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Bidentate N-heterocyclic carbene complex of Manganese as catalyst for hydrosilylation and hydroboration of double and triple bonds

Tesi di laurea sperimentale

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Abstract (IT)

Scopo del presente lavoro di tesi è la sintesi di un complesso di manganese contenente un legante bis N-eterociclico e la sua applicazione come catalizzatore nelle reazioni di idrosililazione e idroborazione di doppi e tripli legami.

I composti organici sililati e borilati sono importanti prodotti intermedi in diversi settori della chimica fine grazie alla loro stabilità e alla loro capacità di essere ampiamente funzionalizzati. La loro sintesi prevedeva l'utilizzo di reazioni poco sostenibili da un punto di vista ambientale, mentre idroborazione e idrosililazione, grazie allo sviluppo di catalizzatori appositi, permettono di ottenere questi composti riducendo coprodotti, sottoprodotti e condizioni operative estreme. Generalmente i catalizzatori impiegati industrialmente contengono metalli di transizione come palladio, platino e rutenio che risultano costosi, rari e non biocompatibili. Per questo motivo negli ultimi anni la ricerca si è concentrata sullo sviluppo di nuovi catalizzatori a base di metalli della prima serie di transizione tra cui il manganese, noto per essere abbondante sulla crosta terrestre, economico e biocompatibile.

I composti N-eterociclici (NHC) sono una classe di leganti tra le più utilizzate poiché oltre a una grossa variabilità di caratteristiche steriche ed elettroniche, consentono di stabilizzare la specie metallica. I complessi N-eterociclici di manganese, a differenza di altri metalli della prima serie di transizione, sono stati scarsamente applicati nelle reazioni di idroborazione e idrosililazione. Per questo motivo, il gruppo dove ho svolto il mio tirocinio si è dedicato a questo tipo di ricerca, sintetizzando e testando un complesso bis-NHC di manganese nell'idrosililazione di carbonili e solfossidi. Il mio lavoro si inserisce all'interno di questo ampio progetto, applicando nuovamente lo stesso complesso su una serie di substrati e reazioni differenti. In particolare, l'idrosililazione è stata applicata su alchini, alcheni e su carbonili (in questo caso attivando il complesso con la luce visibile). Inoltre, si è testata l'attività catalitica del complesso nell'idroborazione di alchini.

Abstract (EN)

The aim of this thesis was the synthesis and application of a manganese bis-N-heterocyclic complex (bis-NHC) as a catalyst in the hydrosilylation and hydroboration of double and triple bonds.

Silylated and borylated compounds are important intermediates in fine chemistry industries because of their stability and capability to be applied in different organic transformations.

Their traditional synthesis involves environmentally unsustainable reactions involving Grignard or lithium reagents. In comparison, catalytic hydroboration and hydrosilylation provide a sustainable method for the preparation of these compounds producing less waste and using less extreme reaction conditions.

Most industrially applied catalysts are based on expensive, scarcely available and toxic metals. For these reasons, research in this area is currently focused on the development of first row transition metal-based catalysts. Among others, manganese is known to be abundant in Earth's crust, cheap and biocompatible making this metal appealing for "green" catalysis.

NHCs are a class of compounds frequently used as ligands in metal catalysed reactions. They possess high electronic and steric tunability, and they enable the stabilisation of the metallic fragments. Manganese NHC complexes, in contrast to other first row metals complexes, have been scarcely applied as catalysts in hydrosilylation and hydroboration processes. For this reason, the group in which I performed my traineeship focus their studies on the synthesis and application of bis-NHC manganese complexes for hydrosilylation of unsaturated functional groups, such as carbonyls and sulfoxides. The goal of my work was to study the hydrosilylation of alkynes, olefins and carbonyls using Mn-NHC complexes as catalysts under visible light. Investigations were extended to explore the activity of Mn-NHC complexes in hydroboration of alkynes.

SUMMARY

INTRODUCTION

THE IMPORTANCE OF CATALYSIS IN CHEMICAL INDUSTRY [1] [2]

Nowadays, chemical industry products play a vital role in our daily life. Polymers, detergents, semiconductors, inks, drugs are examples of products that surround us improving our quality of life. Chemistry is a sector in which innovation is based on research and development to reduce costs, environmental impact and maximize efficiency and profits[3]. A catalyst is one of the main actors in the process of innovation, helping reducing time and costs due to its ability to accelerate and/or use milder conditions in chemical reactions. For example, by lowering the temperature and/or the pressure at which the process operates is possible to save fuel, which is one of the major costs in a large-scale chemical process. Furthermore, it reduces the amounts of reactants used preventing the formation of by-products.

Catalysis is so important that is generally associated with underpinning approximately 30% of the gross domestic products in European economies[4]. Catalyst can operate under homogeneous or heterogeneous media. Homogeneous catalysts are in the same phase of the reactants and they have a homogeneous distribution of active sites. On the contrary, heterogeneous catalysts are in a different phase, usually solid, with dimensionally different active sites.

The use of a homogeneous catalyst offers many advantages in industrial applications, for example, high selectivity on substrate and products obtained, better control of the reaction conditions and high contact between catalyst and substrate. For these reasons, several industrial processes use homogeneous catalysts, and one of the most important is the hydroformylation of olefins that uses cobalt or rhodium-based catalysts.

ORGANOMETALLIC AND N-HETEROCYCLIC CARBENE COMPLEXES

Organometallic complexes are a class of compounds in inorganic chemistry that have a metal-carbon bond, and are frequently used as catalysts. Their chemistry developed enormously during the 20th century and nowadays exist several of these compounds (Figure 1). Many different ligands can be coordinated to the metal centre, according to different interactions. These ligands can be classified depending on difference on δ and π donor-acceptor behaviour. There are different organometallic compounds with single, double, triple metal-carbon bond. The metal-carbon bond involves covalent sharing of electrons between the metal and the carbon in a sigma fashion, with more or less significant ionic contribution to the bonding[5].

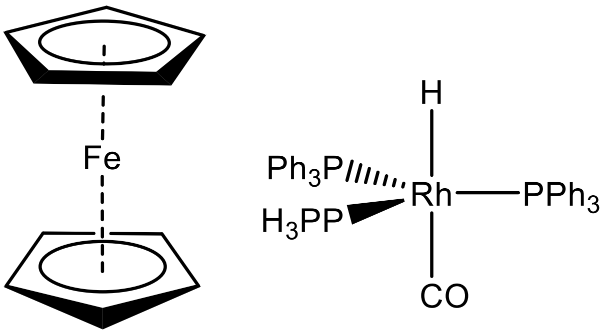


Figure 1 Examples of organometallic compounds: Ferrocene (left) and Carbonyl hydrido tris(triphenylphosphine)rhodium(I) (right)

Many reactions of these compounds involve a change in metal coordination number by the gain or loss of ligands and when there is no change in the oxidation number of the metal, the process is called addition or dissociation. On the contrary, if the metal oxidation state also changes, they are termed oxidative addition or reductive elimination process[5].These compounds have a wide variety of oxidation states and ligands with whom they can engage in different interactions and geometries opening a world of combination and modification. Organometallic compounds undergo a rich variety of reactions that sometimes can be combined into useful catalytic processes, for this reason organometallic reactions are of great interest industrially as they solve one of the most fundamental problem: they can convert relatively inexpensive feedstocks into molecules of greater commercial value[5].

Generally, the most used metal ions for homogeneous catalyst preparation are those from the second and third row of the transition block of the periodic table like: ruthenium, rhodium, palladium and many others. One of the biggest problems with these metals is their cost and supply as they are not only expensive but also their prices can change depending on the balance between availability and exploitation. Another big issue associated with the use of these metals is their relatively high toxicity. If they are used in the preparation of pharmaceuticals, for example, their presence in the final product is subject to strict regulatory control, limiting their use in the process. Therefore, the investigation of Earth-abundant metal complexes constitutes an intriguing challenge, thanks to their lower cost and lower toxicity[6].

Earth-abundant first row metals[7] like iron, nickel, cobalt and manganese (Figure 2) started to be investigated as metal ions to synthesise new catalysts.

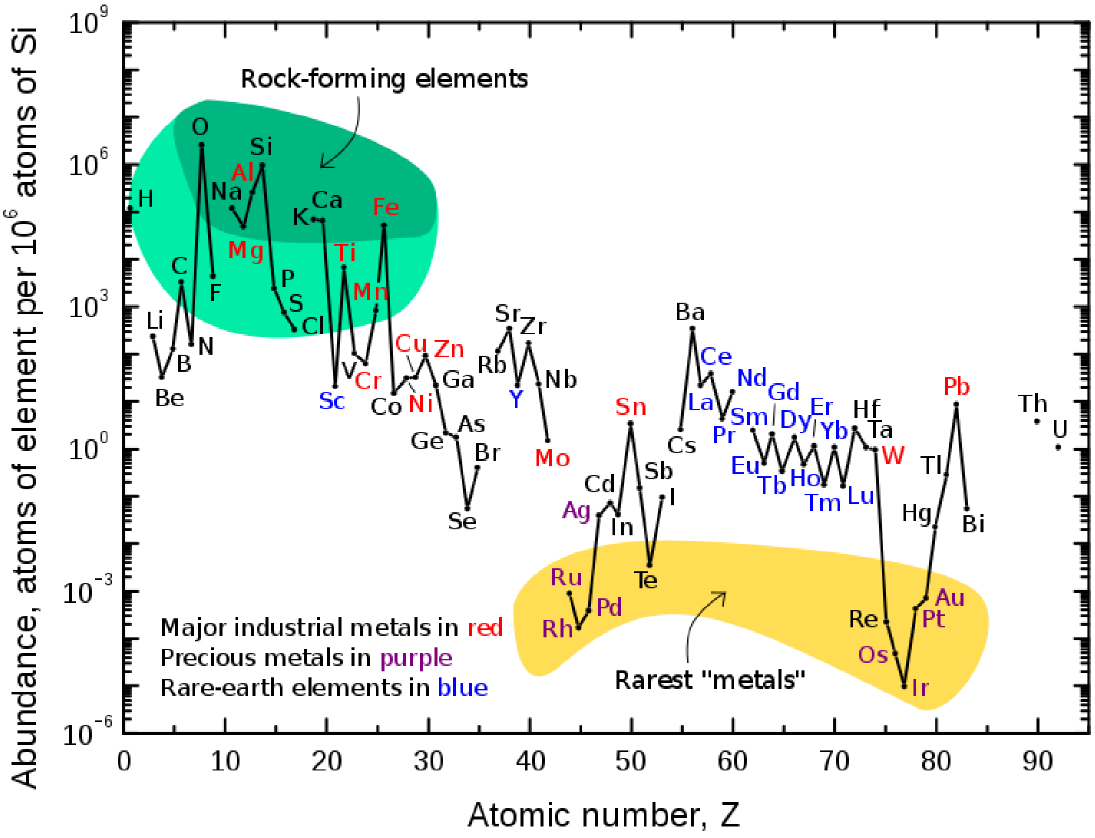


Figure 2 Abundance of elements in Earth's crust related to Silicon atoms. Adopted from ref 7

Whereas noble metal compounds have been the most explored, earth-abundant metal-based catalysts have remained undeveloped. Although organometallic chemistry has its roots in compounds of manganese, iron, cobalt, nickel and copper, these molecules frequently did not exhibit catalytic activity[8].

In order to develop a more sustainable chemistry, many researchers focused their studies on the use of these metals in catalysis. These new studies can help to develop synthetic processes that address cost, supply, toxicity and the minimization of environmental impact, and many examples can be reported nowadays, starting from hydroelementation of alkenes[9] to hydrosilylation of CO[10]. Among all these first row transition metals, manganese is very interesting one as it is the third most abundant metal in earth´s crust and has low toxicity and price[11] .

Manganese, as many other Earth-abundant metals, has extensive applications in different fields such as metallurgy, electronics, as additive in polymers, glass and ceramics industries. It also has many biological roles and it is considered an essential element for living organism, as an example is its well-known role in photosynthesis[11]. From the chemical point of view, Mn displays many oxidation states (from -3 to +7) and this gives to the metal a high potential in organic synthesis. Therefore, in the last century, this metal attracted the attention of the chemist community aiming to develop a “greener” and more sustainable chemistry.

From the catalytic point of view, manganese has been used in the beginning in some cross-coupling reactions between alkenyl lithium reagents and in different application as Grignard’s reagents. Subsequent studies used manganese catalysts for different cross-coupling processes, carbonylation and some reactions with alkenes and alkynes have been also studied[12].

Recent papers show the use of Mn catalysts to activate C-H bonds[13], cyclization[12], dehydrogenation[12] and hydrosilylations of C=O bonds[10]. Many different ligands have been used with this metal centre like ciclopentadienones or diketonates[12], while NHCs remained poorly explored.

The first isolation and characterisation of a NHC occurred in 1991 and soon was clear that these compounds would play an important role in homogeneous catalysis. Starting as excellent ligands for transition metals, NHCs have found multiple applications in some of the most important catalytic transformations. Not only as metal ligands but also as organocatalysts, or in the coordination to block-*p* elements or as metallofarmaceuticals (Figure 3)[14].

NHCs are defined as heterocyclic species containing a carbene carbon and at least one nitrogen atom in the ring structure. The great stability of these compounds is due to both steric and electronic effects. The steric effects are influenced by the two groups (wingtips) bound to the nitrogen atoms. Generally, NHCs have bulky substituents next to the carbene carbon, which helps to stabilize the structure by sterically disfavouring decomposition to the corresponding olefin. However, the most important effect is provided by the electronic stabilisation given by the nitrogen atoms. In contrast to classical carbenes, NHCs have the highest occupied molecular

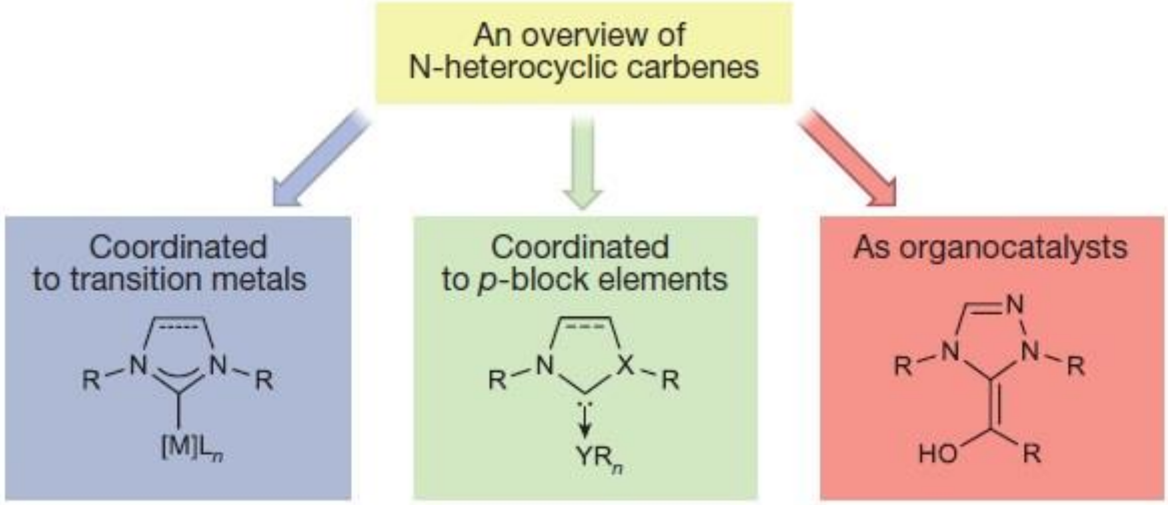


Figure 3 Major applications of NHCs adopted from ref. 14

orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) best described as a formally sp^2-hybridised lone pair and an unoccupied *p*-orbital at the carbon, respectively (Figure 4). The adjacent nitrogen atoms thanks to their electron-withdrawing and π-electron-donating effects stabilize this structure, by lowering the energy of the occupied *δ*-orbital and mesomerically donating electron density into empty *p*-orbital[14].

Usually, transient carbenes are considered to be electrophiles, but the planar structure of the heterocyclic ring of the NHCs makes them nucleophilic. This effect causes them to act as δ-donors and bind to a wide range of metallic and non-metallic species, from metals, semimetals and elements from *p*-block. This donor ability can be improved by modifying the scaffold of the carbene. For example, if the nitrogen atoms stabilise less the carbene carbon, this induces an enhance in the acidity of the carbenic site with obvious consequences for its formation and stability. Thus, when the carbene is coordinated to a metal centre it induces a higher basicity of the ligand which means stronger donor properties. As we have a large variability of *N*-heterocyclic scaffolds, the donor properties theoretically can be fine-tuned over a large range of possibilities[14].

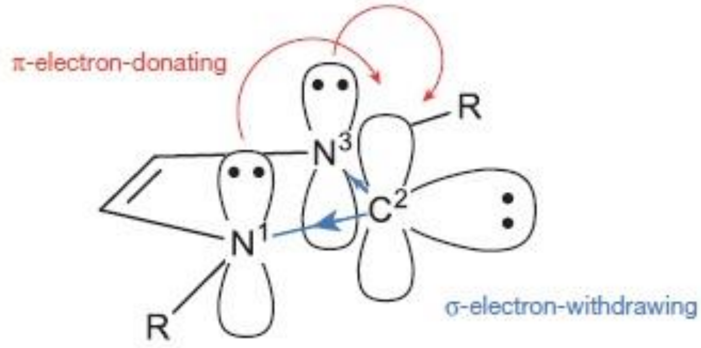


Figure 4 Electronic effects in the NHCs structure. Adopted from ref.14

Due to these important characteristics, in the last years researchers from all over the world started to work on these compounds. Thanks to the easiness of the synthetic steps, diverse analogues can be prepared and a lot of new NHCs have been prepared, opening a new branch in chemistry.

Many different types of NHCs has been synthetised, containing different number of atoms in the ring, with the lone pair in a different carbon atom or with a double NHCs system bounded to the metal (Figure 5).[15] For most classes of N-heterocycles, simple variation of the starting materials in a modular synthetic sequence allows for facile modification of the steric and electronic properties of the resulting carbene.

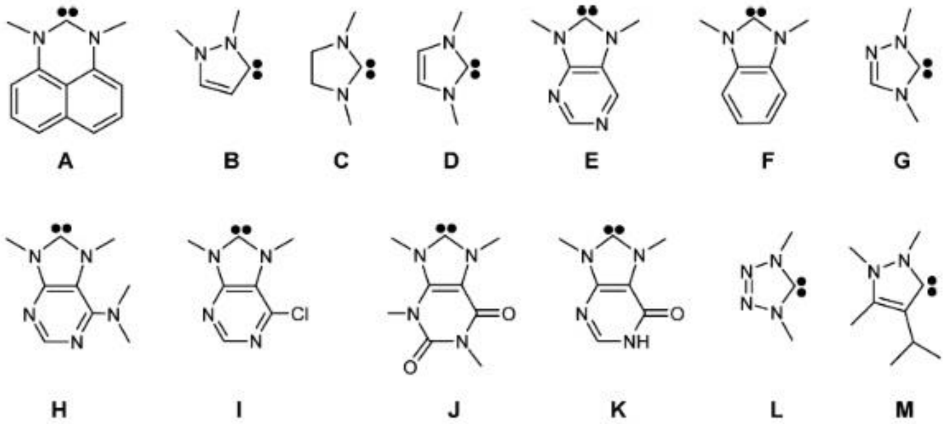


Figure 5 Examples of different types of NHC systems used in literature. Adopted from ref. 15

The main synthetic procedures for NHCs precursors are cyclization reactions[16], or alkylation reactions of an imidazole derivative[17,18].

After the synthesis of the NHC precursor, the carbene is generated upon deprotonation, and then coordinated to a metal center by direct treatment with the appropriate metal precursor[15]. Other synthetic routes to metal-NHC complexes are transmetallation using silver NHC adducts[19] and cyclization reactions[20,21]. As previously reported, most applications of NHCs involve their coordination to transition metals. When coordinated to low oxidation state metal centres, the NHC ligands display high coordination ability due by their donor ability of the formal sp^2-hybridised lone pair available, that donates electron density into a δ-accepting orbital of the transition metal. On the other hand, the contribution of both π-back-bonding into the carbene p-orbital from the metal makes the metal-NHCs bond stable[14]. Nowadays, numerous examples of catalytic applications have been reported using different metals such as iridium[22], ruthenium[23] or gold[24].

As mentioned before, in the recent years many research groups are trying to substitute expensive second and third row transition metals with those from the first. Interestingly, NHCs have been used as suitable ligands for first row transition metals, giving high stability to metal complexes of manganese[25], iron[26], nickel[27].

MANGANESE-NHC COMPLEXES

NHC-containing manganese complexes were among the first isolated species within this family of ligands[28]. Manganese complexes with NHC ligands have been less studied when compared to the analogous complexes of other late 3d transition metals (Fe-Cu)[29]. However, this metal exhibits notable characteristics, discussed previously, which distinguish it from the other transition metals being an intriguing candidate for organometallic chemistry. In the last few years, there has been an increasing interest in manganese-NHC complexes .

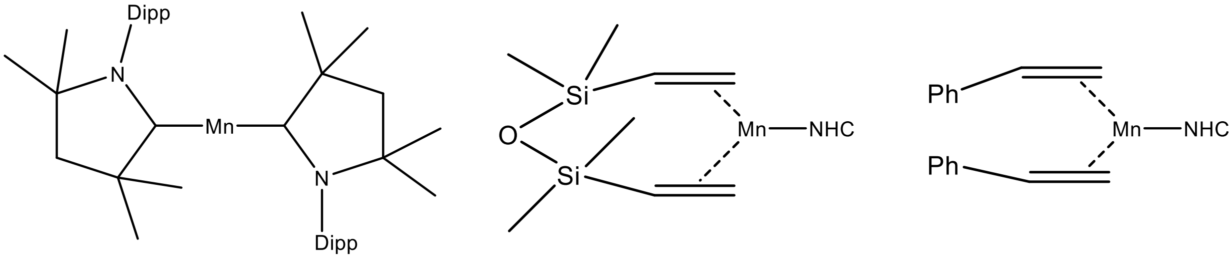
MANGANESE(0)-NHC COMPLEXES

Manganese(0)-NHC complexes with low coordination number are not so studied when compared to other metals like iron or cobalt[30]. The importance of these complexes is their role as key intermediates in several transition-metal-catalysed and -mediated reactions. The most difficult part in preparing a low-coordinate with low-valent transition-metal complex, is due to the low stability of the metal centre. It tends to bind ligands in order to achieve coordination saturation and to undergo oxidative addition reactions because of their reduction potency. In this regard, one could reason that among the metals in the same row of the periodic table, low-coordinate low-valent early transition-metal complexes should be highly reactive and could be more challenging to access than their late transition-metal analogues[30].

The first complex reported in literature is from Roesky *et al.* in 2013. This group reported a manganese complex with a linear geometry supported by a cyclic aminoalkyl carbene (cAAC) ligand[31] (Figure 6, complex A). This complex shows an interaction with H_2, that causes a transformation of the cAAC ligand into an alkyl ligand. In 2018, a study reported the synthesis, characterisation, and reactivity of the first manganese three-coordinate formal zero-valent complex [(NHC)Mn(dvtms)] (dvtms = divinyltetramethyldisiloxane) employing different NHC ligands[30]. These complexes were prepared from one-pot reactions of $MnCl_2$ with the NHC ligand, dvtms, and KC_8 (Figure 6, complex B). These low-coordinate manganese complexes are found to be reactive toward alkenes, alkynes, and allenes at room temperature to form seven-membered manganase(II) complexes, representing the first examples of reductive couplings of alkenes and alkynes mediated by well-defined manganese complexes[30]. These complexes were found to react with H_2O to give mono-alkene $EtMe_2SiOSiMe_2CH=CH_2$, with H_2 to form Mn(II) dialkyl compound, and with I_2 to give Mn(II) diiodide complexes. In addition, they and can undergo a ligand-substitution reaction with CO to form a Mn(0) carbonyl complex[30].

