476 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>770</td>
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<tr>
<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.270 to 37.99°</td>
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<tr>
<td>Index ranges</td>
<td>-11 ≤ h ≤ 13, -30 ≤ k ≤ 30, 17 ≤ l ≤ 17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>13013</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>13013 [R(int) =?]</td>
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<tr>
<td>Completeness to theta = 37.399°</td>
<td>98.1%</td>
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<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.624 and 0.48</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>13013/ 0 /193</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.057</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0521, wR2 = 0.1383</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0609, wR2 = 0.1423</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.641 and -2.048 e. Å³</td>
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</tbody>
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**Table A2.4** Representative bond lengths [Å] and angles [°] for 1.

<table>
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<th>Bond</th>
<th>Length [Å]</th>
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<tr>
<td>Br1-Mn1</td>
<td>2.5744(3)</td>
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<tr>
<td>Mn1-C10</td>
<td>1.782(2)</td>
</tr>
<tr>
<td>Mn1-C12</td>
<td>1.810(2)</td>
</tr>
<tr>
<td>Mn1-C13</td>
<td>1.819(2)</td>
</tr>
<tr>
<td>Mn1-C1</td>
<td>2.0412(19)</td>
</tr>
<tr>
<td>Mn1-C6</td>
<td>2.043(2)</td>
</tr>
<tr>
<td>C10-Mn1-C12</td>
<td>89.69(9)</td>
</tr>
<tr>
<td>C10-Mn1-C13</td>
<td>89.26(9)</td>
</tr>
<tr>
<td>C12-Mn1-C13</td>
<td>88.12(9)</td>
</tr>
<tr>
<td>C10-Mn1-C1</td>
<td>91.60(9)</td>
</tr>
<tr>
<td>C12-Mn1-C1</td>
<td>92.65(9)</td>
</tr>
<tr>
<td>C13-Mn1-C1</td>
<td>178.84(8)</td>
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<td>C10-Mn1-C6</td>
<td>91.90(8)</td>
</tr>
<tr>
<td>C12-Mn1-C6</td>
<td>177.29(9)</td>
</tr>
<tr>
<td>C1-Mn1-C6</td>
<td>85.11(8)</td>
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<tr>
<td>C10-Mn1-Br1</td>
<td>178.96(7)</td>
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<tr>
<td>C1-Mn1-Br1</td>
<td>89.21(5)</td>
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<tr>
<td>C6-Mn1-Br1</td>
<td>87.52(5)</td>
</tr>
</tbody>
</table>

**Crystal preparation:** Crystals of 1 were grown by slow diffusion of hexane in CH₂Cl₂. The crystals for this samples were selected using a Zeiss stereomicroscope using polarized light and prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.
Data collection: Crystal structure determinations were carried out using a Apex DUO Kappa 4- axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 lus using MoK$_\alpha$ radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus ($T = -173 \, ^\circ C$). Programs used: Bruker Device: Data collection APEX-2,$^1$ data reduction Bruker Saint$^2$ V/.60A and absorption correction SADABS$^3$ or TWINABS$^4$.

Structure Solution and Refinement: Crystal structure solution was achieved using the computer program SHELXT$^5$. Visualization was performed with the program SHELXL$^6$. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least- squares refinement on $F^2$ using all measured intensities was carried out using the program SHELXL 2015$^7$. All non-hydrogen atoms were refined including anisotropic displacement parameters. The collected data were processed with TWINABS taking in account overlapping reflections (citation: TWINABS Version 2012/1 Bruker AXS Blessing, Acta Cryst. (1995) A51 33-38). The CHECKCIF-cif shows a B-alert which was properly commented.

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Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO$_2$ Reduction to CO


A2.4 Computational details
Figure A2.34 Top) Selected Kohn-Sham orbitals of the proposed intermediate species $1^+$, $1^-$ and $1^-$. $L = \text{bis-MeNHC}$. Bottom) Comparison of the HOMO orbitals of $1^-$ (Left) and $2^-$ (Right).