Another study from 2019 showed the synthesis of the three-coordinate formal zero-valent Mn styrene complexes achieved by the one-pot. The reaction consisted in stirring the mixture of

$MnCl_2$ with 1 equivalent of NHC in THF followed by the addition of styrene and potassium graphite at room temperature. They found that styrene with monodentate NHC is an effective ligand set for the stabilization of three-coordinate manganese(0) complexes in the form of $[(NHC)Mn(h2\text{-}CH_2CHPh)_2]$[32] (Figure 6, complex C).



Roesky, 2013
A

Cheng, 2018
B

Chen, 2019
C

Figure 6 Structures of low coordination Mn(0)- NHC complexes.

MANGANESE(I)-NHC COMPLEXES

Manganese(I)-NHC complexes are the most common Mn-NHC complexes. The first report was published by Lappert and Pye in 1977, who synthetized the complexes **1** and **2** heating metal precursors ($CpMn(CO)_3$ for **1** and $Mn(CO)_3Br(PPh_3)_2$ for **2**) in the presence of the NHC ligands[33].

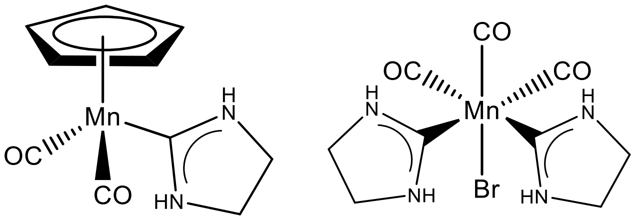


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Figure 7 Lappert and Pye's complexes

An alternative synthetic route was reported by Aumann and Heinen, who described the synthesis of NHC Mn complexes via a ketenimine manganese intermediates obtaining a convenient three component reaction to access a whole plethora of stable, abnormal Mn(I) NHC complexes[34] (Figure 8).

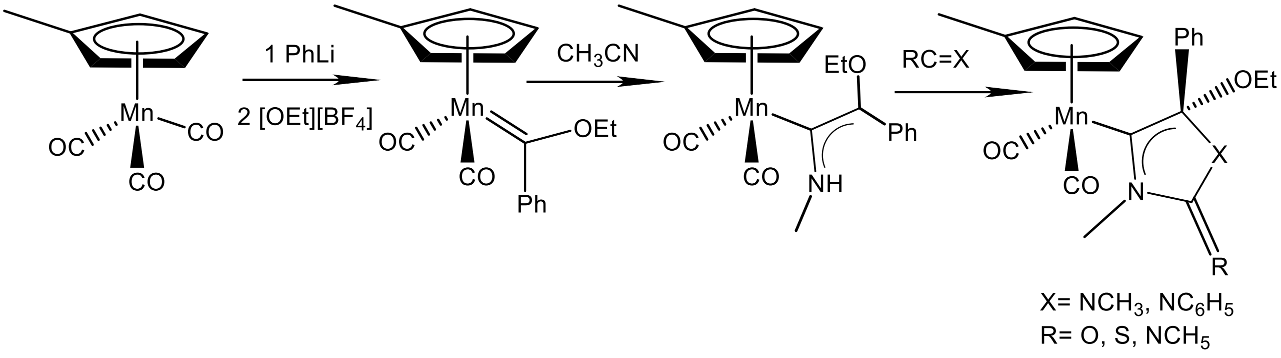


Figure 8 Aumann and Heinen's synthesis of Mn(I)NHCs

With a similar reaction, Fehlhammer’s group described multi-component reactions of manganese(I) complexes obtaining different heterocycles such as oxazoles and imidazoles bounded to the metal[35]. Ruiz and co-workers reported the synthesis of Mn (I) N-heterocyclic carbenes, consisting in the coupling of coordinated isocyanide ligands with propargylamines and propargylic alcohols[20] (Figure 9). The same group later demonstrated that NHC–Mn(I) complexes bearing an N–H residue in the carbene ligand can be used as carbene transfer agents, allowing the isolation of several NHC–Au(I) complexes by this way[36].

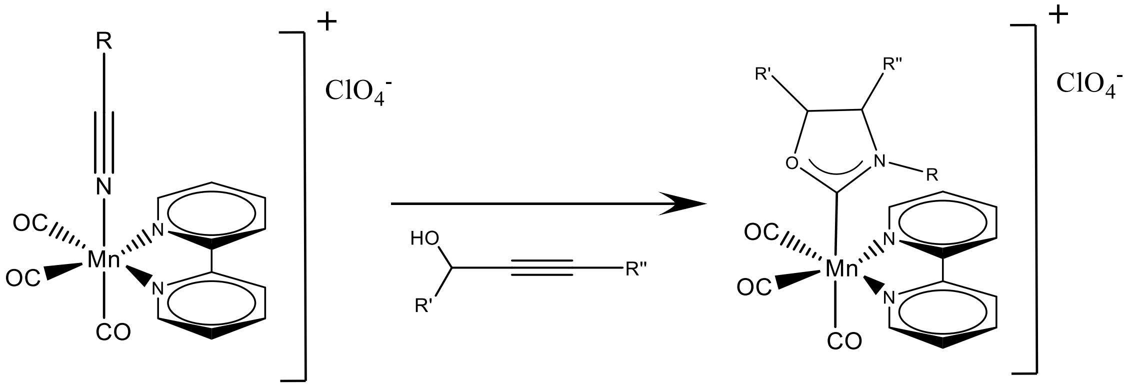


Figure 9 Example of Ruiz and co-workers’ syntheis

Another synthetic route, this time towards N-borane-substituted Mn(I) NHC complexes, was presented in 1998 by Siebert and co-workers in which they describe the reaction between $Mn(CO)_5Br$ and a highly reactive N-borane ligand, in order to synthesize the respective complex **3** in dry THF[37].(Figure 11, complex **3**)

Edwards, Hahn and co-workers treated $Mn(CO)_5Br$ with aminophosphineimine yielding to a NHC ligand formed via a cyclisation reaction on the metal centre and elimination of triphenylphosphioxide [21].(Figure 10)

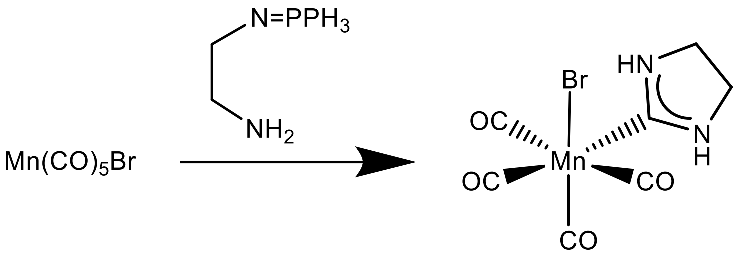
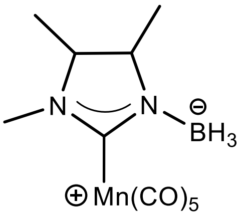


Figure 10 Edwards and Hahn's syntheis

In a subsequent study, starting from the same Mn-NHC complex, they obtained a macrocyclic PCP pincer in a meridional arrangement of the diphosphine and the NHC ligands[38]. (Figure 11, complex **4**)



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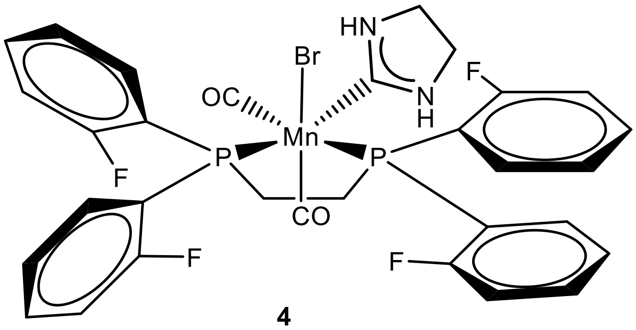

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Figure 11 Complexes 3 and 4

Whittlesey and co-workers treated the manganese pentacarbonyl precursor with different ligands: IiPr$_2$Me$_2$ (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) . In this way they obtained different manganese (I) NHC complexes (Figure 12, complexes **5** and **6**) that after halide removal led to the formation of cationic 16e- species[39] (Figure 12, complexes **7**,**8**,**9** and **10**).

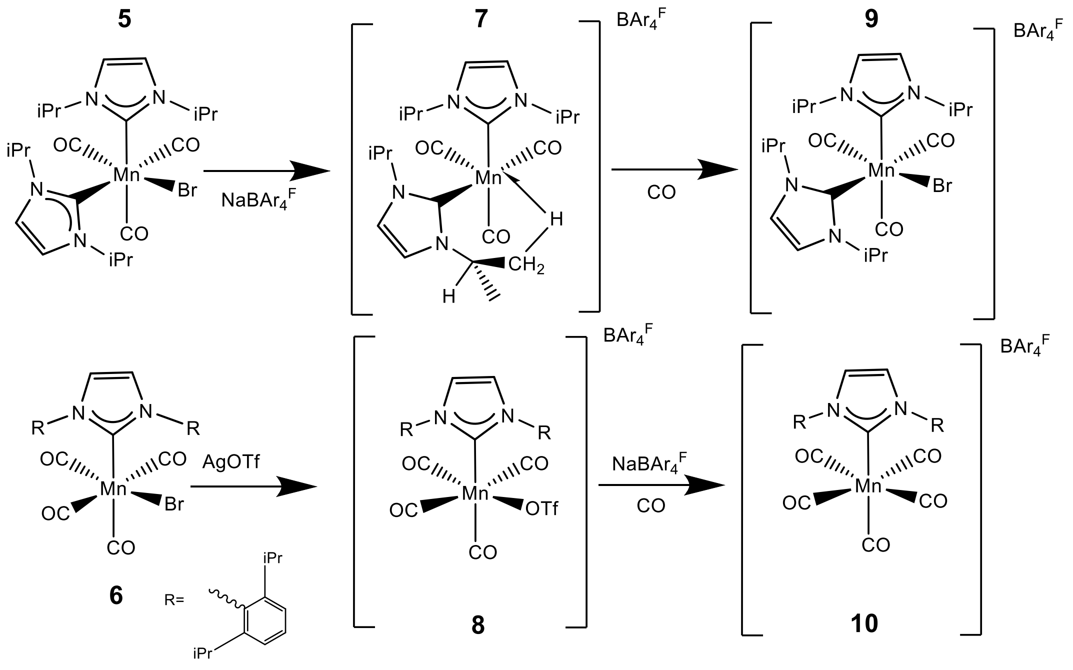


Figure 12 Whittlesey and co-workers' complexes

Later, the same group described the synthesis of four new stable complexes (Figure 13, complexes from **11** to **14**) prepared from CpMn(CO)$_3$ and the appropriate ligands. When these complexes were exposed to UV light, they release CO[40]. In 2014, Schaefer and co-workers described the synthesis of two new manganese NHC complexes: [MnBr(N-methyl-N'-2-pyridylbenzimidazol-2-ylidi-ne] and [MnBr(N-methyl-N'-2-pyridylimidazol-2-yli-ne)(CO)$_3$ (Figure 13, complexes **15** and **16**). These new complexes showed their ability of mediating a two-electron reduction of CO$_2$ to CO[41]. Starting from **16**, Agarwal and co-workers studied the effect of the substitution of the axial ligand on the CO$_2$ electroreduction, synthetizing complexes **17** and **18** (Figure 13)[42]. The results evidenced that there is a difference in the photodecomposition behaviour of these complexes; the cyanide-containing compounds persist longer than the other species, and those compounds with a pseudohalogen (NCS and CN) display poor faradaic efficiencies in the conversion of CO$_2$ to CO, preferring the reduction of protons to form H$_2$.

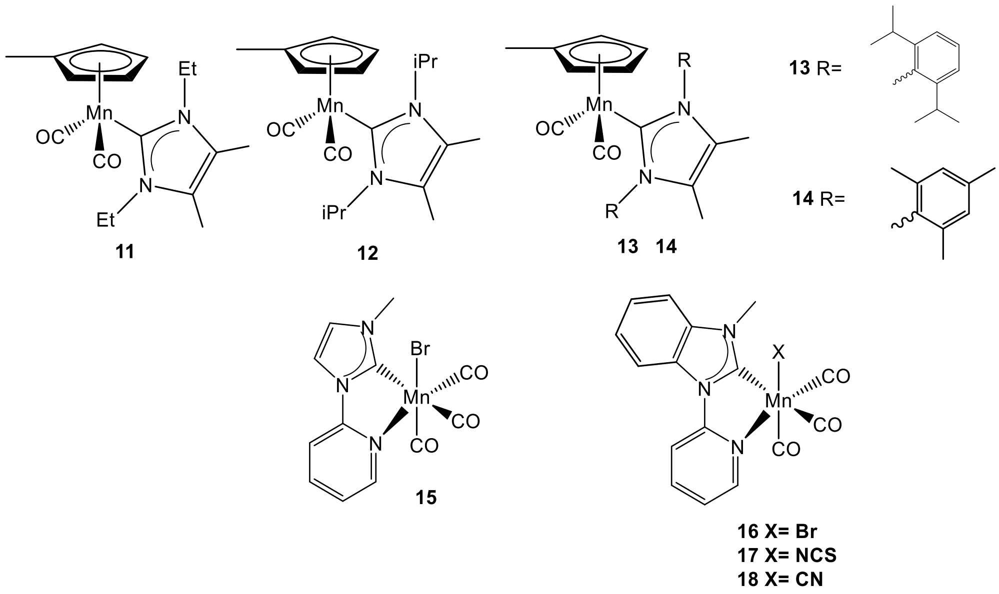


Figure 13 Mn(I)NHC complexes

Darcel and co-workers in 2014 synthetized and tested manganese NHC compounds in the hydrosilylation of carbonyl compounds under UV irradiation[43]. Half-sandwich complexes were obtained in one step from produced cymantrene and were tested with a large variety of aldehydes (13 examples) and ketones (11 examples). In all the cases reported, the substrates were efficiently reduced under mild conditions, and the most active is reported below (Figure 14, complex **19**). Subsequently, in 2016, inspired by this article, the same group published a work in which they synthetized two sandwich complexes bearing Cp tethered NHC ligands: $[(Cp(CH_2)NHCMes)Mn(CO)_2]$ and $[(Cp(CH2)_2NHCMes)Mn(CO)_2]$[44](Figure 14, complexes **20** and **21**). These two complexes were synthetized with a novel synthetic strategy based on the anchoring of an imidazolium moiety to the coordinated Cp ligand (Cp = cyclopentadiene), followed by an intramolecular photochemical CO substitution for the pendent NHC moiety generated *in situ* upon addition of a base. Both complexes showed good activity in the hydrosilylation of ketones in the presence of UV light at toom temperature, and the group succeeded in isolating the corresponding silane σ-complexes, that are the primary products of the photochemical CO substitution of the silylating agent on the catalyst (Figure 14, complexes **22** and **23**).

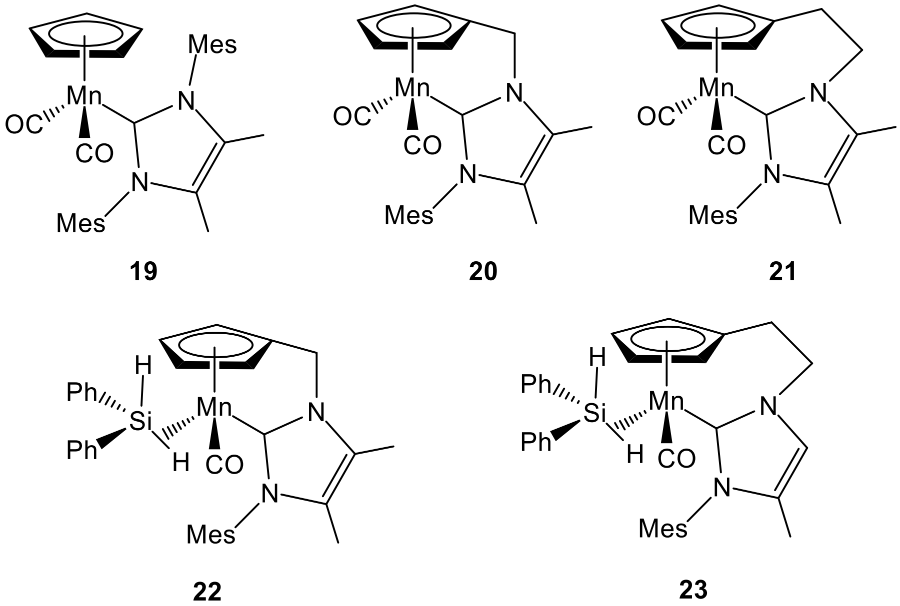


Figure 14 Darcel's manganese NHC complexes

Fraser's group continued to explore the universe of this family of complexes, synthetizing mono and dimetallic manganese compounds, and characterizing them with different techniques including single crystal X-ray analysis and DFT studies. They reported that in dimetallic complexes, the NHC ligand is located in *trans* respect to the metal-metal bond, while in the monometallic complex is situated *cis* to halides[45] (Figure 15, complexes from **24** to **27**). In 2018, Royo's group described the catalytic activity of two manganese complexes bearing bis-NHC ligands in the electrocatalytic reduction of CO_2 to CO[25]. They noticed that the replacement of a pyridine ring by an NHC unit had a significant impact in the catalytic performance of the Mn complexes, improving the turnover frequency and selectivity for CO production. In this work, they synthetized [Mn$(CO)_3$(py-MeNHC)I] (Figure 15, complex **28**) and a bis-NHC Mn(I) complex, which resulted to be the most active, as discussed later.

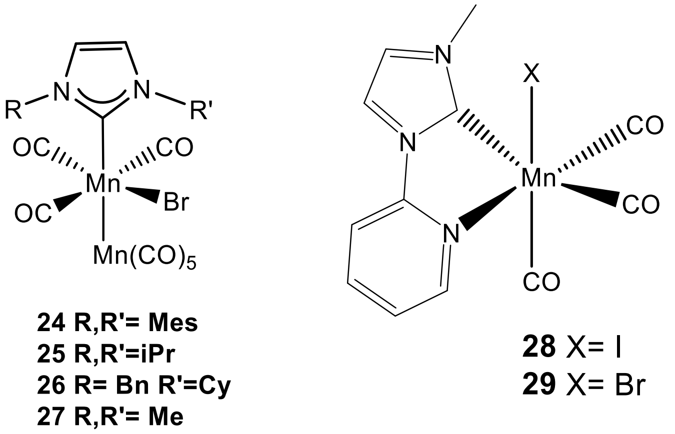
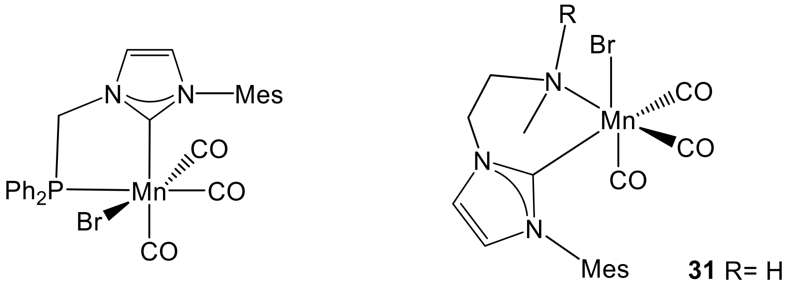


Figure 15 From 21 to 22 dimetallic complexes and Royo's group electrocatalyst 25

Going back talking about cymantrene-like complexes, Wu's group characterized a stable 17-electron complex, formed by a cymantrene analogue substituted with an NHC $MnCp(CO)_2$(IDiiP) (Figure 13, complex **12**) oxidized electrochemically or by the ferrocenium ion in dichloromethane[48]. In this study they report that this class of compounds form stable radical cations at redox potentials which are more negative than those reported for any other $MnCp(CO)_2L$ complex. Comparison of the oxidation potential of the cymantrenyl carbene with those of other $MnCp(CO)_2L$ complexes provides a measure of the donating power of the carbene ligand, a factor that is widely considered to be of central importance to its effects in organometallic chemical reactions.

Lugan, Canac, Sortais and co-workers started exploring phosphine-NHC manganese complexes as hydrogenation catalyst. Inspired by previous works on pincer-type phosphine-pyridine complexes capable to activate H_2, they developed a new hydrogenation catalyst (Figure 16, complex **30**), active on the reduction of different ketones. This catalyst shows an unconventional hydrogen activation mode through a metal ligand cooperation opening new prospective on homogeneous catalysis[49].



30

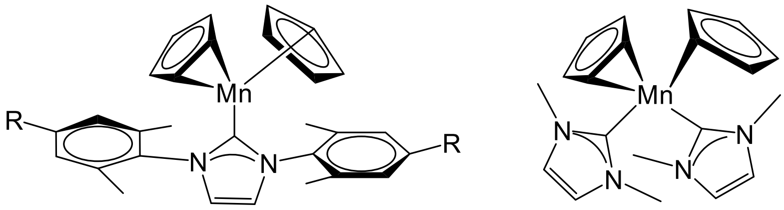
31 R= H
32 R= Me

Figure 16 Manganese-NHC catalyst for hydrogenation (30) and transfer hydrogenation of ketones(31-32)

Another important transformation in which manganese (I) NHC complexes have been applied is the reduction of ketones to their corresponding alcohols. Catalytic transfer hydrogenation (TH) is an attractive and sustainable alternative to the stoichiometric approaches[50] and van Putten, Benschop, de Munck et al. reported the synthesis of the manganese(I) NHC complexes **31** and **32** **(**Figure 16**),** and their catalytic activity for transfer hydrogenation of ketones with iPrOH. The results showed a high maximum TON (at least 17.000) for **31** and no activity for **32**. Complex **31** is capable to reduce ketones at very low catalyst loadings, enabling quantitative alcohol yields at only 75 ppm Mn.

MANGANESE(II)-NHC COMPLEXES

Manganese in oxidation state II shows a different chemical behaviour respect to other metals due to considerable ionic contribution to the Mn(II)–carbon bond[51]. There are only very few examples of articles about Mn(II)NHC complexes and the first report is from Cowley, Jones and co-workers with a reaction between manganocene with different NHC ligands at room temperature in THF for 24 h, obtaining the complexes **33** to **35**[52] (Figure 17))



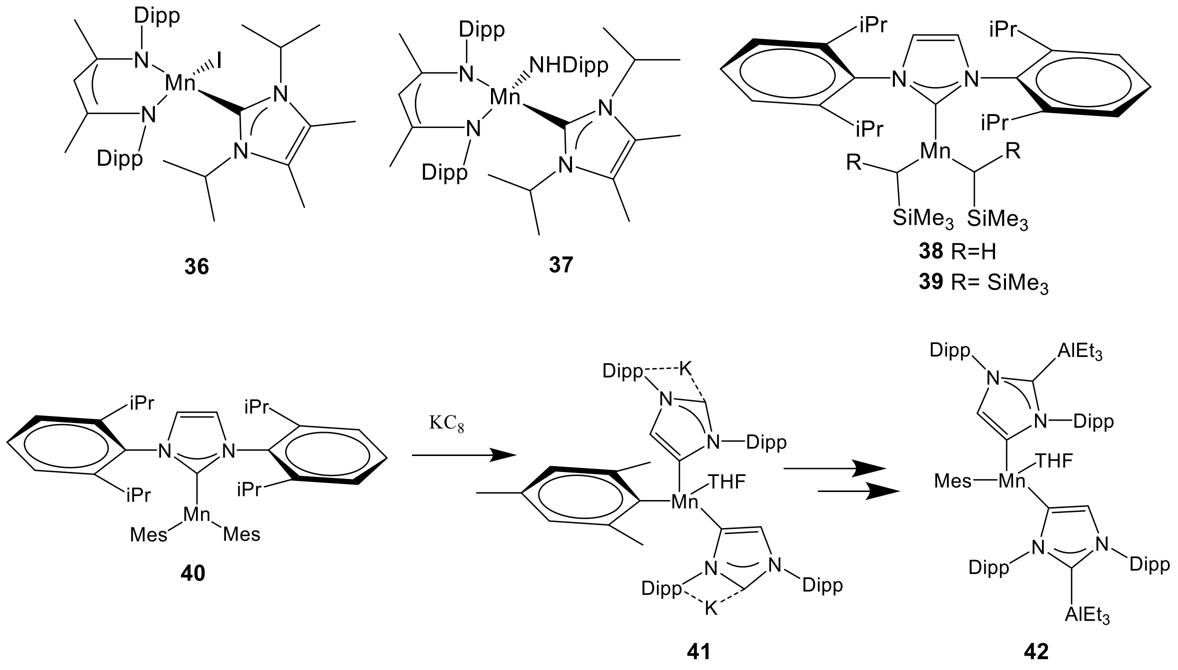
33 R= Me
34 R= Br

35

Figure 17 First manganese(II)NHCs complexes

The group of Roesky discovered another route to obtain Mn(II) complexes, by reacting MnI$_2$ with a chelating diamine and a NHC ligand obtaining complex **36** (Figure 18). Subsequently they proceeded with an halogen abstraction and the addition of a second NHC ligand, resulting in compound **35** (Figure 18)[53]. Later, same group isolated several compounds of the same type Mn(II)X$_2$(I^{i}Pr$_2$Me$_2$)$_2$ (with X = Cl, I, MeCOO) using similar procedures, demonstrating that these compounds could serve as reagents for preparing other Mn(II) NHC complexes generated via halide abstraction[54]. Mulvey, Robertson and co-workers were the first to synthesize a variety of three coordinate Mn(II) NHC complexes by reacting two different trimethylsilyl Mn(II) precursors with the NHC ligand[55] (Figure 18, complexes **38**, **39**).

The group of Goicoechea reported the synthesis of Mn(II) complexes bearing anionic N-heterocyclic dicarbene ligands, obtained by reacting Mn$_3$(Mes)$_6$ in the presence of NHC ligands (Figure 18, complex **40**). Treating the latter with KC$_8$ yielded abnormally bound Mn(II) bis(carbene) NHC complex **41**. After subsequent treatment removing potassium they obtained the bis carbene compound **42** (Figure 18)[56].

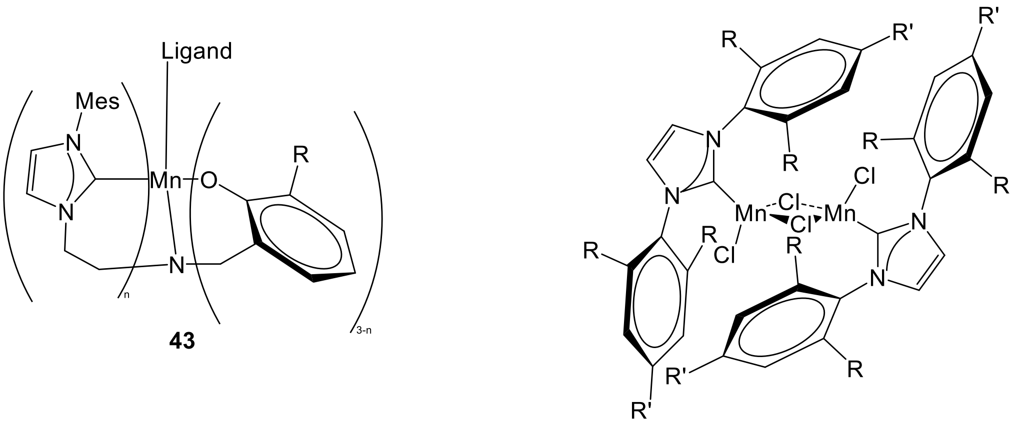


36 **37** **38** R=H **39** R= SiMe$_3$

40 **41** **42**

Figure 18 Manganese(II) NHCs complexes

In 2014, Käß's group synthetized and characterized manganese complexes with tripodal phenolate/N-heterocyclic carbene ligands. All of these complexes can be resumed with the graphical representation reported below (Figure 19, **43**). The importance of these complexes is due to their high tunability, in term of steric and electronic environment at the metal centre[57].In order to see if there were any correlations between the catalytic activity of other 3d metals like iron or cobalt in oxidation state (II) in cross-coupling reactions, Al-Afyouni's group obtained aryl-substituted NHC complexes of Mn(II). Chloride complexes of Mn(II) containing the NHC ligands 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (Figure 19, **44**) and 1,3-dimesitylimidazol-2-ylidene (IMes) (Figure 19, **45**). They demonstrated that these complexes can be prepared straightforwardly by direct carbene addition to MnCl$_2$. They exist in solution as chloride-bridged dimers of formula [Mn$_2$Cl$_2$(μ- Cl)$_2$(NHC)$_2$]. Unfortunately, these complexes didn't show good activity in coupling reactions involving alkyl electrophiles[58].



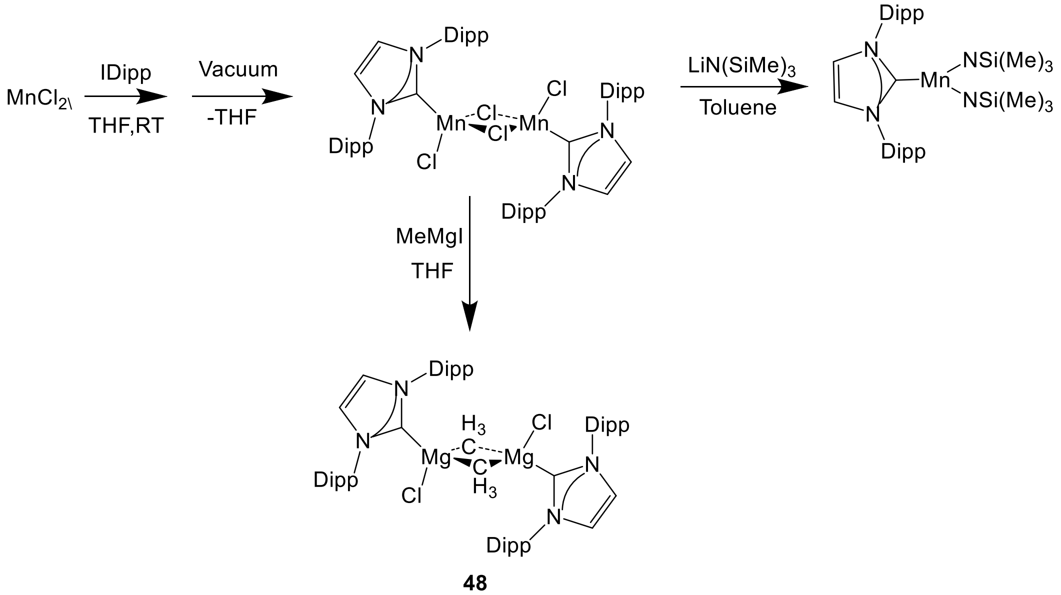
43

R=iPr R'=H **44**
R=Me R'=Me **45**

Figure 19 Mn(II) NHCs complexes

Among low coordination manganese NHCs complexes, Stefan Pelties in 2016 reported a convenient gram scale synthesis for the NHC-stabilized manganese(II) chloride (Figure 20, complex **46**). Then, they investigated its ability to work as a precursor for low-coordinate NHC-stabilized manganese(II) compounds. The reaction between this precursor and $LiN(SiMe_3)_2$ resulted in a unique trigonal planar amide (Figure 20, complex **47**). This compound represents a rare example of a three-coordinate NHC-stabilized manganese(II) complex. Reacting the chloride precursor with MeMgI led to the transfer of the IDipp and the chloride ligands from manganese to the magnesium atom, demonstrating the lability of the manganese(II)−carbon bonding[59](Figure 20, complex **48**).

46 **47**



48

Figure 20 Stefan Pelties manganese (II) NHCs complexes

Other low-coordinate manganese NHC complexes bearing bulky trimethylsilylamide ligands were synthesized by Oliver Hemming in 2019. In this work, the autors described the reaction of manganese amide $[Mn(NSi(Me_3)_2]$ with different bulky NHC ligands, obtaining different low-coordinate complexes[29] (Figure 21, complexes **49**-**55**).

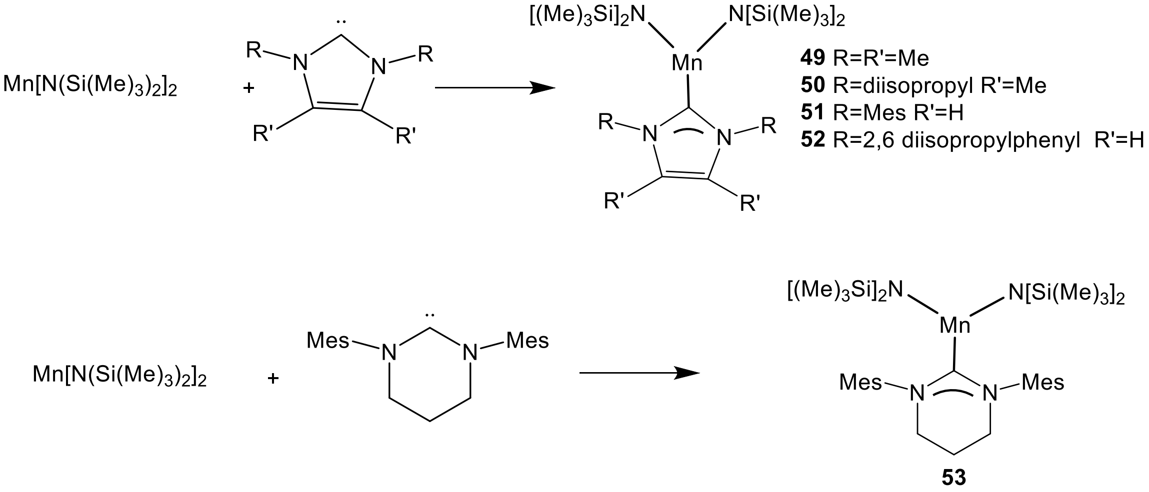


Figure 21Oliver Hemming's synthesis part 1

Another synthetic route described for the preparation of these Mn complexes, was the aminolysis of the amide with imidazolium salts, which allows the synthesis and characterization of complexes **54** and **55** (Figure 22,). The reactivity of these complexes towards primary phosphines were investigated for the synthesis of metal-phosphinidene complexes, which may have potential as phosphinidene transfer agents in a similar manner to that observed for the cobalt analogues. NHC complexes react with primary phosphines to afford a range of NHC-ligated manganese phosphide complexes, leading to a range of manganese-NHC complexes bearing bis(trimethylsilyl)amide ligands (Figure 22, complexes **56** and **57**). These compounds represent the first examples of manganese complexes bearing terminal phosphide ligands[29].

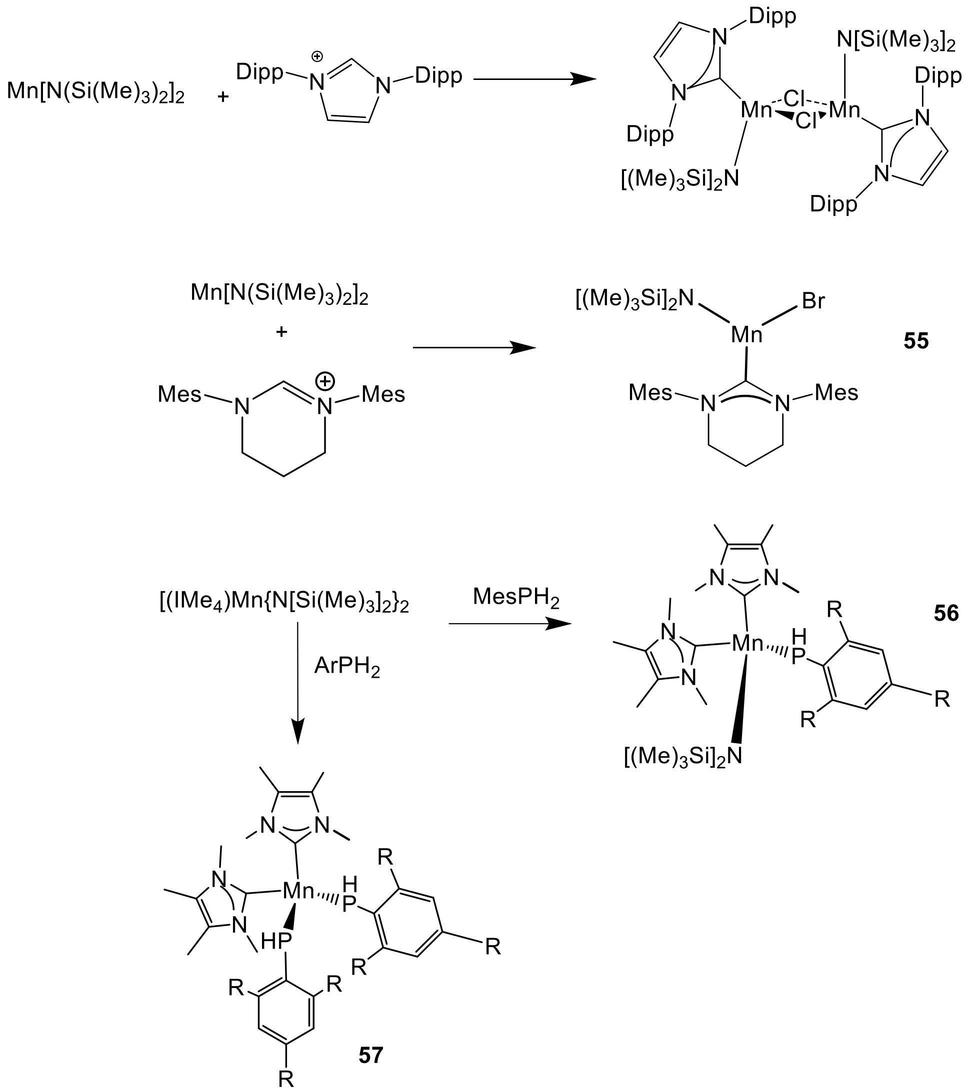


Figure 22 Oliver Hemming's synthesis part 2

MANGANESE (III- IV-V) -NHC COMPLEXES

Bellemin-Laponnaz published the first work on a Mn(III) NHC complex. The group reacted the carbene ligand with Mn(acac)$_3$ in THF obtaining the compound **58** (Figure 23), that showed a five coordinate geometry in the shape of a slightly distorted square pyramid[60]. Smith and co-workers reported the synthesis of a Mn(IV) NHC complex by the reaction of Mn(CO)$_5$Br with pivalonitrile, which leads to the precipitation of the dimer [MnBr(CO)$_3$(tBuCN)]$_2$ (Figure 23, complex **59**). Compound **59** was then treated with the NHC ligand, and oxidised by air and KOTf (or AgOTf only) to form compound **60** (Figure 23). This complex was also synthesized in a two steps synthesis by reacting the carbene ligand with MnBr$_2$ followed by further oxidation with AgOTf [61].

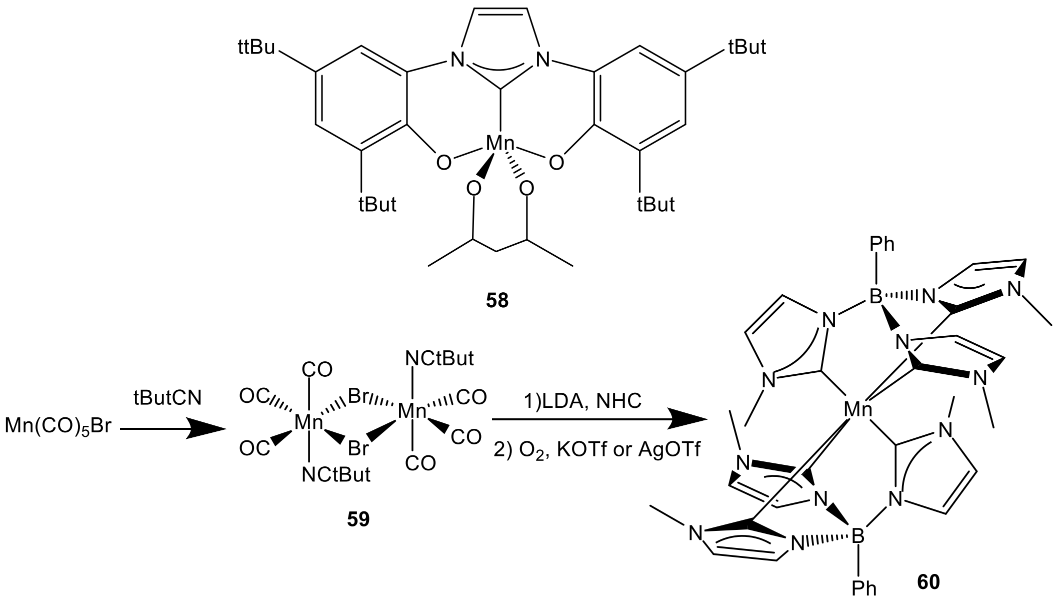


Figure 23 Manganese (III)-(IV) complexes

Meyer's group reported a series of manganese (III, IV, V) complexes bearing amine-linked tris(NHC) ligand XylTIMEN (tris[2-(3-xylylimidazol-2-ylidene)ethyl]-amine) (Figure 24, complexes from **61** to **69**). The group then discovered that pentacoordinate nitride complexes (XylTIMEN)Mn(V) can coordinate additional ligands to form the six-coordinate nitride complexes **63-69**[62–64] (Figure 24).

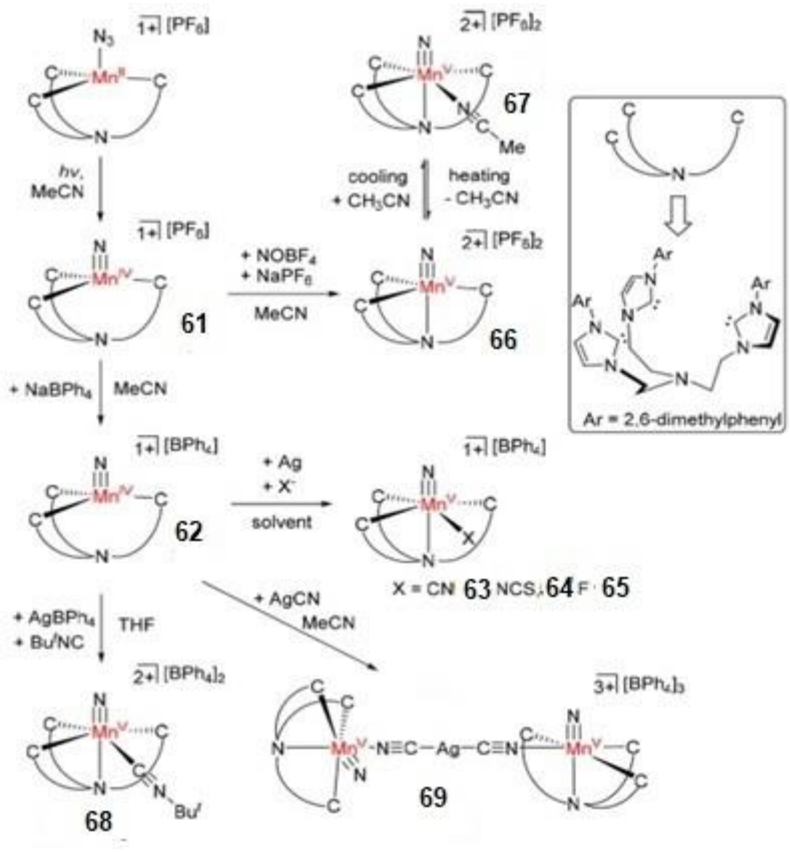
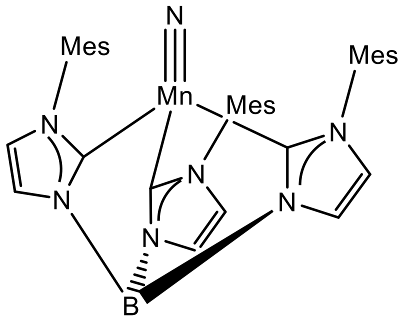


Figure 24 Synthesis scheme of high oxidation states MnNHCs complexes. Adopted by ref. 58

Tris(NHC) ligands showed a high capability to support high oxidation-state manganese nitride complexes. Interestingly, this ability is not restricted to the TIMEN ligand; tris(NHC)borate ligand is also amenable to the task. For this reason, Smith and co-workers synthetized manganese(IV) nitride complex $[PhB(MesIm)_3Mn(N)]$ (Figure 25, complex **70**) by reacting the N-mesityl-substituted manganese(II) complex $[PhB(MesIm)_3MnCl]$ with NaN_3 under UV irradiation[65].



70

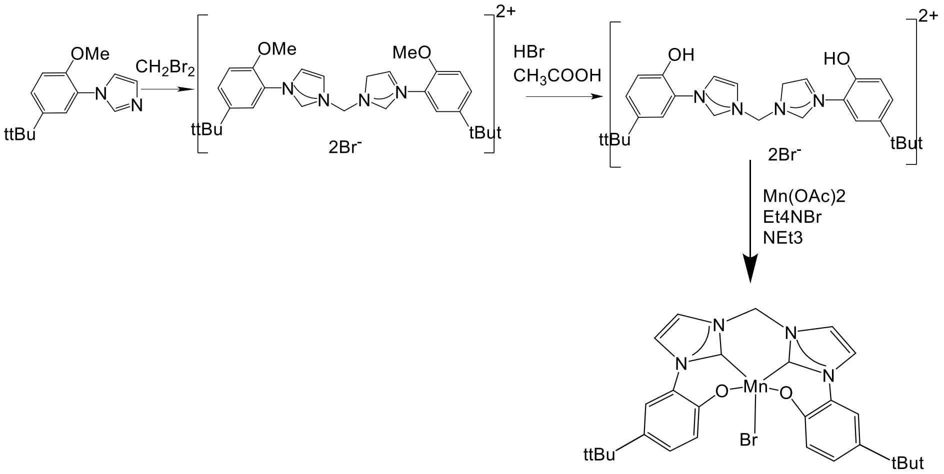
Figure 25 Smith's [PhB(MesIm)3Mn(N)]

MANGANESE BIS-NHC COMPLEXES AND THEIR CATALYTIC APPLICATIONS

Despite a large variety of manganese NHCs complexes have been described in the literature, only few of them have been applied in catalysis. Most of the examples of Mn bis-NHC complexes contain a pincer ligand composed by two NHC ligands and an additional N-donor group. Some examples of tridentate NHC ligands were reported by several research groups in order to stabilise manganese high oxidation states, but no catalytic activity was described[60–64,66].