Figure A2.35 Energy profile for the catalytic cycle of CO$_2$ reduction to CO of 1 starting from the $1^-$. CH$_3$CN. Energies are given in kcal·mol$^{-1}$. TDTS (TOF-determining transition state).
Figure A2.36 Energy profile for the catalytic cycle of CO\textsubscript{2} reduction to CO of 2 starting from the \textsuperscript{2}+ CH\textsubscript{3}CN. Energies are given in kcal·mol\textsuperscript{-1}. TDTS (TOF determining transition state).

Figure A2.37 Comparison of the energy profiles for the TDTS (TOF-determining transition state). For complexes 1 (black) and 2 (green). Energies are given in kcal·mol\textsuperscript{-1}.
Figure A2.38 Transition state structures for the mono (top) and di addition (middle) of CO$_2$, and the C-O bond cleavage (bottom) with complex 1.
Figure A2.39 Transition state structures for the mono (top) and di addition (middle) of CO₂, and the estimated energy maximum in the C-O bond cleavage scan (bottom) with complex 2.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO$_2$ Reduction to CO

Figure A2.40 PES of the O-C bond cleavage PES with complex 2 (blank dots $\Delta E$, red dots $\Delta G$).

Figure A2.41 Selected structures from the O-C bond cleavage PES.
Chapter 2: A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

A2.5 References


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CHAPTER 3: MANGANESE N-HETEROCYCLIC CARBENE COMPLEXES FOR CATALYTIC REDUCTION OF KETONES WITH SILANES

A3.1 NMR data of complexes 2 and 5
A3.2 IR spectra for 2 and 5
A3.3 MS (ESI-TOF) spectra for 5
A3.4 NMR spectra of the alcohol products
A3.1 NMR data of complexes 2 and 5

Figure A3.1 $^1$H NMR (DMSO-d$_6$, 400 MHz) for 2.

Figure A3.2 $^{13}$C NMR (DMSO-d$_6$, 400 MHz) for 2.
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.3 $^1$H NMR (acetonitrile-d$_3$, 400 MHz) for 5.

Figure A3.4 $^{13}$C NMR (acetonitrile-d$_3$, 400 MHz) for 5.
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

A3.2 IR spectra for 2 and 5

Figure A3.5 IR (KBr) for 2.

Figure A3.6 IR (KBr) for 5.
A3.3 MS (ESI-TOF) spectra for 5

![MS (ESI-TOF) spectra for 5](image)

Figure A3.7 MS (ESI-TOF) in acetonitrile for 5.

A3.4 NMR spectra of the alcohol products

Note that in some cases spectra are performed using $n$-tetradecane as an internal standard

![NMR spectra of the alcohol products](image)

Figure A3.8 $^1$H NMR (CDCl$_3$, 400 MHz).
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.9 $^1$H NMR (CDCl$_3$, 400 MHz).

Figure A3.10 $^1$H NMR (CDCl$_3$, 400 MHz).
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.11 $^1$H NMR (CDCl$_3$, 400 MHz).

Figure A3.12 $^1$H NMR (CDCl$_3$, 400 MHz)
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.13 $^1$H NMR (CDCl$_3$, 400 MHz).

Figure A3.14 $^1$H NMR (CDCl$_3$, 400 MHz).
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.15 $^1$H NMR (CDCl₃, 400 MHz).

Figure A3.16 $^1$H NMR (CDCl₃, 400 MHz).
Chapter 3: Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.17 $^1$H NMR (CDCl$_3$, 400 MHz).

Figure A3.18 $^1$H NMR (CDCl$_3$, 400 MHz).
Chapter 3: Manganese N-Heterocyclic Carbone Complexes for Catalytic Reduction of Ketones with Silanes

Figure A3.19 $^1$H NMR (CDCl$_3$, 400 MHz).

Figure A3.20 $^1$H NMR (CDCl$_3$, 400 MHz).
CHAPTER 4: (DI)TRIAZOLYLIDENE MANGANESE COMPLEXES IN CATALYTIC OXIDATION OF ALCOHOLS

A4.1 NMR and IR spectra of complexes 2 and 3
A4.2 Catalytic procedures
A4.3 NMR spectra of the products isolated from the catalytic oxidation of alcohols using 3 as catalyst
A4.4 Electrochemical analysis of complexes 2–5
A4.5 In operando IR analysis of alcohol oxidation
A4.6 IR measurements under catalytic conditions
A4.7 Crystallographic details
A4.8 References
A4.1 NMR and IR spectra of complexes 2 and 3

Figure A4.1 $^1$H NMR spectrum of 2 at 25 °C in DMSO-d6.

Figure A4.2 $^{13}$C ($^1$H) NMR spectrum of 2 at 25 °C in DMSO-d6. Insight shows selected range of HSQC spectrum indicating the coinciding $^{13}$C NMR frequency of the N–CH$_3$ group and the DMSO.
Figure A4.3 IR spectrum of 2 in KBr.

Figure A4.4 $^1$H NMR spectrum of 3 at 25 °C in DMSO-d$_6$. 
Chapter 4: (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols

Figure A4.5 $^{13}$C($^1$H) NMR spectrum of 3 at 25 °C in DMSO-d$_6$.

Figure A4.6 IR spectrum of 3 in KBr
### A4.2 Catalytic procedures

**Table A4.1** Reported Mn-catalysed oxidation of benzyl alcohol to benzaldehyde

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<tr>
<th>entry</th>
<th>cat</th>
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<th>TOF /h⁻¹</th>
<th>yield (%)</th>
<th>Loading (mol %)</th>
<th>conditions</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn^{II}(N₄)X₂</td>
<td>97</td>
<td>170ʰ</td>
<td>47</td>
<td>0.5</td>
<td>H₂O₂ (4 equiv), AcOH (10 equiv)</td>
<td>[A5.1]</td>
</tr>
<tr>
<td>2</td>
<td>[Mn^{V}(N)(CN)₄]²⁻</td>
<td>66</td>
<td>133ʰ</td>
<td>&lt;10</td>
<td>0.1</td>
<td>Co^{III}/Ru^{II} photocatalytic, buffer</td>
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</tr>
<tr>
<td>3</td>
<td>Mn^{II}(N₄)X₂</td>
<td>86</td>
<td>43ʰ</td>
<td>86</td>
<td>1</td>
<td>H₂O₂ (6 equiv), acid (0.5 equiv) ³</td>
<td>[A5.3]</td>
</tr>
<tr>
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<td>Mn^{II}(NO₃)₂</td>
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<td>TEMPO (5 mol%), pyrCOOH ⁴</td>
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<td>84</td>
<td>100</td>
<td>2</td>
<td>TEMPO (2 mol%), pyrCOOH, NaNO₃ ⁴</td>
<td>[A5.5]</td>
</tr>
<tr>
<td>6</td>
<td>Mn^{II}(N₄)Cl₂</td>
<td>80</td>
<td>14ʰ</td>
<td>37</td>
<td>0.5</td>
<td>H₂O₂ (4 equiv), HNO₃aq,</td>
<td>[A5.6]</td>
</tr>
<tr>
<td>7</td>
<td>MnO₂</td>
<td>0.1</td>
<td>---</td>
<td>77</td>
<td>10</td>
<td>no other oxidant</td>
<td>[A5.7]</td>
</tr>
</tbody>
</table>
Table A4.1: Catalytic Oxidation of Alcohols with Manganese Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>TOF</th>
<th>Conversion</th>
<th>Selectivity</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Literature Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Mn$^{III}$(N$_2$O$_2$)Cl</td>
<td>1000$^a$</td>
<td>960 min$^{-1}$</td>
<td>50</td>
<td>0.05</td>
<td>(NBu$_4$)HSO$_5$ (1.7 equiv), MeCN</td>
<td>[A5.8]</td>
</tr>
<tr>
<td>9</td>
<td>Mn$^{III}$(N$_2$O$_2$)Cl</td>
<td>100</td>
<td>2000$^{ae}$</td>
<td>95</td>
<td>1</td>
<td>(NBu$_4$)HSO$_5$ (1.7 equiv), MeCN</td>
<td>[A5.8]</td>
</tr>
<tr>
<td>10</td>
<td>Mn$^{II}$(N$_4$)X$_2$</td>
<td>170</td>
<td>74</td>
<td>85</td>
<td>0.5</td>
<td>H$_2$O$_2$ (1 equiv), MeCN</td>
<td>[A5.9]</td>
</tr>
<tr>
<td>11</td>
<td>Mn(bpy)$_2$X$_2$</td>
<td>152</td>
<td>n.a.</td>
<td>90</td>
<td>0.8</td>
<td>TBHP (1.6 mol%)</td>
<td>[A5.10]</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>84</td>
<td>25</td>
<td>84</td>
<td>1</td>
<td>TBHP (1.5 equiv), MeCN</td>
<td>This work</td>
</tr>
</tbody>
</table>