Oxygen transfer reactions

A method to obtain an active catalytic species is to design a coordinatively unsaturated site or labile ligand around the metal centre, and for this reason, Yagyu and co-workers reported the preparation of a NHC ligand consisting of two carbene carbon atoms and two aryloxy oxygen atoms, acting as a tetradentate ligand for complexation with a manganese(III) ion[67]. The synthesis of the ligand consists in copper-catalysed coupling reaction of 2-iodo-4-tert-butylanisole with imidazole in the presence of an excess of dibromomethane leading to an imidazolium salt intermediate (Figure 26). This intermediate was then refluxed in presence of HBr and CH_3COOH, and subsequently was stirred in presence of $Mn(OAc)_2{\cdot}4H_2O$ with H_4LBr_2, Et_4NBr and NEt_3 in EtOH obtaining the complex **71**. This complex is similar to the Mn"Salen" complexes (a metal bound to a N,N′-bis(salicylidene)ethylenediamine derivate) that are known to be good catalysts for different oxygen transfer reactions. Thus, its catalytic activity in epoxidations was examined attempting the oxidation of styrene with PhIO for 4 h at 40 °C giving styrene oxide (38%) and benzaldehyde (3%).



71

Figure 26 Synthesis of a Mn(III) bis-NHC system

Elecrocatalytic reduction of CO_2 to CO

One of the biggest environmental issues today consists in the big amounts of CO_2 released in the atmosphere. A way to produce value-added chemicals and fuels from renewable energy and CO_2 as feedstock would help to improve the sustainability of industrial processes[68]. In 2018, Royo, Lloret-Fillol and co-workers published the synthesis and the catalytic activity of the first purely organometallic *fac*-[$Mn(CO)_3$(bis-NHC^{Me})Br] (**72**,Figure 27) complex (bis-NHC^{Me} = bis-N-methylimidazolium), which displayed an unprecedented activity for the selective electrocatalytic reduction of CO_2 to CO[25]. Complex **72** was prepared from the reaction of the pro-ligand bis-NHC^{Me} imidazolium salt with [$MnBr(CO)_5$] in the presence of KO^tBu.

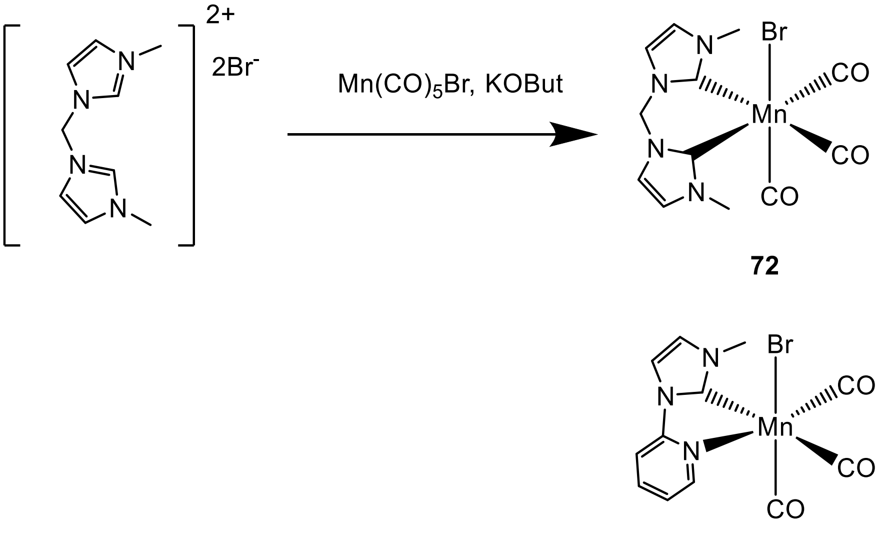


Figure 27 Synthesis of Mn bis-NHC tricarbonyl ***72*** *and its analogue* ***73***

The analysis of the electrochemical behaviour of complex **72** in the reduction of CO_2 shows a turnover frequency (TOF max) value of 2100 s^{-1} in the selective reduction of CO_2 to CO when the reaction is performed in CH_3CN. The TOF max value of **72** is more than 2000 times higher than the value of the analogous pyridyl-NHC catalysts **73** under more favourable conditions (CH_3CN+5%H_2O) and about 50 times higher than the highest CO_2 reduction TOF ever reported for an NHC-containing Mn(I) catalyst[69]. Based on spectroelectrochemical studies and DFT calculations, a mechanism for the electroreduction of carbon dioxide mediated by **72** was proposed (Figure 28) shows the proposed mechanism.

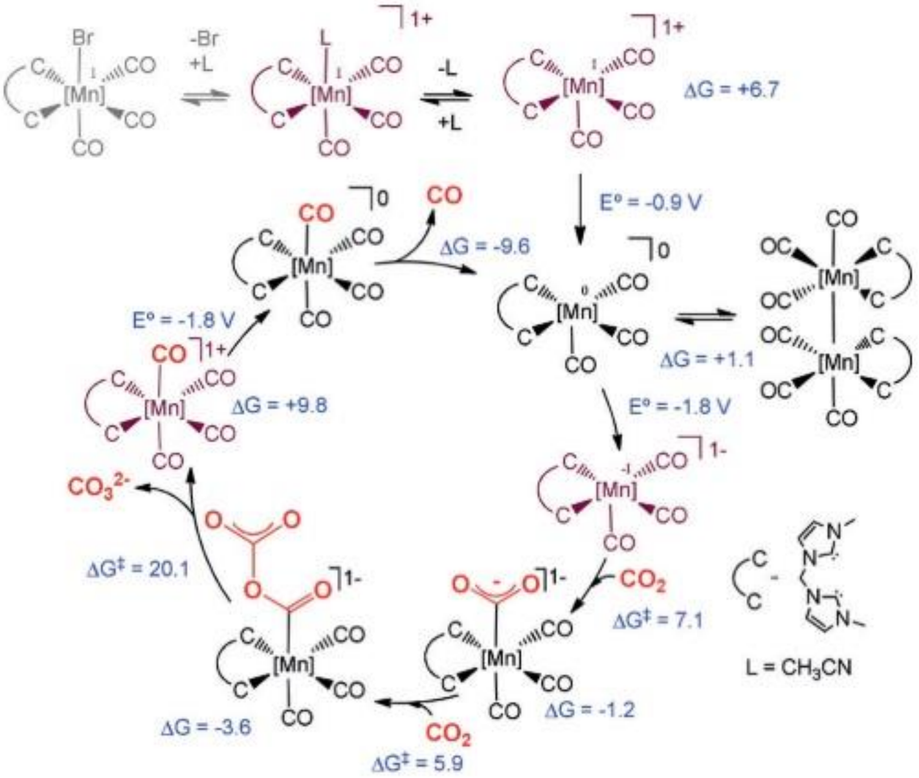
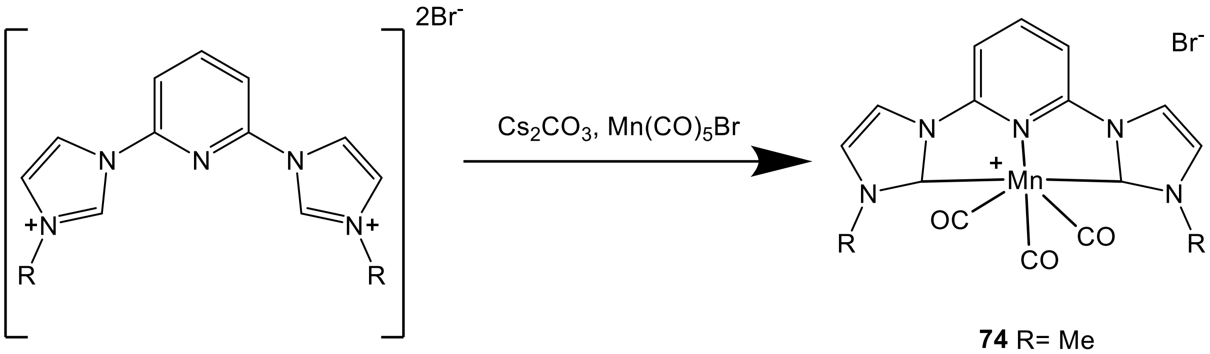


Figure 28 Proposed mechanism for the electroreduction of carbon dioxide. Adopted from ref. 25

This work represented the first purely organometallic NHC-based tricarbonyl Mn(I) complex that is active in the electrocatalytic reduction of CO_2 to CO. It was demonstrated that the replacement of a pyridine ring by an NHC unit had a significant effect on the catalytic performance, converting carbon dioxide into CO using anhydrous aprotic organic solvents. Complementary IR-SEC measurements and computational data suggested that the strongly nucleophilic character of the Mn atom is likely responsible for the positive ligand effect on catalysis. Later, the same group used these family of Mn tricarbonyl complexes bearing bis-NHC and mixed NHC-py ligands in the reduction of ketones with silanes[17], that is reported in the next paragraph.

Soon later, Myren’s group focused on the preparation of a bis-NHC tridentate ligand framework for the same reaction[70]. The synthesis of the complexes **74** and **75** (Figure 29) started from the synthesis of the two ligands (reported in previous works[71,72]), followed by a reaction with $Mn(CO)_5Br$ in the presence of Cs_2CO_3 in MeCN at 60 °C (Figure 29).



74 R= Me
75 R=Bn

Figure 29 Myren's group synthesis of complexes 74 and 75

Complexes **74** and **75** were characterised by single crystal X-Ray diffraction, Normal Pulse Voltammetry and Diffusion Ordered Spectroscopy. Based on Normal Pulse Voltammetry and Diffusion Ordered Spectroscopy studies, the authors proposed that the reduction of **74** and **75** occurs irreversibly as a $1e^-$ step. During the experiment conducted with CO_2 saturation, they observed a large catalytic current enhancement with good faradaic efficiencies for CO production and an increase in the amounts of protons produced a rise in the current and overall faradaic efficiency for CO production eroded at more negative potentials.

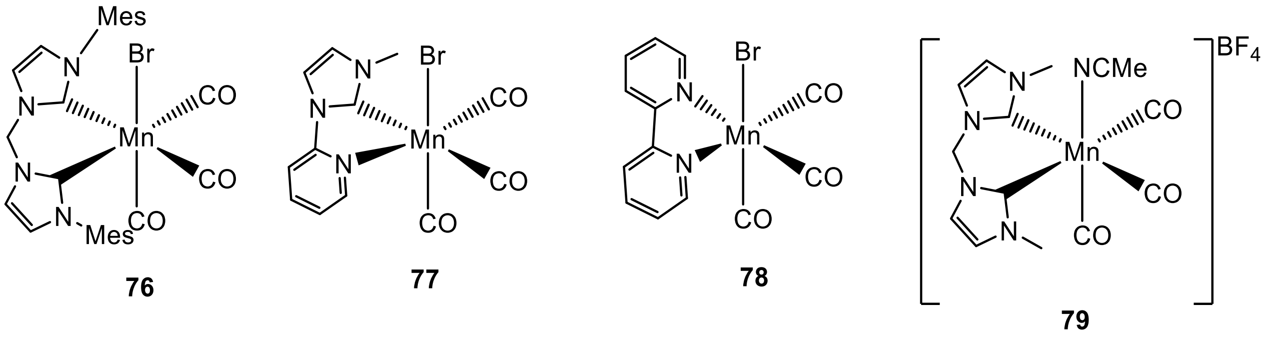
Hydrosilylation of polar unsaturated bonds

Hydrosilylation offers a useful alternative for the reduction of unsaturated carbon-heteroatom bonds, that can be done under mild conditions and avoiding dangerous reagents[26].

Reduction of carbonyl groups: Ketones and Esters

Up to date, all the Mn complexes developed for catalytic reduction of carbonyl groups were coordination compounds bearing N-, O-, and P-based ligands. In 2018, Royo et al. described the use complexes **72** (Figure 27) and **76** (Figure 30) as catalysts for the reduction of ketones, and compared their activity with those of mixed NHC-pyridyl **77**, and bipyridyl ligands **78** Mn complexes (Figure 30). Catalytic essays were performed using benzaldehyde as benchmark substrate, phenylsilane as reducing agent and benzene as solvent at 80°C. Bis-NHC complexes showed the highest activity, illustrating that the presence of the strong donating NHC ligands improved the catalytic efficiency of Mn tricarbonyl complexes. Interestingly, treatment of **72** with $AgBF_4$ in acetonitrile afforded the corresponding cationic species $[Mn(CO)_3(\text{bis-NHC}^{Me})(NCMe)][BF_4^-]$ **79**, which displayed higher catalytic activity than **72**. The group also demonstrated the possibility of using different silanes, such as Ph_2SiH_2 and the cheap and readily available polymethylhydrosiloxane (PMHS). Mechanistic studies indicated that the reaction follows a radical pathway differing from the Mn-based catalysts reported in the literature, where Ojima-like mechanism has been proposed to be operative[73–75].

The same group, later, extender their work with manganese bis-NHC systems to the selective reduction of esters to alcohols through hydrosilylation. Complex **72** represents the first Mn-mediated reduction of esters using the cheap and readily available PMHS as reducing agent under air, without any auxiliary additives[76]. Initially, the reaction was attempted using methyl benzoate in the presence of **72** (1 mol%) and $PhSiH_3$ as reducing agent, in neat conditions at 100°C. To observe the importance of the bis-NHC ligand in the catalyst sity tructure, its reactivity was compared with the mixed NHC-pyridine complex **77**. The results evidenced a lower activity of the latter. Catalysts **72** can be reused up to 5 cycles, reaching an overall TON number of 485. The possibility of using less expensive silanes, such as Ph_2SiH_2, PMHS, and TMDS was studied. Good conversion (88%) of esters was obtained with PMHS, while Ph_2SiH_2 and TMDS resulted inactive. Different substrates were screened showing that the catalytic system can reduce a lot of different cyclic, aliphatic, chlorated and differently substituted ketones in good yields. The only limitations are referred to the reduction of alkyl benzoates bearing the NO_2, NH_2, and CN substituents.



76 **77** **78** **79**

Figure 30 Complexes used in the reduction of ketones and esters

Reduction of sulfoxides

The efficiency of **72** in the reduction of sulfoxides with silanes was also described by Royo and co-workers[77]. The catalytic activity of **72** was studied using methyl phenyl sulfoxide as a model substrate and phenylsilane as a reductant under solvent-free conditions, at 100°C with a catalyst loading of 2 mol%. The complex revealed a high catalytic activity, converting methyl phenyl sulfoxide in the corresponding sulfide in 10 minutes in a non-inert atmosphere and with no additives. A turnover frequency, TOF of 788 h^{-1} was obtained representing the highest TOF value reported so far for a metal-based catalyst, in reduction of sulfoxides with silanes. Moreover, the group discovered that the catalyst could be reused up to 9 cycles. A wide variety of sulfoxides were tested in order explore the scope of the reaction. All symmetric, asymmetric, diaryl, dialkyl, acyclic, cyclic sulfoxides were readily reduced affording excellent yields (mostly up to 80%) of the corresponding sulfides. In addition, halogenated, alkyl, ester, cyano, and nitro functional groups were reduced with excellent selectivity and good yields obtained (from 50 to 84%), whereas olefinic groups were not tolerated. The possibility to use different silanes was also explored, replacing phenylsilane by cheaper and safer silanes like Ph_2SiH_2, triethylsilane (Et_3SiH), tetramethyldisiloxane (TMDS) and PMHS. Interestingly, a variety of sulfoxides were reduced using diphenylsilane and TMDS; representing the first application of TMDS as a reducing agent in Mn-mediated reactions. Experiments with TEMPO and other radical scavengers such as Ph_2NH and $CBrCl_3$ produced a significant decrease in the activity of the catalyst, demonstrating the involvement of radical intermediates in the reduction of sulfoxides.

Borrowing hydrogen

The borrowing hydrogen/hydrogen autotransfer (BH/ HA) has been emerging as a versatile method in synthesis, providing a more sustainable way to obtain carbon-carbon bonds, using non-activated renewable alcohols as starting materials. Usually, the catalysts for this reaction work with a bifunctional outer-sphere metal−ligand cooperation or through an inner-sphere mechanism but the introduction of additional functional site(s) or hemilabile arm(s) to the ligands implies expensive, air-sensitive, and problems in the synthesis at a large scale. In this regard, Lan and co-workers wanted to explore another reaction path: the non-bifunctional outer-sphere mechanism[47]. They applied for the first time this strategy with a non-noble transition metal in the BH/HA C−C bond formation in α-alkylation of ketones with alcohols and in the Friedländer annulation, using a bis-NHC-Mn system **72**. They compared the latter with NHC-pyridine **77**, and bipyridine manganese **78** complexes, obtaining that in the α-alkylation of ketones the most active complex is **72**. The reaction, using different alcohols and ketones as substrates, proceeds smoothly reaching good or excellent yields (from 38 to 96% after two hours). In the Friedländer annulation, several ketones with different substituents underwent straightforward delivering of the quinolines in good yields (from 46 to 83% after two hours). Again, DFT studies allowed to propose a plausible mechanism for the reaction and it is reported below (Figure 31).

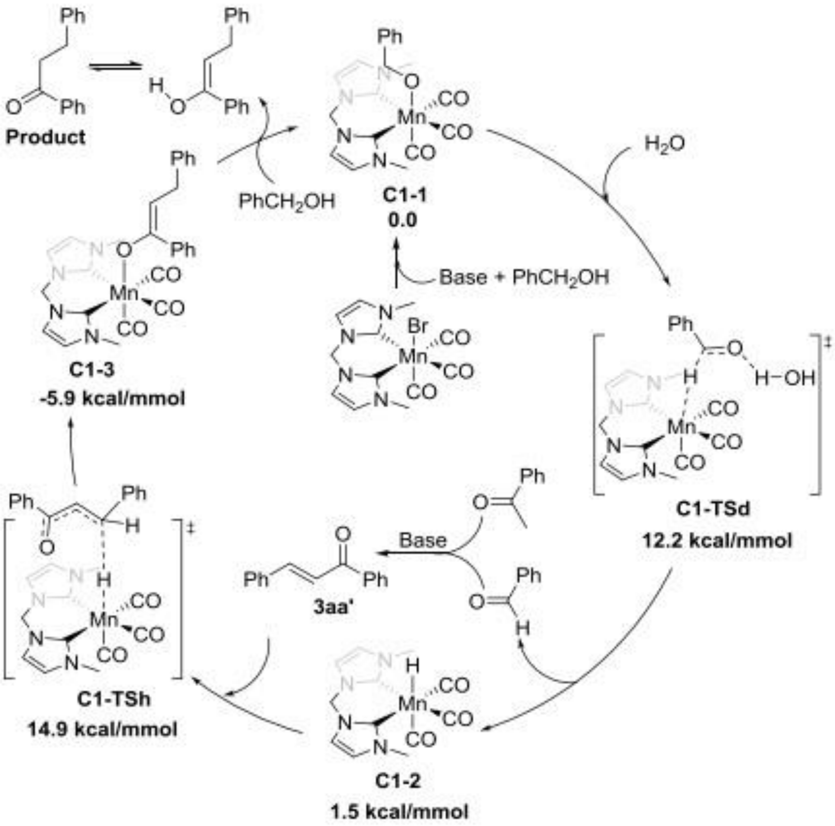
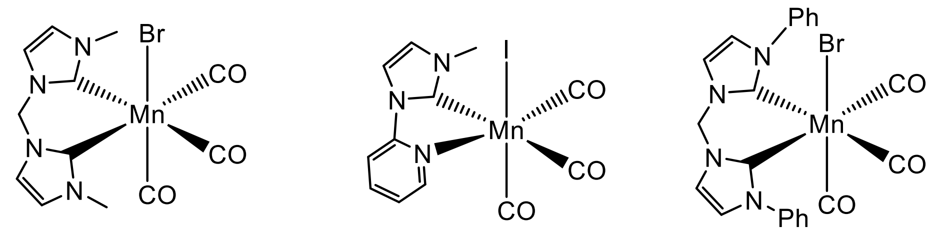


Figure 31 Proposed mechanism α-alkylation of ketones with alcohols. Adopted from ref.47

The borrowing hydrogen (BH) or hydrogen auto- transfer (HA) methodology can also be applied in the dehydrogenative coupling of alcohols with amines, in order to obtain a more sustainable N-alkylation. Huang and co-workers tested catalysts **72**, **80, 81** (Figure 32) in this reaction, trying to find a methodology for *N*-akylation avoiding harsh reaction conditions and phosphine-containing ligands that are usually required[46] . In this case, they tested the catalysts in a benchmark reaction between aniline and benzylalcohol in the presence of a base (KO^tBut) at room temperature, obtaining high activity for the complexes **72** and **81**. To test the robustness of the catalyst, they made a screening using a wide range of aromatic amines resulting in a good tolerance of the catalyst **72** (chosen as optimum catalyst) towards different substituents and C=C group containing anilines. Only alkylation of aliphatic amines was unsuccessful. A wide range of alcohol were tested and even Citronellol (with an unsaturated C=C bond), phenylpropanol and methanol were able to be used and converted.

DFT studies indicated that the catalyst acts with an outer-sphere mechanism without the dissociation of the CO ligand.



72 **80** **81**

Figure 32 Complexes tested by Huang and co-workers

HYDROSILYLATION AND ITS RELEVANCE

The hydrosilylation is an important reaction nowadays. Organosilicon compounds are usually stable, non-toxic, easy to handle and highly attractive building blocks in organic synthesis and industry. These products can be used as reagents and synthons directed toward the construction of natural products offering a powerful tool in organic synthesis[78]. Nevertheless hydrosilylation is used for crosslinking of silicone polymers to elastomers and silicone-based coatings, and for coupling of silanes and siloxanes to organic polymers[79]. Organosilicon compounds represent the starting materials of emulsifiers, softeners, adhesives, silicone, rubber, herbicides, fungicides and many others[10]. The name hydrosilylation refers to the addition of organic and inorganic silicon hydrides on multiple bonds, in particular carbon-carbon and carbon-heteroatom (for example carbonyls). This reaction can be applied also to heteroatom-heteroatom bonds (for example N=N or N=O)[80]. The derivatives are generally less polar, more volatile and thermally stable[81]. The silylating agents used for these reactions are silanes. These compounds contain silicon-hydrogen bound (they are the corresponding of the saturated hydrocarbons but less stable than their analogues)[82]. There are many different silane compounds, with different groups bond to the silicon atom that can influence the stereoselectivity of the reaction.

The first example of hydrosilylation, was a reaction occurring between trichlorosilane and 1-octene in the presence of acetyl peroxide in 1947 reported by Leo Sommer[83](Figure 33) .

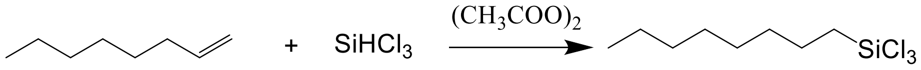


Figure 33 Leo Sommer hydrosilylation

This reaction was mediated by free radicals generated in situ[83] but nowadays catalysis uses transition metal complexes (but also supported metals) that accomplish the process through different mechanisms[80].

The discovery of hexachloroplatinic acid in 1957 as a very efficient precursor of the Pt-catalyst by John L. Speier was the starting point for a wide exploration of other platinum catalyst for this reaction[79]. This led to the application of this reaction as a fundamental and elegant method explored over the next years for laboratory and industrial synthesis of organosilicon compounds and other organic silyl derivatives[80]. One of the most affected industrial field is polymer industry, that from 1967 developed new technologies for this reaction for more than 50 years [84]. Industrially relevant aspects of hydrosilylation are dominated by the selectivity, activity (TOF or TON) of hydrosilylation catalysts. Platinum catalysts have different industrial drawbacks, primarily high price, pushing companies and universities to focus their research on a more responsible use of precious metal consumption. The seek for price-efficient and durable catalysts led to more active, selective and employing lower-priced transition metal catalysts[79]. This research for alternative platinum-free catalysts containing low-cost-transition metals has been performed extensively and year after year hydrosilylation receives more attention (Figure 34)[84].