n.d. = not discussed

$^a$ estimated TOF based on the single time/conversion point provided in the article

$^b$ n.d. = not discussed, selectivity nuclear

$^c$ acid = adamantyl-COOH, only cinnamylalcohol (conjugated alcohol) as substrate

$^d$ AcOH as solvent, aerobic conditions, only substituted BnOH as substrate

$^e$ The Haddad system (entries 8,9) is peculiar with phenomenally high rates, but also conversions that seem to take place only in the first seconds of the reaction, but this unusual behavior has not been addressed

Earlier report on 100% selectivity and yield with a Mn$^{II}$(terpy)Cl$_2$(H$_2$O) complex$^{[A5.7]}$ was found to be heterogeneous in nature$^{[A5.8]}$ and is therefore not listed in Table A4.1. Entries 8 and 9 report very high activity, though the absence of
kinetic data do not allow for differentiating between a homogeneous catalyst and a heterogeneization (with an apparent turnover of 1000 within the first min, and then no turnovers for the subsequent 2 h). The notion of a heterogeneous catalyst is supported by the previously noted tendency of Mn complexes with N-donor ligands to heterogeneize during activation. \[A5.8\]

**Table A4.2** Reported Mn-catalysed oxidation of 1-phenylethanol to acetophenone.

<table>
<thead>
<tr>
<th>entry</th>
<th>cat</th>
<th>TON</th>
<th>TOF</th>
<th>yield (%)</th>
<th>loading (mol%)</th>
<th>conditions</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn$^{II}$(N$_4$)$_2$</td>
<td>200</td>
<td>400$^a$</td>
<td>84</td>
<td>0.5</td>
<td>H$_2$O$_2$ (4 equiv), AcOH (10 equiv)</td>
<td>[A5.1]</td>
</tr>
<tr>
<td>2</td>
<td>[Mn$^V$(N)(CN)$_4$]$^{2-}$</td>
<td>44</td>
<td>88$^a$</td>
<td>&lt;5</td>
<td>0.1</td>
<td>Co$^{III}$/Ru$^{II}$ photocatalytic, phosphate buffer</td>
<td>[A5.2]</td>
</tr>
<tr>
<td>3</td>
<td>Mn$^{II}$(N$_4$)$_2$</td>
<td>95</td>
<td>47$^a$</td>
<td>95</td>
<td>2.5</td>
<td>H$_2$O$_2$ (6 equiv), adamantylCOOH (0.5 equiv)</td>
<td>[A5.3]</td>
</tr>
<tr>
<td>4</td>
<td>Mn$^{II}$(NO$_3$)$_2$</td>
<td>25</td>
<td>9$^a$</td>
<td>100</td>
<td>4</td>
<td>TEMPO (5 mol%), pyrCOOH (6 mol%)$^b$</td>
<td>[A5.4]</td>
</tr>
<tr>
<td>No.</td>
<td>Complex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Mn^{II}(NO_3)_2</td>
<td>TEMPO (2mol%), pyrCOOH (3 mol%), NaNO_3</td>
<td>A5.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Mn^{II}(N_4)Cl_2</td>
<td>H_2O_2 (4 equiv), HNO_3aq</td>
<td>A5.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Mn^{III}(N_2O_2)Cl</td>
<td>(NBu_4)HSO_5 (1.7 equiv), MeCN</td>
<td>A5.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Mn^{II}(N_4)X_2</td>
<td>H_2O_2 (1 equiv), MeCN</td>
<td>A5.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Mn(N_4)X_2</td>
<td>H_2O_2 (1.5 equiv), HOAc (1 equiv), MeCN</td>
<td>A5.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Mn(N_4)X_2</td>
<td>H_2O_2 (1.2 equiv), H_2SO_4 (0.3 equiv), MeCN</td>
<td>A5.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Mn(OAc)_2</td>
<td>TBHP (2.5 equiv), TFA (0.1 equiv)</td>
<td>A5.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>TBHP (1.1 equiv), MeCN</td>
<td>This work</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[^a]: See references [A5.5] and [A5.6] for details on the reactions.
A4.3 NMR spectra of the products isolated from the catalytic oxidation of alcohols using 3 as catalyst

Figure A4.7 $^1$H NMR spectrum of acetophenone (CDCl$_3$, 400 MHz).

Figure A4.8 $^1$H NMR spectrum of cyclohexanone (CDCl$_3$, 400 MHz).
Chapter 4: (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols

Figure A4.9 $^1$H NMR spectrum of benzaldehyde (CDCl$_3$, 400 MHz). *Benzoic acid.

Figure A4.10 $^1$H NMR spectrum of propiophenone (CDCl$_3$, 400 MHz).
Figure A4.11 $^1$H NMR spectrum of cyclopropyl methyl ketone (CDCl$_3$, 400 MHz).

Figure A4.12 $^1$H NMR spectrum of 2-hexanone (CDCl$_3$, 400 MHz).
Chapter 4: (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols

A4.4 Electrochemical analysis of complexes 2–5

Figure A4.13 Overlaid CV plots of 0.5 mM solutions of [Ru(bpy)$_3$](PF$_6$)$_2$ and Ferrocene (grey), and blank solution (blue) in 0.1 M [NBu$_4$]PF$_6$ in MeCN, scan rate 500 mV s$^{-1}$.

Complex 2

Figure A4.14 Overlaid CV plots of 0.5 mM solutions of complex 2 and ferrocene as internal standard (grey), and blank solution (blue) in 0.1 M [NBu$_4$]PF$_6$ in MeCN, scan rate 100 mV s$^{-1}$.

Table A4.3 Electrochemical data from a 0.5 mM solution of complex 2 at different scan rates.

<table>
<thead>
<tr>
<th>Scan rate (mV)</th>
<th>I$_{pa}$ (μA)</th>
<th>I$_{pc}$ (μA)</th>
<th>I$<em>{pc}$/I$</em>{pa}$$^a$</th>
<th>E$_{pa}$ (V)</th>
<th>E$_{pc}$ (V)</th>
<th>E$_{1/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>15.01</td>
<td>10.70</td>
<td>0.71</td>
<td>0.368</td>
<td>0.233</td>
<td>0.301</td>
</tr>
<tr>
<td>750</td>
<td>12.47</td>
<td>9.30</td>
<td>0.74</td>
<td>0.366</td>
<td>0.233</td>
<td>0.299</td>
</tr>
<tr>
<td>500</td>
<td>10.47</td>
<td>7.59</td>
<td>0.72</td>
<td>0.356</td>
<td>0.233</td>
<td>0.294</td>
</tr>
<tr>
<td>200</td>
<td>6.78</td>
<td>4.95</td>
<td>0.73</td>
<td>0.351</td>
<td>0.236</td>
<td>0.293</td>
</tr>
<tr>
<td>100</td>
<td>5.01</td>
<td>3.25</td>
<td>0.65</td>
<td>0.348</td>
<td>0.241</td>
<td>0.294</td>
</tr>
<tr>
<td>50</td>
<td>3.97</td>
<td>2.64</td>
<td>0.66</td>
<td>0.346</td>
<td>0.243</td>
<td>0.294</td>
</tr>
</tbody>
</table>
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The \( I_{\text{pc}}/I_{\text{pa}} \) ratio of the redox process is fairly constant over a broad scan rate. Together with the small potential difference between \( E_{\text{pc}} \) and \( E_{\text{pa}} \) (\( \Delta E = \text{ca. 120 mV} \)), this indicates an E mechanism with a reversible redox process for complex 2 at +0.30 V (vs Fc+/Fc).