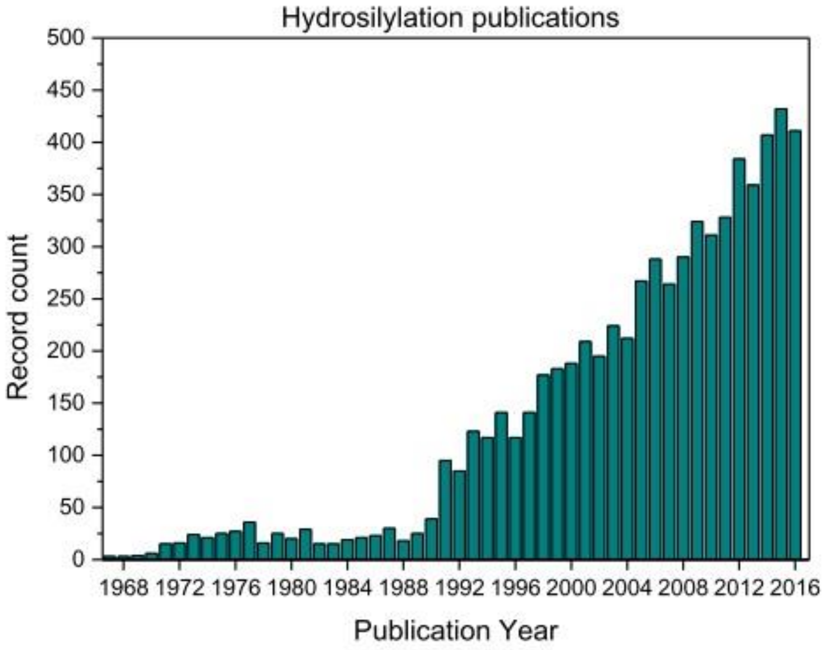


Figure 34 Hydrosilylation publications listed per year. Adopted from ref. 84

HYDROSILYLATION OF ALKYNES

The hydrosilylation of alkynes is the most direct, powerful and atom-economical approach to obtain specific alkenylsilanes. These compounds cover a big variety of applications in organic synthesis and display ease of handling, low cost, minimal toxicity and compatibility with a range of organic transformations. For these reasons, they have greatly stimulated their synthetic advancements[85].

Unsaturated hydrosilylation products are attractive intermediates for further transformations including oxidation, electrophilic substitution, palladium catalysed cross-coupling, rhodium-catalysed nucleophilic addition[86].

Vinylsilanes are other important products of this reactions[78]. They represent important building blocks in organic synthesis and nowadays new more sustainable preparation methods are required. Metal-catalyzed hydrosilylation of terminal alkynes is an efficient and atom economical way for their production[86].

However, the synthetic utility of the alkenylsilanes and vinylsilanes depends on the regio- and stereo- control of their preparation. The hydrosilylation of alkynes offers a greater synthetic challenge because of the potential for a broader product distribution (Figure 35). For example internal alkynes hydrosilylation would potentially give four isomeric addition products: [85]

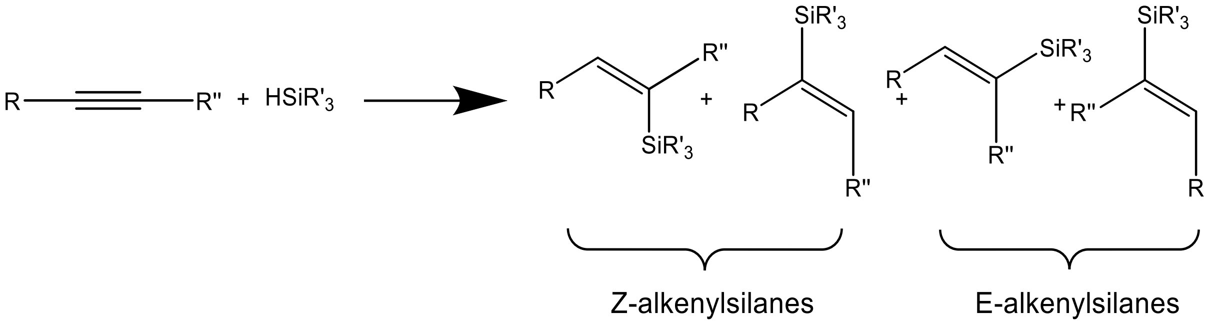


Figure 35 Possible products of hydrosilylation of internal alkynes

The hydrosilylation of terminal alkynes (in the preparation of vinylsilanes) yields, instead, to three regio-isomers: the α, the β-(E), and the β-(Z) isomers (Figure 36).

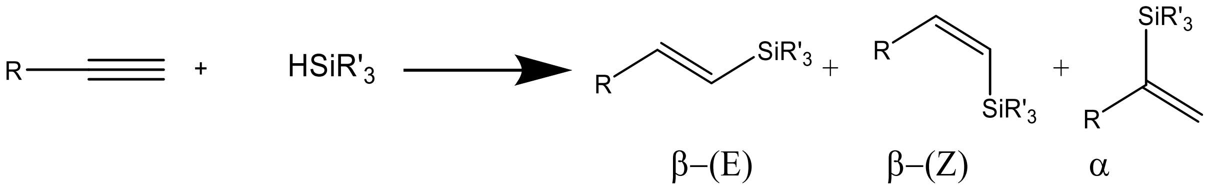


Figure 36 Possible products of hydrosilylation of terminal alkynes

The regio- and stereochemical outcome of this process depends on several factors including the catalytic system (the metal and ligands) and the substituents on the reagents employed. Reaction parameters such as solvent, temperature, catalyst loading or even the sequence of addition of the reagents are other important factors that influence the stereo- and regio- selectivity[87]. Due to the importance of stereo- defined alkenylsilanes in synthetic chemistry, efficient and selective catalysts that lead to the formation of each of a specific isomer are strongly desirable[85,88].

The hydrosilylation of alkynes can be promoted by a variety of catalysts including radical initiators, chloroplatinic acid[85], and different types of metal catalysts[89]. Transition-metal-catalysed hydrosilylation reactions have made great success over the past few decades, employing specially precious metal complexes like platinum[85,88,90–92], rhodium[85,87,93–98], ruthenium[85,99–102], iridium[85,103] and palladium[85,104,105]. Different ligands have been tested with these metals, in order to enhance catalytic activity, regio- and stereoselectivity. Among all the complexes synthetized, various works used NHC ligands.

Platinum, the oldest metal used for hydrosilylation of alkynes[85], presents different works involving NHC ligands[88,90,91].

In these articles, different working groups demonstrate that these complexes are competent catalysts for the hydrosilylation of alkynes[88,90,91], in which the regioselectivity is governed by both steric and electronic factors both of the alkyne and the NHC substituents[88]. These complexes generally require low catalyst loading[90] and thanks to the easy modification of NHC ligands it had been possible to obtain a water soluble complex, active at room temperature[91].

Rhodium shows several recent works where this metal is bounded with NHC and bis-NHC ligands. These works report good stereoselection and generally high reactivity with internal[98] and terminal alkynes[93,94,96].

Iridium NHC complexes have been largely used in different reactions and these catalysts proved to be active catalysts for the synthesis of vinylsilanes[103].

Palladium reports only an article using NHC ligands in hydrosilylation. This complex was used for the bis(silyl)ation of internal acetylenes using non-activated di-silanes[105].

The current catalytic processes rely on precious metal complexes and are susceptible to unwanted side reactions such as dehydrogenative silylation and over hydrosilylation to the tertiary silane. Early transition metal catalysts show a wide application in carbon–heteroatom double bond hydrosilylation, but only few examples in alkyne hydrosilylation[85].

One of the biggest problems in the modern production of organosilicon compounds, is the huge uptake of platinum in hydrosilylation reactions. It was estimated in a study from 2008 that the silicone industry worldwide depletes ca. 5.6 tons of platinum, which is unrecyclable[106]. Due to this the high cost of platinum, chemical industries need to focus on the development of nonprecious metal catalysts.

The late 3d transition metals like cobalt, iron and nickel are promising candidates for nonprecious metal-based hydro-silylation catalysts due to their abundance, low-cost, and low toxicity. These metals, in their early alkyne hydrosilylation catalysis tests showed that they are capable of catalyse this reaction but the catalytic efficiency is not as high as the noble-metal catalysts[107].

Nowadays the most studied low cost metals for this reactions are cobalt[107–110], nickel[107,111,112], and iron[89,113] but few examples are reported using NHC ligand. Cobalt NHC is reported once in the to be active in the hydrosilylation of alkynes[114]. This complex was a low-coordinate Co(I) alkyl complex bearing bulky IAd ligand (IAd = 1,3-diadamantylimidazol- 2-ylidene), producing syn-adducts of vinylsilanes with high efficiency, selectivity, and good functional group compatibility[114].

In 2011 a work published by Bearding and al. reported the only known NHC nickel complex active in the hydrosilylation of alkynes. In this work they showed that the catalytic activity of the various nickel complexes is dependent on the ligand substituents and they are active in the hydrosilylation of internal alkynes with triethylsilane[111,115]. Titanium and iron still don't have any NHC complex active in the hydrosilylation of alkynes so far[26,115].

Manganese in hydrosilylation of alkynes

Manganese, as other promising low-cost metal for catalysis, has been intensively studied in hydrosilylation of carbonyls. Only sporadic terminal olefins were preliminarily tried for hydrosilylation of carbon – carbon unsaturated bonds. The first and only manganese-catalysed hydrosilylation of alkynes has been reported in 2018 from Wang and co-workers[116]. This reaction, compared to the hydrosilylation of alkynes, results more challenging due to the lower polarity of the carbon – carbon triple bond (compared to the C=O), the control of stereo- and regio-selectivity for unsymmetrical alkynes and the undesired formation of hydrogenation byproducts[85].

The group found that catalytic use of mononuclear $MnBr(CO)_5$ with the ligand $AsPh_3$ could deliver the E-products in excellent stereoselectivity. On the contrary, di-nuclear $Mn_2(CO)_{10}$ in the presence of laurylperoxide (LPO) enabled the formation of Z-products in a reversed stereoselectivity[10] (Figure 37).

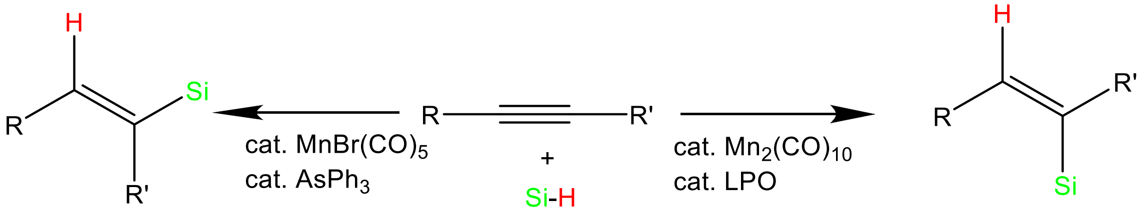


Figure 37 Schematic rappresentation of Yang and Wang's work

Diphenylacetylene and diphenylsilane were chosen as the model substrates to optimize the reaction conditions. The use of $[Mn(CO)_5Br]$ yielded a low amount of silylated products, instead the reaction produced noticeable amounts of hydrogenative by-products. Adding $AsPh_3$ as a ligand optimized the yield of the E product and the stereoselectivity over the Z product. The group then started to test a series of silanes, including mono-, di-, and tri-substituted aliphatic and aromatic silanes showing that the catalyst tolerated these groups and in all the cases E-configured products where obtained in high yields with excellent selectivity.

Detailed mechanistic studies were conducted, leading to a proposed catalytic cycle of the [$Mn(CO)_5Br$]/$AsPh_3$ -catalysed E-selective hydrosilylation of alkynes (Figure 38).

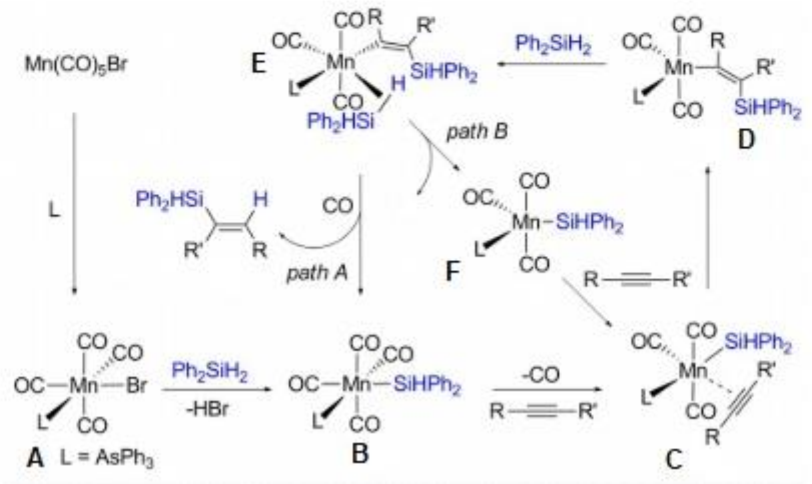


Figure 38 Proposed mechanism for E-selective hydrosilylation. Adopted from ref. 8

Manganese pentacarbonyl bromide exchanged a carbonyl with the ligand $AsPh_3$ generating an intermediate **A** that underwent a δ-metathesis reaction with silane resulting in the specie **B**. Subsequently this complex coordinated the alkyne (**C**) and an insertion on the alkyne took place, leading to an alkenyl–manganese intermediate **D**. This intermediate, then, coordinated another silane molecule (generating the specie **E**), and through a δ-metathesis the desired product is produced, closing the catalytic cycle (path A). An alternative path for **E** was also described (path B). The desired product could also be released directly from **E**, forming the species **F** that underwent through a coordination of alkyne to give intermediate **C**.

The use of the use of di-nuclear complex [$Mn_2(CO)_{10}$] in presence of lauroylperoxide (LPO) reversed the E/Z selectivity in the hydrosilylation of alkynes. The catalyst tolerated a big variety of substituents on the phenyl moiety and both the internal and the terminal alkynes were successfully reduced. Thanks to the enhancement of yield and selectivity due to the radical initiator LPO and that the reaction could take place under UV irradiation, a radical mechanism was proposed for the Z-selective hydrosilylation process (Figure 39).

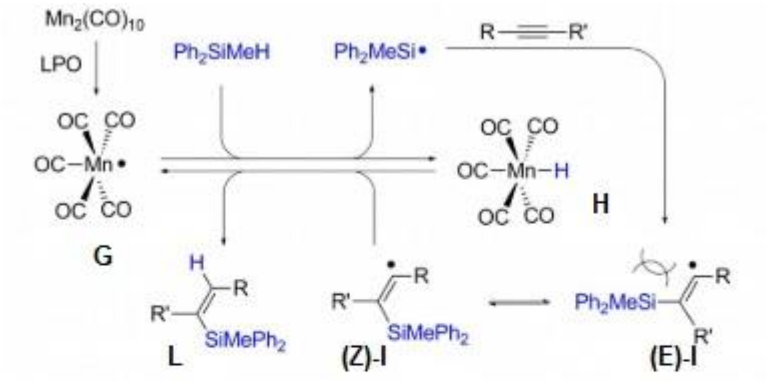


Figure 39 Proposed mechanism for Z-selective hydrosilylation. Adopted from ref. 8

The first step of the cycle is the homolysis of [$Mn_2(CO)_{10}$] that generates manganese radical **G**. This radical intermediate abstracts hydrogen from silane yielding to a silyl radical and manganese hydride **H**. The silyl radical reacts with the triple bond of the alkyne giving the alkenyl radical **(E)-I** in equilibrium with his stereoisomer **(Z)-I**. The equilibrium is shifted to the less hindered radical Z-configured, which reacts with manganese hydride **H** yielding to the product **L**.

In this way the group discovered the first catalytic use of manganese in the hydrosilylation of alkynes, opening new perspective for the use of this metal in this reaction. Due to the lack of early transition metals NHC complexes used in this reaction[111,114,115] and to the scarcity of examples using manganese[10], the group in which I performed my traineeship started to investigate in this direction.

HYDROSILYLATION OF OLEFINS

Alkenes have been perhaps the most studied substrate in hydrosilylation, dating back to the first published reports over 70 years ago[83,120]. The hydrosilylation of alkenes is usually straightforward and one of the most atom-economical and efficient processes for the formation of alkylsilane derivatives[121,122]. This reaction is also important because employs stable, cheap and readily available reagents, enabling the addition of silicon hydrides across C–C multiple bonds[123].

Alkylsilanes like other organometalloids find useful applications in organic syntheses, replacing boron and tin compounds as they are in general less toxic, cheaper and more stable[86,124] and the silicon-carbon bond is the base of organosilicon monomers and polymers of great industrial application[125].

Hydrosilylation of olefins has emerged as one of the largest-scale applications of homogeneous catalysis[126]. This process is employed in the production of organofunctional silanes[127–130] and silicone polymers. Among these products we can find different commodities like silicon oils, silicone-based surfactants[131], functional siloxanes, silicone resins, elastomers[126] coatings and adhesives[79,126]. Organosilicon reagents are commonly used in fine chemical synthesis[132]; these compounds can undergo long synthetic sequences without decomposition[123].

The wide variety of silylated products made the global silicones market reach a volume of 2.1 million metric tons in 2018 and is further projected to reach a volume of 2.8 million metric tons by 2024[133].

The most important problem associated with hydrosilylation of alkenes is the regio and stereo control. For simple olefins, the selectivity issue is limited to the possible formation of two regioisomers anti-Markovnikov and Markovnikov[134,135]. (Figure 40)

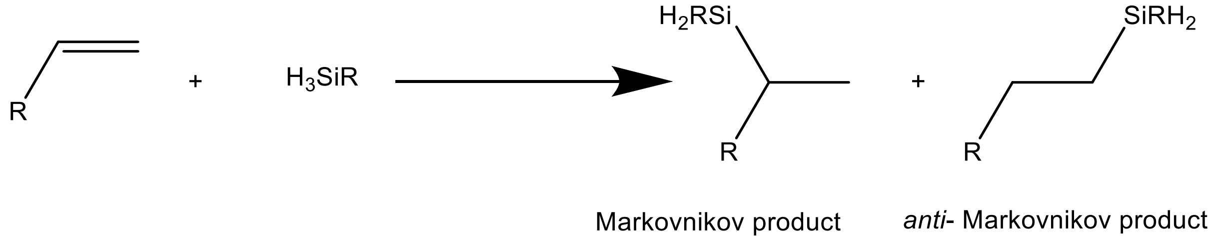


Figure 40 Hydrosilylation of terminal olefins

In some cases, side reactions such as dehydrogenative silylation and alkene hydrogenation, which afford vinylsilane and allylsilane, and alkanes, respectively, can also happen[121].

In order to pursue high yields, selectivity homogeneous late and early TM-complexes have been developed[121]. Among late transition metals, compounds of platinum and rhodium[136] are the most frequently used. Different articles have been published showing these metal compounds binding NHC ligand as catalyst in the hydrosilylation of alkenes and they all show very good performances in terms of activity and selectivity[123,134,137–143].

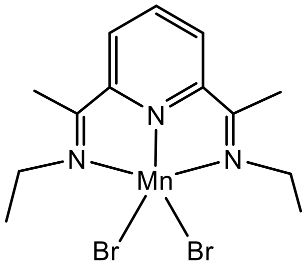
The main drawbacks associated to the use of platinum is associated with intolerance to amino-substituted olefins, a tendency to catalyse side reactions (dehydrogenative silylation, hydrogenation, isomerization, oligomerization and redistribution of hydrosilanes[144]) and the decomposition of the complex to colloidal platinum[136]. Rhodium, by the way, is far more expensive than platinum and characterized by strong price variations. For these reasons is of little interest for low-cost hydrosilylation catalysts because the homogeneous nature of these processes facilitates the loss of the precious metal and this makes metal recovery and recycling extremely difficult[79].

In order to reduce costs and environmental sustainability research focused of low-cost metals catalysts for hydrosilylation of olefins. The most studied metals in this field are nickel[144,145], iron[136,145], cobalt[108,132,145–148] and titanium[144,149]. The use of NHC ligands with these metals in this reaction is limited to few examples[108,147,149–151]. Nickel NHC complexes were tested on the hydrosilylation of styrenes, showing activity and the silylated compounds obtained were mainly the Markovnikov addition products[151]. In another work, nickel NHC complexes were studied with DFT calculations to understand the mechanisms of regio and stereoselectivities in hydrosilylation of allylsilanes[149]. Cobalt NHC systems showed to be active too in the hydrosilylation of 1-octene with PhSiH3 with very high activity and good selectivity[150] and that cobalt(II) amide complexes can be used as catalysts in the hydrosilylation of alkenes with tertiary silanes, avoiding the use of external activator[147].

Manganese in hydrosilylation of olefins

Manganese reports quite few examples as a catalyst in the hydrosilylation of alkenes[10]. The first reported article is from 1983, where [$(CO)_5MnSiPh_3$] is used in the hydrosilylation of 1-pentene with an eight-membered cyclic silane under UV irradiation or heating conditions. The system, when heated, produced a variety of products due to the happening of different side reactions. The UV irradiation, instead, produced high yields of the silylated product[152]. Later, in 1987, another article reported the use of [$Mn_2(CO)_{10}$] to catalyse hydrosilylation of 1-hexene with trietoxysilane, but the yield was very low[153].

Another manganese catalyst was used more than 10 years later by the same group to hydrosilylate a terminal olefin founding this poly(siloxane)-supported dimeric manganese complex very active[154]. In 2017, an article on *Nature Chemistry* described the use of a series of Earth-abundant transition metals (iron and cobalt especially) in the hydrosilylation of olefins[145]. Among cobalt, iron and other metals, they tested a Mn(II) complex **82** (Figure 41) activated with NaOtBu, noticing a 60% conversion of 1-octene with total selectivity on the liner silylated product.



82

Figure 41 Docherty's manganese complex

HYDROSILYLATION OF CARBONYL COMPOUNDS

Catalytic hydrosilylation is one of the most important and convenient methods to obtain a silylether, which have important applications in organic synthesis, synthesis of organosilicon compounds and polymer chemistry[17,26]. In Figure 42 it is reported, as an example of hydrosilylation of a carbonyl compound, the reduction of a generic ketone.

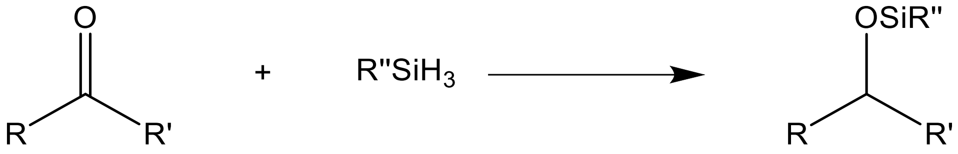


Figure 42 Hydrosilylation of a ketone

Hydrosilylation of carbonyls also offers a useful alternative for the reduction of unsaturated carbon-heteroatom bonds, representing a safer alternative process to hydrogenation[26]. Firstly, it does not employ highly flammable molecular hydrogen and the reaction does not need special pressure equipments, then, liquid hydrosilanes are easy-handling materials that reacts in mild conditions tolerating different functional groups[155]. A lot of different metals have been tested for this reaction and most of them are precious metals like platinum[80,92,156–159], palladium[80,160–162], rhodium[80,163,164], iridium[80,165,166] and ruthenuim[80,167,168]. Complexes of these metals provide usually the most stable and active catalysts but the seek more sustainable alternatives led researchers on the development of Earth-abundant first-row transition metals complexes, making this new trend dominant in the last decade[155].