Figure A4.15 DPV oxidation (blue) and reduction (yellow) of 0.5 mM solutions of complex 2 in 0.1 M [NBu₄]PF₆ in MeCN (0.005 V step potential).

Figure A4.16 Left: Overlaid CV plots of 0.5 mM solutions of complex 2 at different scan rates in 0.1 M [NBu₄]PF₆ in MeCN in a larger potential window (−0.1 V to +1.14 V vs Fc/Fc⁺) reveal further redox processes, although considerably less intense than the redox event at +0.30 V. Right: DPV oxidation (blue) and reduction (yellow) of complex 2 (0.005 V step change).
Figure A4.17 Overlaid CV plots of 0.5 mM solutions of the ligand precursor 1b (grey), and blank solution (blue) in 0.1 M [NBu₄]PF₆ in MeCN (scan rate 500 mV s⁻¹) show that this compound is electrochemically inert in the –0.1 to +1.14 V potential range (vs Fc/Fc⁺).

Complex 3

Table A4.4 Electrochemical data from a 0.5 mM solution of complex 3 at different scan rates.

<table>
<thead>
<tr>
<th>Scan rate (mV s⁻¹)</th>
<th>I_{pa} (µA)</th>
<th>I_{pc} (µA)</th>
<th>I_{pc}/I_{pa}a</th>
<th>E_{pa} (V)</th>
<th>E_{pc} (V)</th>
<th>E_{1/2} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>22</td>
<td>16.2</td>
<td>0.73</td>
<td>0.022</td>
<td>–0.063</td>
<td>–0.021</td>
</tr>
<tr>
<td>500</td>
<td>15.3</td>
<td>9.7</td>
<td>0.63</td>
<td>0.019</td>
<td>–0.060</td>
<td>–0.021</td>
</tr>
<tr>
<td>250</td>
<td>11.15</td>
<td>6.09</td>
<td>0.54</td>
<td>0.017</td>
<td>–0.064</td>
<td>–0.023</td>
</tr>
<tr>
<td>100</td>
<td>7.99</td>
<td>3.64</td>
<td>0.45</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>50</td>
<td>6.77</td>
<td>3.64</td>
<td>0.54</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a The gradual decrease of the I_{pc}/I_{pa} ratio suggests an EC mechanism. However, analysis of the current ratio (I_{pc}/I_{pa}) vs time does not correlate with a first or second order rate law, which may indicate that the electron transfer is not a fully reversible process, i.e. both E and C are not reversible.
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Figure A4.18 Measurement of complex 3 over a larger potential window (−0.5 to +1.12 V vs Fc/Fc). Left: Overlaid CV plots of 0.5 mM solutions of complex 3 and [Ru(bpy)3](PF6)2 as internal standard (grey), and blank solution (blue) in 0.1 M [NBu4]PF6 in MeCN, scan rate 500 mV s⁻¹. Right: DPV oxidation (blue) and reduction (yellow) with step potential = 0.005 V.

Figure A4.19 CV measurements of the ligand precursor 1a (grey; blank solution blue) does not show any redox activity (2 mM di(triazolium) salt in 0.1 M [NBu4]PF6 in MeCN, scan rate 500 mV s⁻¹.

Complex 4

Table A4.5 Electrochemical data from a 0.5 mM solution of complex 4 at different scan rates.