The most common first transition metal used in hydrosilylation of carbonyl is iron, that in comparison with other 3d metals has evolved enormously since the first example of an homogeneous iron catalyst in ketone hydrosilylation was reported by Brunner in 1991[169]. In the last two decades this metal was employed in this reaction with many structurally diverse complexes [26,80,155,170–172]. From monodentate NHC systems to pentadentate and half sandwich complexes, this metal provides catalysts for the reduction of various carbonyls substrates ranging from aldehydes to amides[155].

Cobalt has largely studied for the hydrosilylation of double and triple carbon-carbon bonds[108,110,135,146,173] and only few examples are reported with different substrates like carbonyls[174–177].

Similarly, nickel has been extensively studied for hydrosilylation of unsaturated carbon-carbon bonds[80] while with carbonyls has remained quite unexplored until 2008[80]. From that year, on the contrary, many research groups developed different catalysts showing good activity in the reduction of ketones and aldehydes[161,178–185].

Manganese in the hydrosilylation of carbonyl compounds

Another metal that needs mention is manganese, that has shown to be highly active in hydrosilylation of different carbonyl compounds, showing different mechanisms depending on the catalyst. From the 90's a lot of different studies focused on this metal, involving different structures, from half sandwich to bis-NHCs complexes and considerable progresses have been made in hydrosilylation of carbonyl groups. The first example of active manganese complex in this reaction was reported in 2013 by Du and co-workers[74]. Their catalyst was able to reduce a variety of aliphatic and aryl carbonyl compounds at 80 °C. Previously some other works report the use of manganese in hydrosilylation of organometallic frameworks[186] (organoiron acyl complexes) or ketones, but they offer little opportunity for ligand modification and fine tuning[187–189].

One of the most active catalytic system was reported by Trovitch in 2014, showing a really high TOF (4950 min^{-1}) reducing various ketones and differently substituted aldehydes and esters at room temperature. Compared to all base-metal catalysts that opens potentials application for large scale industries[10,17].

Darcel, Sortais, Lugan and co-workers developed of manganese half-sandwich complexes using n-heterocyclic ligands reducing acetophenone at room temperature under UV light[43,44]. The same group, later, discovered that manganese carbonyl complex $Mn_2(CO)_{10}$ and triethylsilane under UV irradiation at room temperature is active in the selective reduction of carboxylic acids to aldehydes[190].

In 2017 Huang's group achieved the asymmetric hydrosilylation of ketones using a Mn(II) catalyst bearing a chiral ligand. In the article they report to obtain a wide range of chiral secondary silyl-alcohols in good to excellent yields and enantioselectivities[191]. Later, Gade's group developed other enantioselective manganese complexes bearing pincer ligands active in the reduction of acetophenone[192].

On the same year, Turculet and co-workers synthetised and tested a manganese-based N-phosphinoamidate complex found to be capable of reducing aldehydes, ketones, and esters at room temperature with low catalyst loading[193].

Since 2018, Royo et al. explored the use of the already cited complex **1** in the reduction of ketones and compared their activity with those of mixed NHC-pyridyl **1b**, and bipyridyl ligands

1c Mn-complexes (reported in the paragraph “Reduction of carbonyl groups: Ketones and Esters”).

Since the results obtained in the reduction of carbonyls are positive, Royo’s group wanted to continue with this field, improving reaction conditions by lowering the temperature from 80°C to room temperature and activating the catalyst by blue visible light.

HYDROBORATION OF ALKYNES

Hydroboration is the addition of a boron–hydrogen bond across an unsaturated multiple bond to give organoboron compounds[196]; versatile building blocks in organic synthesis.

In particular, carbon−boron bonds are suitable for carbon−carbon bond formation[197,198] and introduction of functional groups, making hydroboration one of the most studied of reactions in organic synthesis[199]. Furthermore, organoboron compounds show stability toward atmospheric oxidation[200] and their ease of handling[201] make them powerful synthetic intermediates in various organic[202–208], natural product syntheses[209] and in several chemical transformations in the pharmaceutical industry[210].

Among organoboron compounds, alkenyl boranes play a central role in synthesis[211]. Their preparation involved the reaction of Grignard or lithium reagents with trialkyl borates[212]; this method was neither functional group tolerant nor atom economical. Hydroboration of alkynes, on the contrary, provided a useful method for their syntheis thank to its tolerance to different functional groups (alkyl halides, NO_2, RCOCl, $RCONH_2$, RCOOR, epoxide, CN, and COOH[213]) and to its atom efficiency.

The addition of a boron-hydride to a triple bond proceeds readily with no need for a catalyst, providing the cis addition product. The alkyne pushes electrons into the boron’s empty p orbital, while the hydrogen on the boron transfers onto the alkyne in a *syn* fashion[214]. The suprafacial delivery of hydrogen and boron to the same p-face of a given alkyne, creates a four- membered transition state[215], allowing the production of the cis product (Figure 43).

In the presence of an unsymmetrical alkyne, the boron tends to be transferred on the less substituted carbon atom[214]

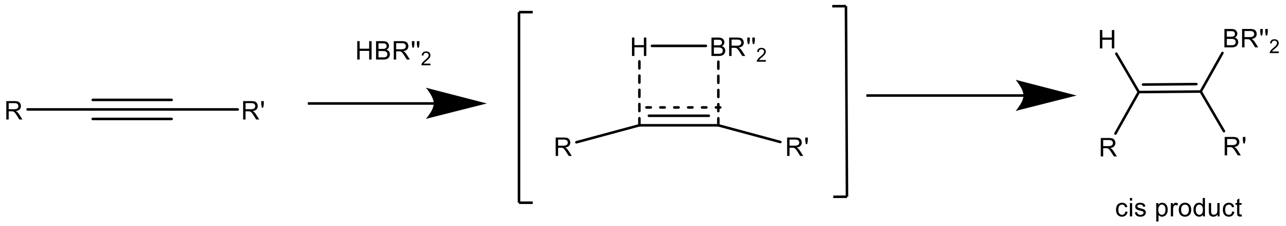


Figure 43 Scheme of alkyne hydroboration

Un-catalysed hydroboration usually requires elevated temperatures, so in order to lower the temperature in 1985 the first use of a transition metal complex as a catalyst was reported[199]. Moreover the chemo-, regio- and stereoselectivity of hydroboration could be influenced by the presence of a catalyst, opening new branches of research[199]. It has to be reported that the syn-addition mode is also strictly obeyed when transition metals are used. Only very few catalysts are reported to induce a different addition mechanism[215].

Rhodium[199,211,213,216] is usually the most common metal used to promote efficiently such reactions although other precious metals like platinum[217], ruthenium[199,215,216,218], iridium[211], silver[219] and copper[220,221] have been used. Those complexes displayed usually high turnover frequencies, but catalysts based on Earth-abundant transition metals are now the target of many research groups considering their low cost and environmental sustainability[212].

Recently, some of these metals have been used for this reaction. The most studied metals in this category are iron[26,200,201,222] and cobalt[212,223–226]. The first work reported using iron complexes for hydroboration of alkynes is from 2013[227] and in 2017 Nishibayashi and co-workers published the most active iron catalyst for this reaction[201]. Cobalt has been almost exclusively used in hydroboration of terminal alkynes[212,223–226] and among those, Trovitch's group reported a cobalt hydride as the most active cobalt catalyst in that reaction[225].

Currently no manganese complexes were tested for this reaction, and this opens new possibility for a future development. From this point, the group in which I did my traineeship started to investigate if it was possible to apply complex **1** as catalyst for the hydroboration of alkynes.

AIM OF THE THESIS WORK

My training period was developed in different research groups. I have had the opportunity to work under the supervision of Dr Beatriz Royo at the Instituto de Tecnologia Química e Biológica Antonio Xavier from Universidade Nova de Lisboa . Her group is developing new manganese bis-NHC complexes for their use as homogeneous catalysts. I was involved in the synthesis of the manganese bis-NHC complex **72** and in the preliminary study of its catalytic activity in the following reactions:

- Hydrosilylation of alkynes;
- Light-Mediated hydrosilylation of ketones;
- Light-Mediated hydrosilylation of aldehydes;
- Light-Mediated hydrosilylation of esters;
- Hydroboration of alkynes.

Due to the pandemic spread across Europe, I was forced to come back to Italy sooner than initially planned, and I had to leave some of the preliminary projects started abroad. Thanks to the supervision of Prof. Rita Mazzoni at Alma Mater Studiorum – Università di Bologna (Italy), I could complete part of my studies using complex **72**. I deepen my studies on the following reactions:

- Hydrosilylation of alkynes;
- Hydrosilylation of alkenes.

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RESULTS AND DISCUSSION

SYNTHESIS OF THE LIGAND 1,1'-METHYLENE-3,3'-DI-METHYLIMIDAZOLIUM DIBROMIDE

The NHC pro-ligand was synthetized using a procedure previously reported in the literature[25], that consists in a double alkylation of two N-methylimidazole with dibromomethane in acetonitrile at 110°C for 72 hours. The identity of the pro-ligand was confirmed by ^{1}H-NMR. The reaction scheme is reported in Figure 44.

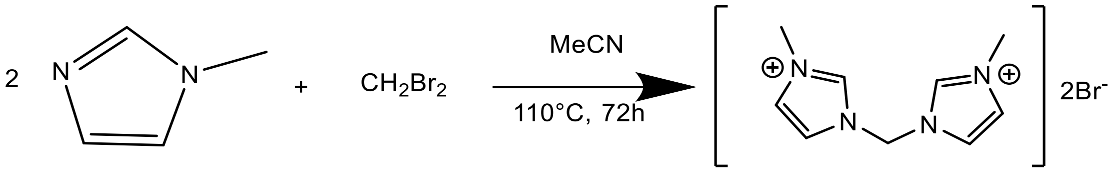
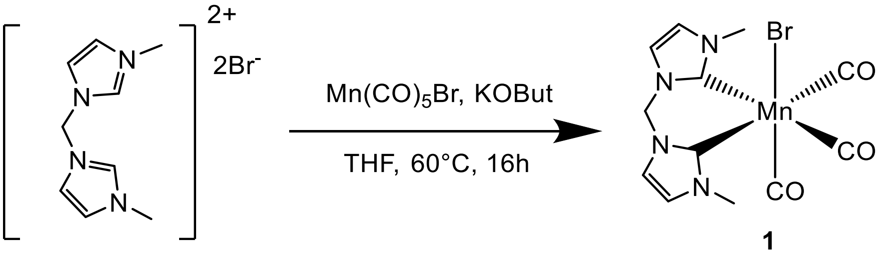


Figure 44 Ligand 1,1'-methylene-3,3'-di-methylimidazolium dibromide synthesis

SYNTHESIS AND CHARACTERIZATION OF COMPLEX 1

The synthesis of the corresponding manganese bis-NHC complex *fac*-[Mn(bis-NHC^{Me})(CO)$_3$Br] (**1**) was achieved following the procedure described by Royo, by treating the precursor Mn(CO)$_5$Br with the imidazolium salt in the presence of potassium *tert*-butoxide in anhydrous tetrahydrofuran. The role of the base is to deprotonate the imidazolium salt to form the corresponding carbene species. Then, the in situ generated NHC reacts with the manganese precursor, Mn(CO)$_5$Br, yielding complex **1** (Figure 45**).**



1

*Figure 45 Synthesis of the complex **1***

After the work up, a yellow powder was obtained and its identity was confirmed by ^{1}H-NMR (Figure 46), ^{13}C-NMR (Figure 47), and FT-IR spectroscopy (Figure 48). Complex **1** is stable to air and moisture.

In the ^{1}H-NMR spectrum (Figure 46), obtained in deuterated dimethylsulfoxide, we can observe the signals corresponding to the hydrogens on the imidazole ring at 7.56 and 7.43 ppm, the signals of the CH_2 bridging between the two rings at 6.61 and 6.01 ppm and signals from the methyls at 3.97 ppm.

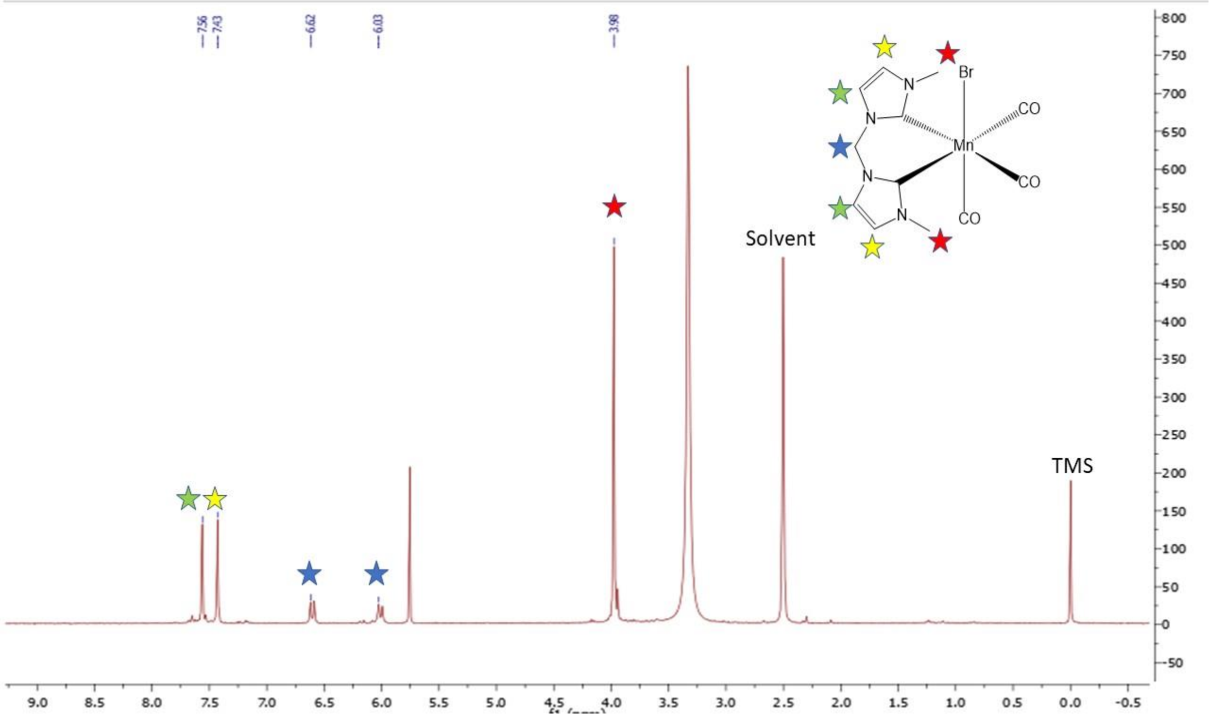


Figure 46 ^{1}H-NMR in DMSO-d_6 spectra of ***1***

^{13}C-NMR spectrum (Figure 47) shows the signal of the carbonyls at 220 ppm, the carbene at 190 ppm, the imidazole carbons at 124 and 122 the carbon in the bridge between the two rings at 62 ppm and methyls at 38 ppm.

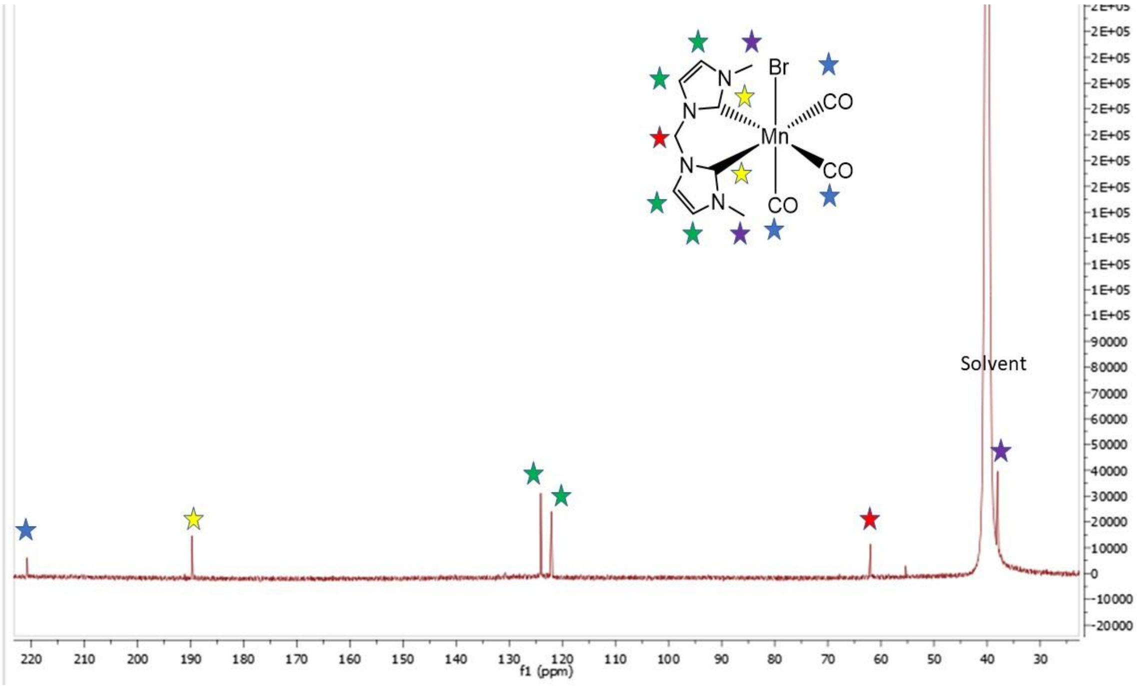


*Figure 47 ^{13}C-NMR in DMSO-d$_6$ spectrum of the catalyst **1***

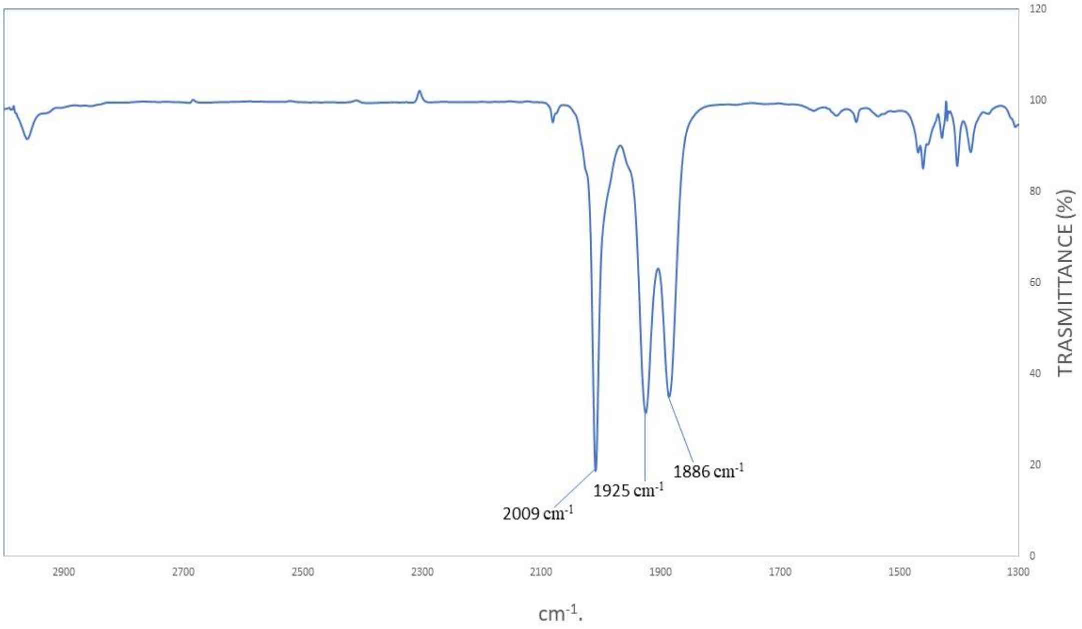


*Figure 48 FT-IR spectra of **1***

The FT-IR analysis was conducted in solution of dichloromethane and shows the three bands corresponding to the carbonyls at 2009, 1925 and 1886 cm^{-1}.

HYDROSILYLATION OF DIPHENYLACETYLENE

The catalytic activity of **1** was tested in the hydrosilylation of alkynes (Figure 49). Initially, the reactions were conducted using diphenylacetylene (0.5 mmol) as benchmark substrate at 150°C in toluene, using similar conditions as those reported in the literature for Mn-catalysed hydrosilylation reactions[116] using 5% mol catalyst. Phenylsilane (0.75 mmol) was the silane chosen according to the already reported article,[116] and the conversion of the diphenylacetylene was monitored by GC-FID using n-tetradecane as internal standard. All the preliminary studies were conducted overnight and results are reported in Table 1.

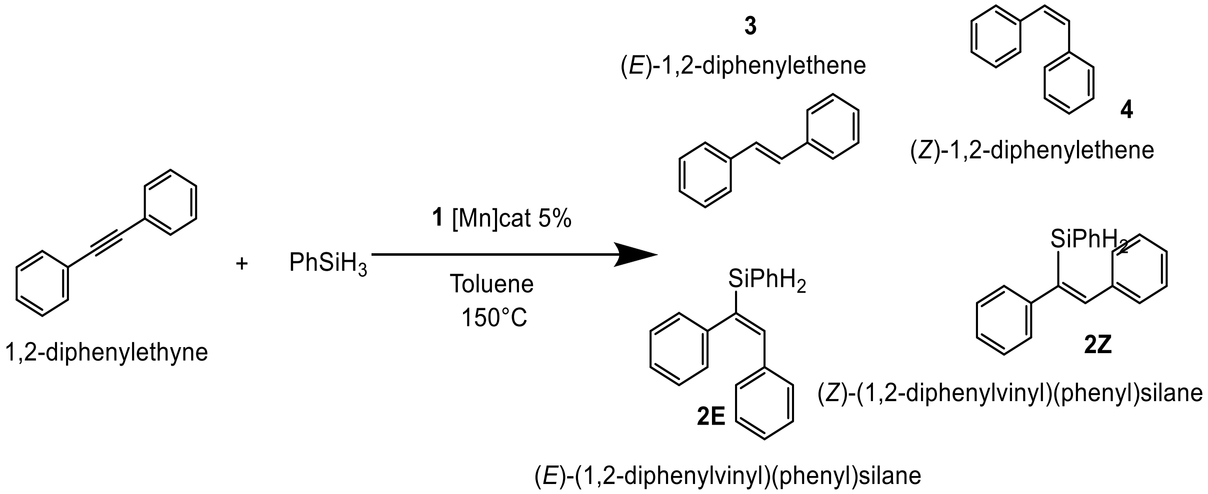


*Figure 49 Reaction scheme of diphenylacetylene hydrosilylation catalysed by **1**.*

Table 1 Hydrosilylation screening reactions

Entry	Catalyst **1** (mol%)	Additive	Conversion (%)
1	5	--	25
2	5	LPO (20%)	51

Complex **1** exhibited low catalytic activity; low conversion to the target products was obtained (Table 1). In order to improve the conversion, we explored the use of the additive laurylperoxide (LPO). This additive has been already employed in a previous study[116] to enhance the conversion. Addition of LPO produced an increase in the conversion of the substrate (entry 2). As reported in literature[116], the reaction usually produces two types of products: hydrosilylated (**2E**-**2Z**) and hydrogenated products (**3**-**4**). Since four different products could be formed, the selectivity in this reaction plays an important role, and we focused our studies on that parameter. Gas chromatographic (GC) analysis of the reaction crude showed only few traces of hydrogenated by-products, so we can assume than **2E** and **2Z** were the only products obtained. Thus we will refer our results in the following on diastereoselectivity in the two hydrosilylated products **2E** and **2Z**.

A significant drawback associated with these two products is that they were not fully characterized in literature. Thus, in order to analyse and confirm the major products of the reaction, we attempted a separation of three reaction mixtures together with a chromatographic column. We eluted with a mixture composed by petroleum ether-EtOAc 40:1. This led to the purification of the products from some minor by-products of the reaction, the internal standard and part of the reagent. We collected the cleaner and most concentrated fractions in the major products (**2E** and **2Z**). To separate the two diastereoisomers, we injected the collected fractions in an HPLC system using a C-18 column in inverse phase, eluting with a solution of 80/20 of azeotropic mixture MeCN- water/ water. Thanks to subsequent injection it has been possible to separately collect the two stereoisomers. After, the solvent was removed yielding two oily products that were analysed by NMR (^{1}H-NMR, ^{13}C-NMR and NOESY experiments). By irradiating the signal of the two protons bounded to the silicon atom at 4,77 ppm, it was possible to distinguish the two stereoisomers. Below it is reported the product referred as **2E** (Figure 53).

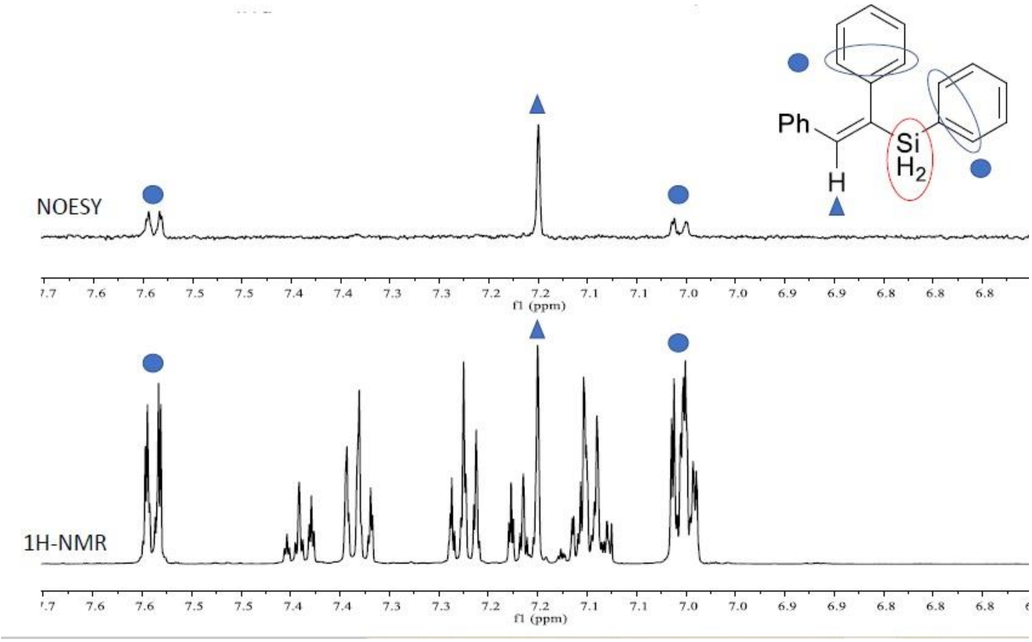


Figure 50 ^{1}H-NMR and NOESY spectra of 2E product in CD_3CN

The other product **2Z** has been identified as the Z product (Figure 54).

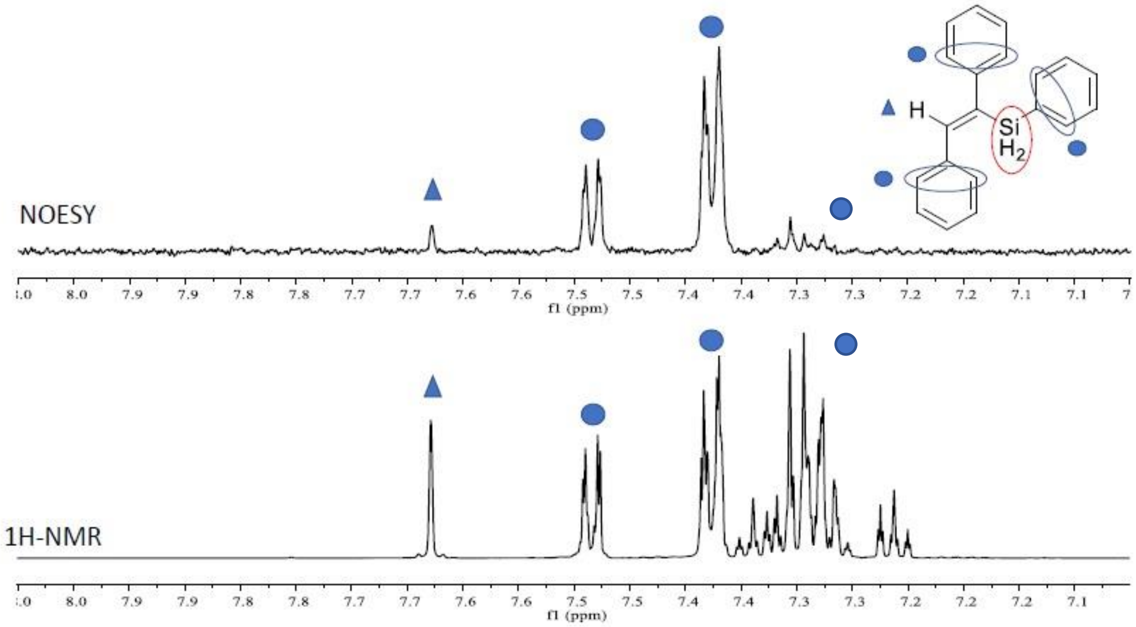


Figure 51 ^{1}H-NMR and NOESY spectra of 2Z product in CD_3CN

In order to explore the diastereoselectivity of the reaction and how it is influenced, we performed different experiments (Table 2).

Table 2 Diastereoselectivity in different experiments

Entry	Catalyst (mol%)	Additive	Conversion (%)	Diastereoelectivity on **2E** (%)
1	0	---	<4	15
2	5	---	25	84
3	5	LPO (20% mol)	51	42

Entry 1 corresponds to the blank of the reaction; in the absence of catalyst no reaction occurs (<4%). Using 5 mol% of catalyst **1,** a 25% conversion was obtained, with a 84% selectivity to isomer **2Z** (entry 2). This finding is in accord with those essays previously reported using LPO (entry 3).

Optimization of the reaction time was performed. The kinetic profile of the reaction using laurylperoxide (20% mol) is shown in Figure 55.

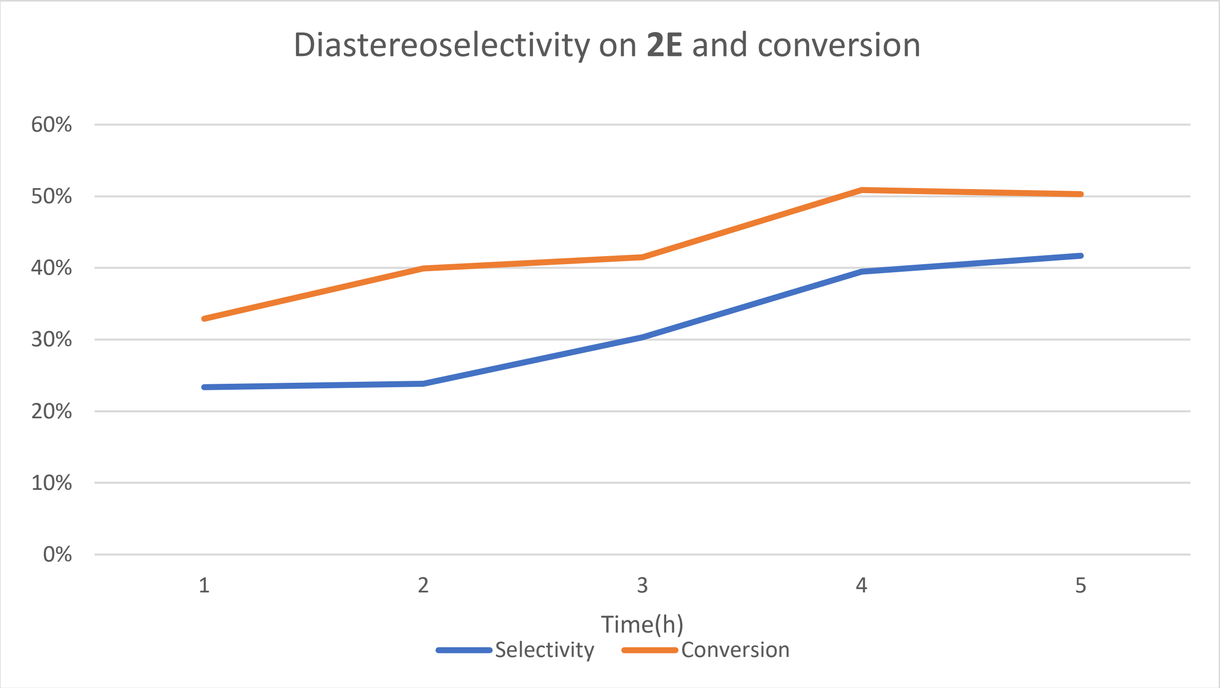


Figure 52 Selectivity and conversion over time in presence of ***1*** *and LPO*

From this graphic is possible to observe that the reaction proceeds in 5 hours, reaching the same conversion observed overnight (Table 1 and Table 2), and that selectivity in the *E* isomer increases with time. This change in selectivity can be explained by the presence of at least two different reaction pathways that produce the two stereoisomers at different speeds. Since in the already cited article[116] no blank in presence of LPO was performed, we set the reaction with the presence of the latter and no catalyst (Table 3).

Table 3 Diastereoselectivity in blank experiment with LPO

Name	Conversion	Diastereoelectivity on **2E**
LPO BLANK	43%	12%

Interestingly the LPO BLANK experiment shows that the reaction is favoured, reaching 43% conversion. Subsequent studies were performed in order to see how fast was the LPO BLANK reaction. Surprisingly, the reaction proceeds in less than one hour. Investigating the eventual dual role of the catalyst **1** in selectivity and of LPO in conversion, it was decided to follow the kinetic profile of the reaction in the presence of catalyst **1** but without the additive LPO (Figure 56).

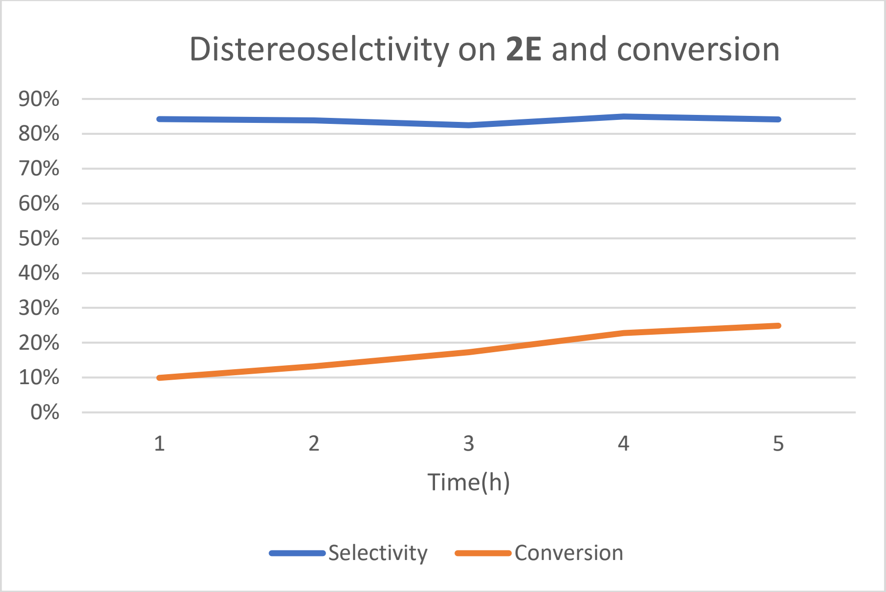


*Figure 53 Diastereoselectivity over time in the reaction with **1** and no LPO*

The reaction reaches the maximum conversion in 5 hours, nevertheless the selectivity on the less favoured stereoisomer is much higher than that obtained in the absence of the catalyst. Taking into consideration both results (Figure 55 and Figure 56), we can conclude that the LPO and the catalyst form two different stereoisomers with different speeds and pathways.

To explore the possible interactions between catalyst and LPO, a reaction reducing the quantity of the LPO to 5% mol was settled. All the obtained results were compared (Table 4).

Table 4 Different conversion, distereoselectivity and 2E yields

Entry	Cat (%mol)	LPO (%mol)	Conversion(%)	Diastereoelectivity(%)	Yield in 2E (%)
1	0	20	41	12	5
2	5	20	51	42	21
3	5	5	33	62	21
4	5	0	25	84	21

From results reported in Table 4 it is possible to observe that the yield in the product **2E** is independent of the quantity of LPO (entries 2,3,4). We can assume that the pathway that generates product **2E** is not influenced by the presence of the radical initiator. This leads us to the conclusion that the LPO increases the conversion generating only the **2Z** diastereoisomer, and it reacts stoichiometrically as a reagent. An equivalent of LPO generates two equivalents of radicals, and it is possible to observe that in entries 1, 2, 3 the improvement in the conversion is similar to the quantity of LPO introduced in the reaction. From these results we can conclude that the LPO is not playing any significant role in the heterolytic path; actually, it can only slow down the speed of this path by deducting diphenylacetylene and converting it in the diastereoisomer **2Z**. Thus, we can consider that the presence of LPO is counterproductive, as it reduces the total selectivity. Therefore, the use of LPO was avoided in the next essays.

Screening of different solvents and temperatures was performed. We tried different solvents with the aim to check the influence of coordination ability and polarity of the solvents: acetonitrile, dichloromethane and petroleum ether (Figure 54).

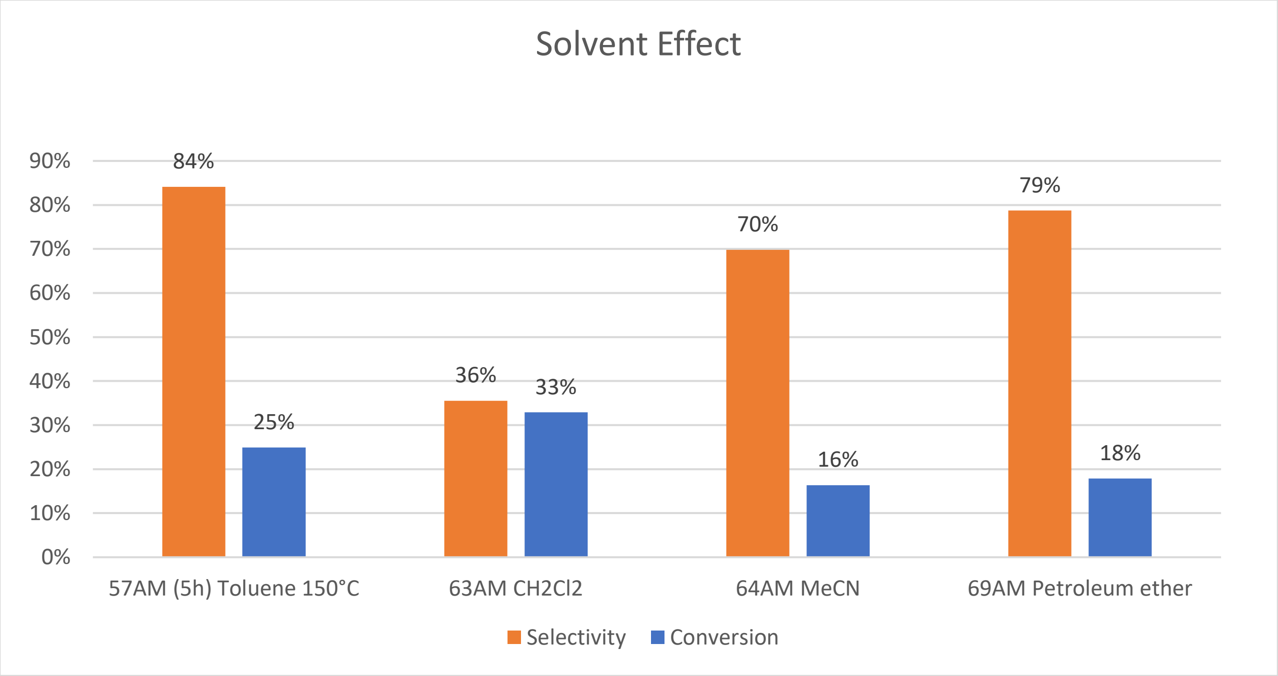


Figure 54 Solvent effect on conversion and diastereoselectivity

The presence of a coordinating solvent (acetonitrile) affects the reaction lowering conversion but the selectivity is still high on the E-isomer. Dichloromethane substantially decreases the selectivity, while the conversion seems to increase. In contrast, petroleum ether did not affect neither selectivity nor conversion. Subsequently, the effect of the temperature on the selectivity and conversion was studied. Four different temperatures were explored: 120°C, 130°C, 140°C and 150°C. Results are reported in Figure 55 .

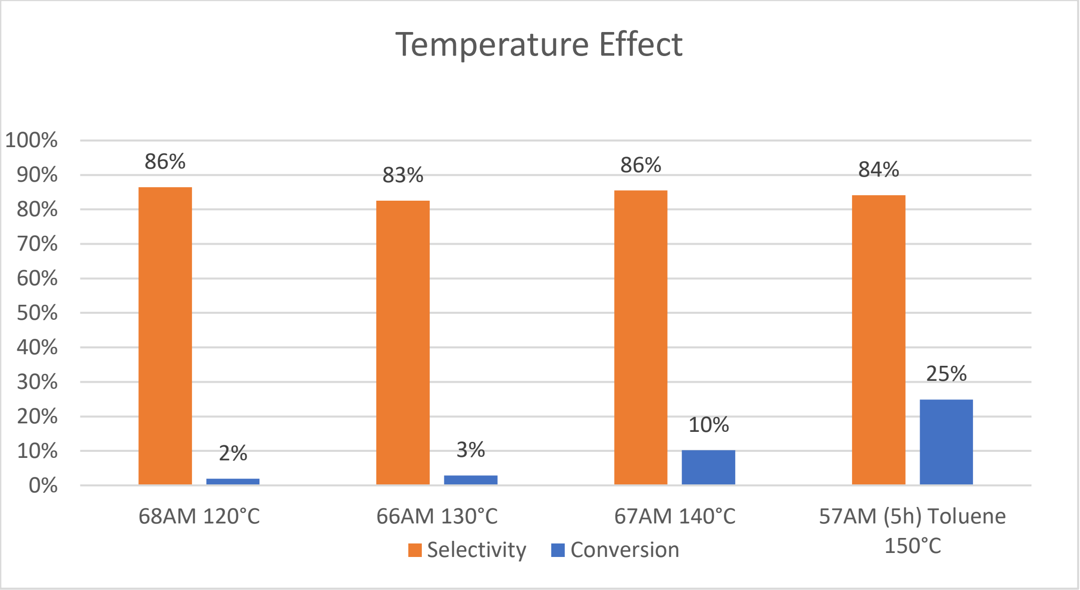


Figure 55 Temperature effect on conversion and diastereoselectivity

From the graph is possible to observe that the selectivity is independent from the temperature, while the conversion is highly affected. The catalyst shows good activity only at high temperatures. In conclusion, the optimized conditions for hydrosilylation of alkynes are using toluene at 150°C.

Since the conversion achieved in the best conditions is still low, the use of different additives was explored. The first additive tested was silver tetrafluoroborate ($AgBF_4$), that has already shown to enhance the activity of the catalyst in the hydrosilylation of ketones in a previous study reported in Royo´s group[117]. This additive was added in stoichiometric quantity to the catalytic reaction using 5 mol% of catalyst and keeping the reaction in the dark during 5 h under stirring at 150°C in toluene. In other experiment, potassium tert-butoxide (tBuOK) was tested as an additive. This additive has already shown to activate earth abundant metal catalysts in hydroboration and hydrosilylation of alkenes[118]. As $AgBF_4$, it was added in stoichiometric amount to the reaction mixture under similar conditions previously described. Conversion and diastereoselectivity of the two reactions attempted are shown in Figure 56.

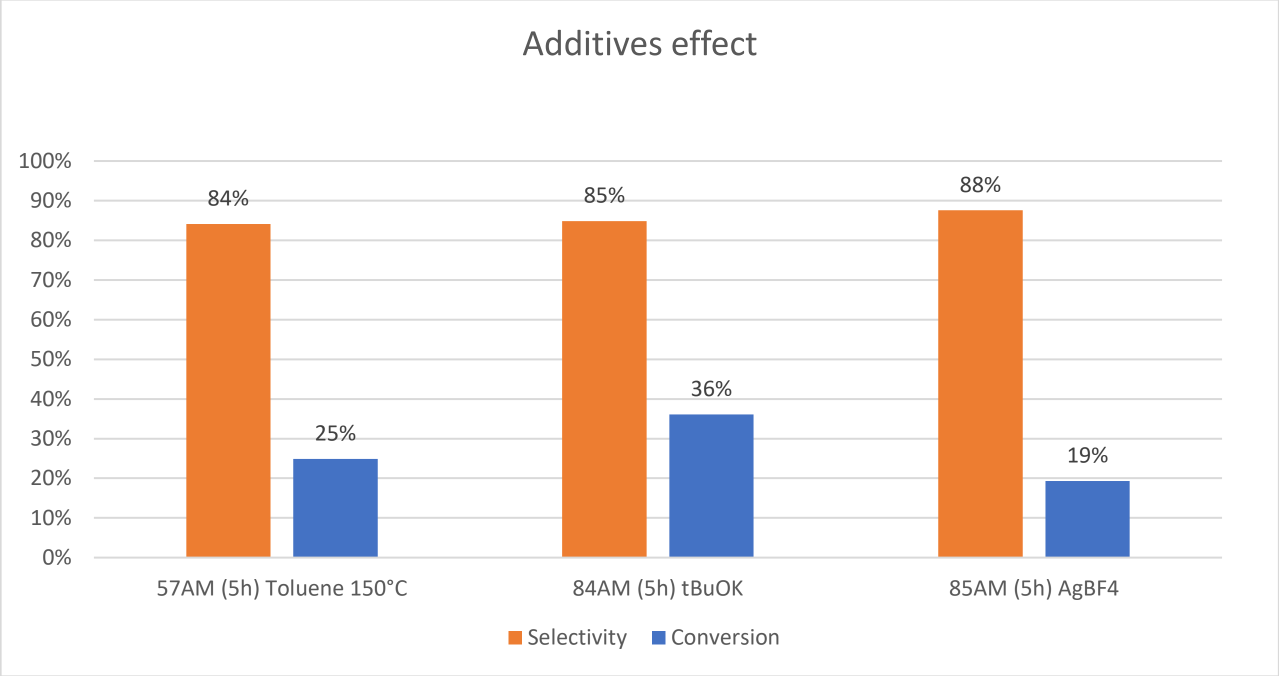
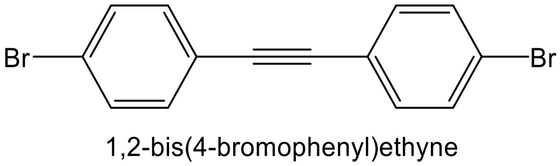


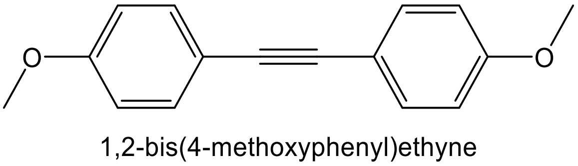
Figure 56 Effects of different additives on diastereoselectivity and conversion

On the left we have the reaction without additives and observing diastereoselectivity we can see that is not particularly affected by the presence neither of tBuOK nor $AgBF_4$. In contrast, potassium tert-butoxide seems to slightly enhance the conversion, while silver tetrafluoroborate does not affect particularly the performance of the catalyst.