<table>
<thead>
<tr>
<th>Scan rate (mV s⁻¹)</th>
<th>Ipa (µA)</th>
<th>Ipc (µA)</th>
<th>Ipca/Ipa¹</th>
<th>Epa (V)</th>
<th>Epc (V)</th>
<th>E1/2 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>26.46</td>
<td>19.78</td>
<td>0.748</td>
<td>0.431</td>
<td>0.348</td>
<td>0.389</td>
</tr>
<tr>
<td>750</td>
<td>23.23</td>
<td>15.8</td>
<td>0.680</td>
<td>0.431</td>
<td>0.346</td>
<td>0.388</td>
</tr>
<tr>
<td>500</td>
<td>19.26</td>
<td>11.55</td>
<td>0.600</td>
<td>0.434</td>
<td>0.339</td>
<td>0.386</td>
</tr>
<tr>
<td>250</td>
<td>13.82</td>
<td>5.94</td>
<td>0.435</td>
<td>0.428</td>
<td>0.350</td>
<td>0.389</td>
</tr>
<tr>
<td>100</td>
<td>9.51</td>
<td>–</td>
<td>–</td>
<td>0.426</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

¹ Analysis of the Ipca/Ipa ratio relative to the scan rate is in agreement with a first order chemical reaction of the oxidized species (linear correlation factor R > 0.99), thus suggesting an EC mechanism.
Figure A4.20 Overlaid CV plots of a fresh solutions of complex 4 (grey) and after standing for 40 min (blue; 0.5 mM complex, 0.1 M [NBu₄]PF₆ in MeCN, 100 mV s⁻¹ scan rate) indicate that complex 4 decomposes over time. Also note that in a larger potential window three oxidation processes are observed at around −0.1 V, 0.4 V, and 0.9 V.

A4.5 In operando IR analysis of alcohol oxidation

Figure A4.21 IR spectra of complex 3 in MeCN at 40 °C (red) and pure solvent (blue).
Figure A4.22 IR spectra of 1-phenylethanol in MeCN at 40 °C (orange) and pure solvent (purple).

Figure A4.23 IR spectra of TBHP in MeCN at 40 °C (blue) and pure solvent (purple).
Figure A4.24 IR spectra of acetophenone in MeCN at 40 °C (purple) and pure solvent (blue).

Figure A4.25 IR spectra of mesitylene in MeCN at 40 °C (orange) and pure solvent (blue).
A4.6 IR measurements under catalytic conditions

Figure A4.26 Catalytic profile for the oxidation of 1-phenylethanol using complex 3 under conditions as described in Figure 4.12. Conversions were determined by $^1$H NMR integration using mesitylene as internal standard (orange line) and time-resolved online MCT FT-IR spectroscopy. The height of the IR band at 1686 cm\(^{-1}\) (blue) shows an excellent correlation with conversions determined by $^1$H NMR spectroscopy (Table 4.3).

A4.7 Crystallographic details

Table A4.6 Crystal data and structure refinement for 3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC No.</td>
<td>1895142</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C18H16Mn2N6O8</td>
</tr>
<tr>
<td>Formula weight</td>
<td>554.25</td>
</tr>
<tr>
<td>Temperature</td>
<td>123(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 14.6208(2)\text{Å}$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$b = 10.59240(10)\text{Å}$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 108.231(2)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 15.2131(2)\text{Å}$</td>
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<td></td>
<td>$\gamma = 90^\circ$</td>
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<tr>
<td>Volume</td>
<td>2237.78(5) Å3</td>
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<td>Z</td>
<td>4</td>
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<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Density</td>
<td>1.645 Mg m$^{-3}$</td>
</tr>
<tr>
<td>(calculated)</td>
<td></td>
</tr>
<tr>
<td>Absorption Coefficient</td>
<td>1.186 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1120</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.353 x 0.154 x 0.106 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.418 to 28.169°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-19 \leq h \leq 19, -14 \leq k \leq 13, -20 \leq l \leq 19$</td>
</tr>
<tr>
<td>Reflections</td>
<td>10803</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2542 [R(int) = 0.0242]</td>
</tr>
<tr>
<td>Completeness to theta = 37.399°</td>
<td>100%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1 and 0.697</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2542 / 0 / 156</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.077</td>
</tr>
<tr>
<td>Final R indices [&gt;2sigma(I)]</td>
<td>$R_1 = 0.0249, wR_2 = 0.0619$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.029, wR_2 = 0.0648$</td>
</tr>
</tbody>
</table>
Chapter 4: (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols

Largest diff. Peak and hole: 1.372 and -0.276 e Å⁻³

Table A4.7 Representative bond lengths [Å] and angles [°] for complex 3.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1-Mnla</td>
<td>2.9389 (4)</td>
</tr>
<tr>
<td>Mn1-C6</td>
<td>1.8072 (17)</td>
</tr>
<tr>
<td>Mn1-C7</td>
<td>1.8361 (16)</td>
</tr>
<tr>
<td>Mn1-C8</td>
<td>1.7946 (16)</td>
</tr>
<tr>
<td>Mn1-C9</td>
<td>1.8377 (16)</td>
</tr>
<tr>
<td>Mn1-C1</td>
<td>2.0440 (15)</td>
</tr>
<tr>
<td>C6-Mn1-C1</td>
<td>172.11 (6)</td>
</tr>
<tr>
<td>C7-Mn1-C1</td>
<td>87.65 (6)</td>
</tr>
<tr>
<td>C9-Mn1-C1</td>
<td>87.82 (6)</td>
</tr>
<tr>
<td>C8-Mn1-C1</td>
<td>173.93 (5)</td>
</tr>
<tr>
<td>C6-Mn1-Mnla</td>
<td>83.98 (5)</td>
</tr>
<tr>
<td>C17-Mn1-Mnla</td>
<td>82.40 (5)</td>
</tr>
<tr>
<td>C9-Mn1-Mnla</td>
<td>85.62 (5)</td>
</tr>
<tr>
<td>C1-Mn1-Mnla</td>
<td>88.12 (4)</td>
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A4.8 References


Chapter 4: (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols


CHAPTER 5: CHELATING BIS-N-HETEROCYCLIC CARBENE COMPLEXES OF IRON(II) CONTAINING BIPYRIDYL LIGANDS AS CATALYST PRECURSORS FOR OXIDATION OF ALCOHOLS

A5.1 NMR data of complexes 1 and 3
A5.2 MS (ESI-TOF) spectra of complexes 1 and 2, and MS (ESI-TOF) spectrum of the reaction of complex 1 with TBHP in acetonitrile.
A5.3 Crystallographic details
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

A5.1 NMR data of complexes 1 and 3

Figure A5.1 $^1$H NMR in MeCN-d$_3$ of iron complex 1 several minutes after preparation of the NMR sample.

Figure A5.2 $^1$H NMR in MeCN-d$_3$ of iron complex 1, after 16h the preparation of the NMR sample.
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Figure A5.3 $^1$H NMR in MeCN-d$_3$ of iron complex 3.

Figure A5.4 $^{13}$C NMR in MeCN-d$_3$ of iron complex 3.
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Figure A5.5 HMQC in MeCN-d$_3$ of iron complex 3.

Figure A5.6 HMBC in MeCN-d$_3$ of iron complex 3.
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Figure A5.7 COSY in MeCN-d$_3$ of iron complex 3.

A5.2 MS (ESI-TOF) spectra of complexes 1 and 2, and MS (ESI-TOF) spectrum of the reaction of complex 1 with TBHP in acetonitrile
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Figure A5.8 MS (ESI-TOF) in acetonitrile of 1.
Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Figure A5.9 MS (ESI-TOF) in acetonitrile of 2.

Figure A5.10 MS (ESI-TOF) of the sample obtained by reaction of 1 with TBHP in acetonitrile.
A5.3 Crystallographic details

Compound 3 crystallises in the monoclinic system, space group $P2_1/n$, with one Fe(II) cation and two I- anions in the asymmetric unit. Selected bond distances and angles are listed in Table A5.1 and crystallographic experimental data and structure refinement parameters are displayed in Table A5.2.

### Table A5.1
Selected bond lengths (Å) and angles (°) for 3.

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<th>Length/Value</th>
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<td>N(7)-Fe(1)-N(6)</td>
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Chapter 5: Chelating bis-N-heterocyclic carbene complexes of iron(II) containing bipyridyl ligands as catalyst precursors for oxidation of alcohols

Table A5.2 Selected crystallographic experimental data and structure refinement parameters for 3.

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<th>Empirical formula</th>
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