Finally, the effect of substitution on the phenyls of the alkynes was studied. The diphenylacetylene was substituted with bis(4-bromophenyl)acetylene (Figure 57, compound **A**) and bis(4-methoxyphenyl)acetylene (Figure 57, compound **B**). It is expected that the introduction of electron-withdrawing or electron-donating groups may influence the results of the reaction.


1,2-bis(4-bromophenyl)ethyne

A


1,2-bis(4-methoxyphenyl)ethyne

B

Figure 57 EWG and EDG substituted diphenylacetylenes

Initially, bis(4-bromophenyl)acetylene (0.5 mmol) was used as a substrate and phenylsilane (0.75 mmol) was chosen as silylating agent. The reaction was performed using the optimized conditions (150°C in toluene for 5 hours), and 5%mol of catalyst. Similar reaction was perfomed using the substrate bis(4-methoxyphenyl)acetylene, that was previously synthesised following the procedure reported in literature[119] by a modified Sonogashira coupling reaction.

Conversions of the substrates were monitored by GC-FID using n-tetradecane as internal standard. The reactions after 5 hours showed in both cases higher conversions compared to the diphenylacetylene, showing that the substitution on the two phenyls improve the conversion (Table 5).

Table 5 Conversion of hydrosilylation on different substrates

Substrate	Conversion
Diphenylacetylene	25%
Bis(4-bromophenyl)acetylene	36%
Bis(4-methoxyphenyl)acetylene	38%

No particular effects of the influence of the difference between electron-withdrawal (EWG) or electron-donating (EDG) groups are observed in terms of the reactivity of the substrate toward hydrosilylation with catalyst **1**.

HYDROSILYLATION OF 1-OCTENE– PRELIMINARY RESULTS

Catalyst **1** was also tested in the hydrosilylation of aliphatic alkenes, using 1-octene as a benchmark substrate (Figure 58).

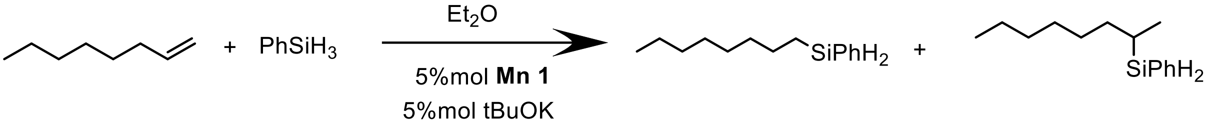


Figure 58 Hydrosilylation of 1-octene

Preliminary reactions were conducted at room temperature in diethyl ether (0.5 mL) with 5 mol % of catalyst, 5mol% of tBuOK and phenylsilane (1.10 mmol), using 1,3,5-trimethoxybenzene added as internal standard. The conversion of the alkene was monitored by ^{1}H-NMR. All the reactions were conducted overnight. No conversion was observed at room temperature, so the reaction was tested at higher temperatures. Unfortunately, the reaction does not proceed at 80°C, 100°C and 150°C.

HYDROSILYLATION OF CARBONYL COMPOUNDS IN PRESENCE OF LIGHT – PRELIMINARY RESULTS

As previously reported in the paragraph “Reduction of carbonyl groups: Ketones and Esters”, Royo et al. explored the use of the already cited complex **1** in the hydrosilylation of different carbonyl compounds. Since the outcome was promising, the group wanted to explore the catalytic performance of complex 1 using visible light. The effect of light was explored in the hydrosilylation of acetophenone with phenylsilane, at room temperature under blue visible light. Initially, the reactions were conducted in THF using 1 mol% catalyst **1**. The reaction mixture was stirred for 66 hours. The conversion of the substrate was monitored by GC-FID using n-tetradecane as internal standard. Unfortunately, the conversion under these conditions was very low (Table 6).

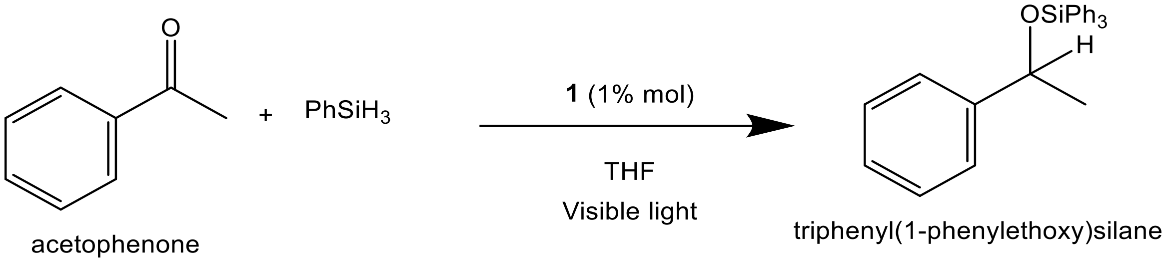


Figure 59 Scheme of hydrosilylation of acetophenone

Table 6 Conversion of acetophenone at room temperature

Entry	Conversion
1	7%

Interestingly, when this reaction is performed in the presence of Me_3NO (Figure 60), high conversion was obtained in 16 h (Table 7).

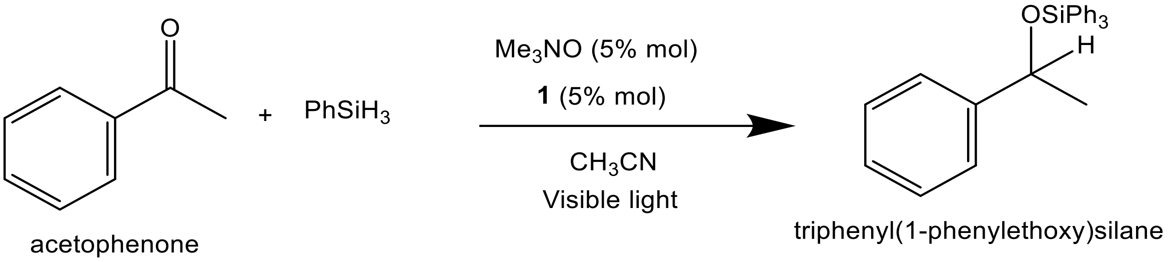


Figure 60 Scheme of hydrosilylation of acetophenone in presence of trimethylamine N-oxide

Table 7 Acetophenone conversion in presence of Me_3NO

Entry	Conversion
1	86%

Hydrosilylation of aldehydes in presence of light and Me_3NO

Since this catalyst is active in the hydrosilylation of ketones in presence of light and Me_3NO, we attempted the same reaction in presence of aldehydes using benzaldehyde (1 mmol) as reference substrate and phenylsilane as reducing agent (1,2 mmol) .The catalyst **1** loading was the same used with acetophenone (5% mol) and even in this case we checked the overnight conversion using n- tetradecane (0,5 mmol) as internal standard on a GC-FID (Figure 61).

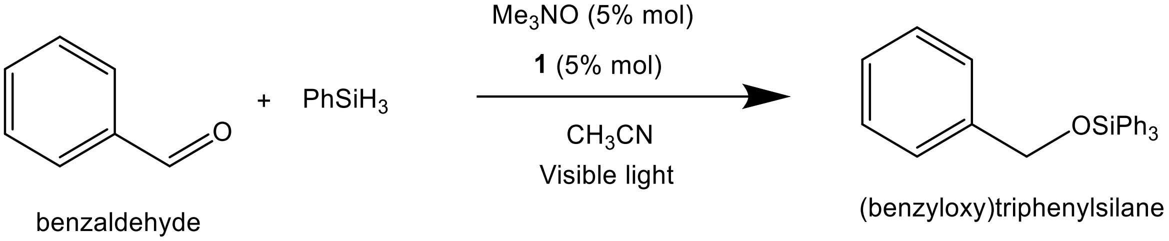


Figure 61 Hydrosilylation of benzaldehyde

The reaction occurred, as expected, with high conversion overnight (97%). We proceeded testing less activated carbonyl substrates such as esters

Hydrosilylation of esters in presence of light and Me_3NO

In this reaction we used methyl benzoate (1 mmol) as reference substrate because it has been already employed by Royo's group for the same reaction in a previous article[76]. The silane chosen is phenylsilane (1,2 mmol) and even in this case the internal standard for GC-FID analysis is n-tetradecane (0,5 mmol). The catalyst **1** loading was the same used with other carbonyls substrates (5% mol). Since this reaction has been already tested at 90°C with no light irradiation, the group wanted to see if it was possible to reduce the temperature to 25°C with the help of light (Figure 62). For this reason, the conditions are the same used in previous studies about the reduction of esters: air atmosphere and neat reaction[76].

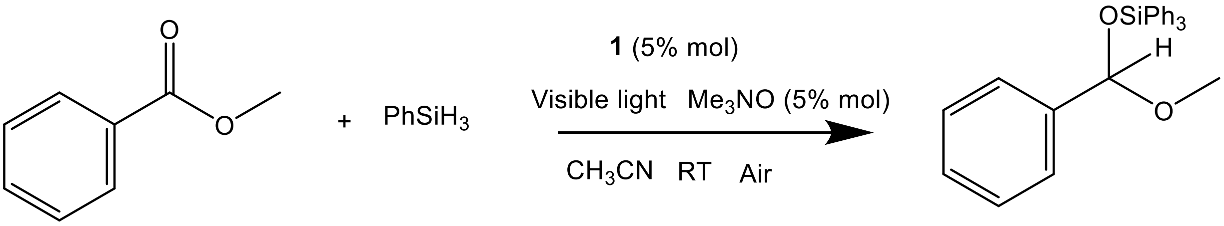


Figure 62 Hydrosilylation of methyl benzoate

The reaction was conducted overnight and then over the weekend to see if differences in the conversion were detectable (Table 8).

Table 8 Methyl benzoate conversion

Reaction time	Conversion %
Overnight	5%
3 Days	8%

No significant difference in the conversion was detectable. The ester group is less reactive than the ketone one so it might need some additive or an increase in the temperature. Further studies are proceeding in Royo's laboratory.

Investigation on the role of the additive trimethylamine N-Oxide

From the previous blanks experiments it is possible to conclude that the presence of light, catalyst and Me_3NO is required for the success of the reaction. In order to understand better the roles of the species in the reaction mixture, we planned different experiments.

*Investigation on the interaction between the catalyst **1** and Me_3NO*

Since it was expected that this additive could induce the release of a carbonyl on the complex, we set a stoichiometric reaction between **1** and Me_3NO (Figure 63).

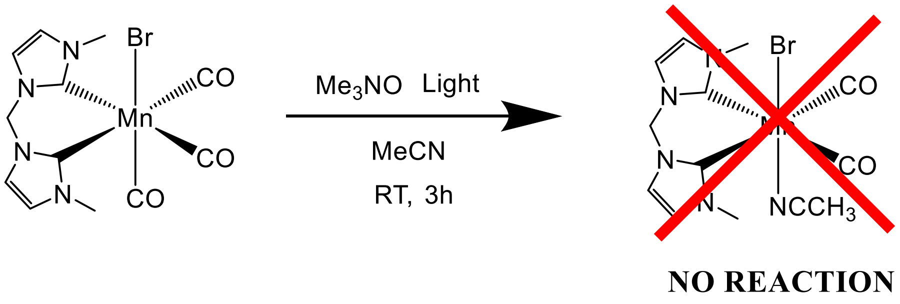


Figure 63 Stoichiometric reaction between catalyst and additive

At the end of the reaction a dark orange solid was obtained. FT-IR analysis of the latter did not show any difference in the pattern of the carbonyl region, meaning no reaction has occurred. We also did the same reaction in the same conditions for a longer time (overnight), but in this case the FT-IR showed the degradation of the complex.

HYDROBORATION OF DIPHENYLACETYLENE WITH PINACOLBORANE – PRELIMINARY RESULTS

The catalytic performance of catalyst **1** in hydroboration of alkynes was explored. The first attempt was conducted using 2 mmol of diphenylacetylene, pinacolborane (2,2 mmol) and the catalyst **1** (1% mol). The reaction mixture was stirred at room temperature for 30 minutes under nitrogen atmosphere. The conversion was then measured by GC-FID technique using n-tetradecane as internal standard. The reaction did not show any conversion, for this reason we modified the conditions. The first modification introduced was the adding of an additive: potassium tert-butoxide (1 mol%). We kept the same reaction time and temperature, but the conversion was not detectable. Increasing the temperature to 80°C do not significantly improve the conversion rate as shown in Table 11.

Table 9 Diphenylacetylene conversion over time

Entry	Time (h)	Conversion %
1	1	11
2	2	11
3	3	12
4	4	12

CONCLUSIONS

Complex **1** has been synthetized and characterised by different techniques involving ^{1}H-NMR, ^{13}C-NMR, and FT-IR. Subsequently, it has been employed as a catalyst in the hydrosilylation of internal alkynes showing to be active in the reduction of diphenylacetylene. The complex shows a good diastereoselctivity (84%) promoting the formation of the E-diastereoisomer and surprisingly. In contrast to the previous study involving manganese, no hydrogenated by-products were detected. The reaction reaches the maximum conversion (25%) in 5 hours and the optimised temperature was found to be 150°C. A decrease in the temperature led to a significant decrease in substrate conversion, but no significant differences were found in the diastereotopic distributions of the products.

The best performing solvent was toluene or apolar non-coordinating solvents as petroleum ether. Acetonitrile, a strong coordinating solvent, showed a decrease in the diastereoselctivity and in the conversion, while dichloromethane increased the conversion and inverted the diastereotopic distribution on the two isomers favouring the product **2Z**.

Another parameter studied was the presence of different additives. Laurylperoxide, an additive already used in a previous study[116], resulted to be a stoichiometric reagent that creates a radical mechanism where the catalyst **1** is not involved, favouring the production of the diastereoisomer **2Z**.

Potassium tert-butoxide, added in catalytic amounts, showed to increase the conversion of the substrate reaching 36% while keeping diastereoselectivity high (85%). Silver tetrafluoroborate, on the contrary, seems not to affect neither diastereoselectivity nor conversion.

The use of differently substituted diphenylacetylenes with EWG or EDG groups demonstrated that their presence helps the reaction to happen. Bis(4-bromophenyl)acetylene and bis(4-methoxyphenyl)acetylene converts in larger extend than the unsubstituted diphenylacetylene but no relevant differences can be seen depending on the EWG or EDG group nature.

Regarding the hydrosilylation of terminal alkynes, the complex did not show activity in the under the conditions tested. Since this part of the work furnished only preliminary results, subsequent studies, in order to achieve the conversion of the substrate, need to be conducted. New catalytic reaction could test different reaction conditions. Since manganese has not been used frequently in this important reaction, this kind of studies can open new branches of research leading to industrially relevant results.

In concern to hydrosilylation of carbonyl substrates in presence of light, the catalyst was found to be able to activate ketones and aldehydes in presence of phenylsilane and Me_3NO, reaching high conversions overnight. Esters are found to be unreactive in the conditions tested in this work. The role of the additive is still under investigation and all the reactions performed with light in this work are at the early preliminary stages.

Unfortunately, regarding the hydroboration of alkynes, no more studies on this reaction were performed due to the lack of time. However, it is possible to observe that manganese catalyst **1** is active and new studies could be performed. Manganese could provide a new class of Earth-abundant transition metal that can be applied for this reaction

EXPERIMENTAL PART

GENERAL INFORMATION

All reactions were carried out under nitrogen or argon atmosphere unless otherwise reported. All the reagents were used as received without further purification unless otherwise noted. The synthesis of the ligand bis-NHC^{Me} (bis-N-methylimidazolium = 1,1′-methylene-3,3′-di-methyllimidazolium dibromide) and of the complex **1** were carried following the reported procedures, already published in previous articles[25], using Schlenk techniques and dry solvents. The manipulation of the complex **1** was carried under reduced light conditions. All ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance II 500 MHz, on a Varian Mercury Plus VX 400 (^{1}H, 399.9; ^{13}C, 100.6 MHz) or on Varian Inova 600 (^{1}H, 599.7; ^{13}C, 150.8 MHz) spectrometers at 298 K ;chemical shifts were referenced internally to residual solvent peaks. GC-FID analysis were performed with a Thermo Scientific Trace 1300 Gas Chromatograph with a flame ionization detector (FID) using a TR-5MS column (L x I.D 30m x 0,25mm, average thickness 0,25µm) or on a Agilent Technologies 7890A GC system with a flame ionization detector (FID) using a TR-5MS column (L x I.D 15m x 0,32mm, average thickness 1µm). Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum Two FT-IR spectrophotometer. ESI-MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in CH_3CN

SYNTHESIS OF THE LIGAND BIS-N-METHYLIMIDAZOLIUM

In a dried Schlenk tube 1,91mL (28,8 mmol) of 1-methylimidazole and 0,85 mL (12,11 mmol) of Dibromomethane were dissolved in 25 mL of acetonitrile and stirred at 110°C for 72 hours. The solution was filtered and the white solid washed with diethylether (3 x 25 mL). The solid, after vacuum drying was characterized with ^{1}H-NMR.

^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9,43 (s, 2H, CH_{imid}), 8,00 (m, 2H, CH_{imid}), 7,79 (m, 2H, CH_{imid}), 6,68 (s, 2H, NCH_2N), 3,88 (s, 6H, NCH_3)

SYNTHESIS OF THE COMPLEX 1

$MnBr(CO)_5$ (0,3522g 1,3 mmol) was dissolved in 25 mL of anhydrous THF at room temperature. Potassium tertbutoxide (0,2680g 2,4 mmol) was added in the mixture, followed by 1,1'-methylene-3,3'-di-methylimidazolium dibromide (0,34g 1,0 mmol). The mixture was heated at 60°C for 16h under stirring. All the solvent was removed under vacuum and the residue was washed with Et_2O (4 x 20 mL) and then dissolved in dichloromethane (100mL).

This solution was washed with 100 mL of water and the organic extract dried with anhydrous sodium sulfate. The organic solution was concentrated to dryness and the residue dried under vacuum to yield a yellow powder, which was characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR spectroscopy and HRMS ESI-MS. Mass obtained 0,2325g, yield 45%. Crystals of the complex suitable for X-ray diffraction analysis were obtained thanks to layering technique using a dichloromethane /hexane double layer.

^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 7,56 (s,2H, CH_{imid}), 7,43 (s,2H, CH_{imid}), 6,61(d, 1H, NCH_2N), 6,03(d, 1H, NCH_2N), 3,97 (s, 6H, NCH_3)
^{13}C-NMR (150.8 MHz, DMSO-d_6, 25°C): δ ppm 220 (*C*O), 189 (Mn-$C_{carbene}$), 124 ($CH_{\text{imidazole}}$), 122 ($CH_{\text{imidazole}}$), 62 (NCH_2N), 38 (NCH_3);
IR(CH_2Cl_2): ν 2009 (CO), 1925 (CO), 1886 (CO) cm^{-1}

GENERAL PROCEDURE FOR HYDROSILYLATION OF ALKYNES

In a closed Schlenk tube vial were dissolved 0,5 mmol of alkyne, 0,75 mmol of silane and 0,50 mmol of n-tetradecane as internal standard in 0,25 mL of solvent. The catalyst **1** was added in catalytic amount 0,025mmol (5% mol). The reaction mixture was stirred overnight at 150°C under nitrogen atmosphere. The conversion was then measured by GC-FID technique using calibration curve of the alkyne using n-tetradecane as internal standard.

GC Temperatures

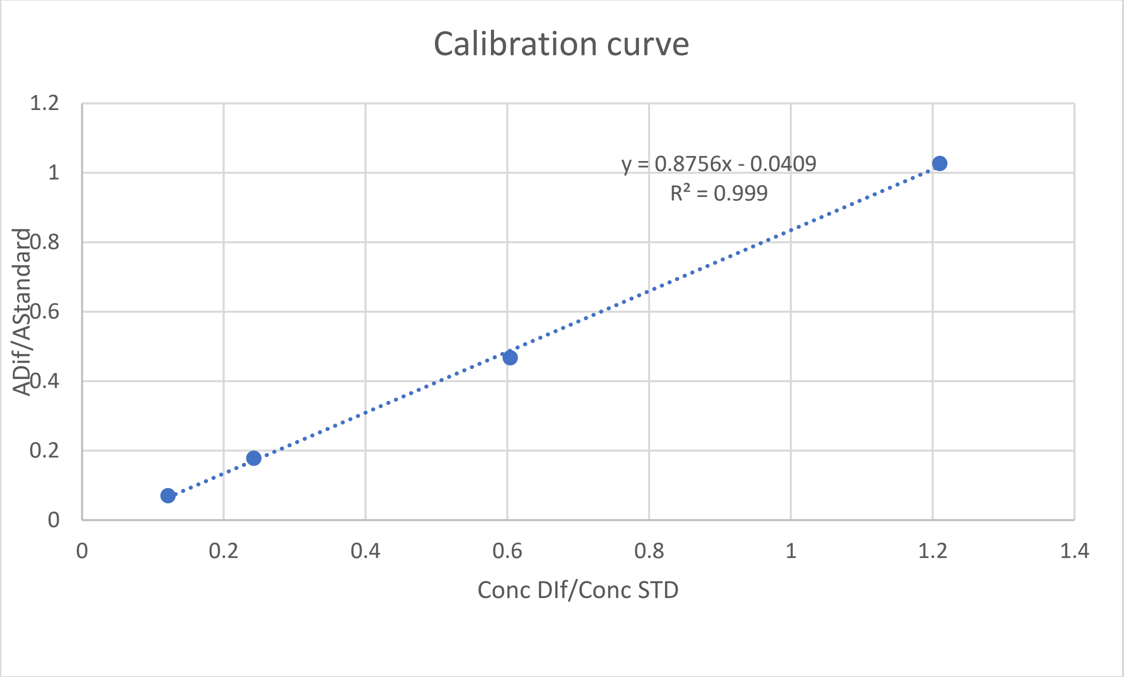
Initial Temperature: 80°C

Initial Hold Time: 2 min

Ramp 1: 15°C/ min

Ramp 1 Final Temperature: 280°C

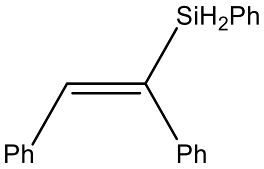
Final Hold Time: 10 min



Silylated alkenes products characterization

Three reaction mixtures were collected together, dried over silica and put on the head of a chromatographic column containing silica gel. The colum was eluted with a mixture composed by petroleum ether-EtOAc 40:1. After the separation, the fractions containing the two products in major quantities were united and all the volatiles were removed under vacuum obtaining a transparent and oily liquid. The products were diluited with acetonitrile and injected in an HPLC system using a C-18 column in inverse phase, eluting with a solution of 80/20 of azeotropic mixture MeCN- water/ water. Collecting at different times the two diastereoisomers and after the solvents were removed, it had been possible to obtain them pure. Two transparent oily products were visible at the bottom of the flask. We then subjected the two products to ^{1}H-NMR, ^{13}C-NMR and NOESY experiments.

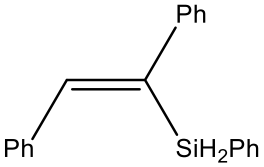
(E)-(1,2-diphenylvinyl)(phenyl)silane **2E**



^{1}H-NMR (600MHz, CD_3CN) δ 7.61 (d,2H), 7.44 (m, 1H), 7.37 (m, 2H), 7.27 (m, 2H), 7.22 (m, 1H), 7.20 (m, 1H), 7.15 (m, 2H), 7.05 (m, 4H), 4.77 (s, 2H, SiH_2)

^{13}C-NMR (MHz, CD_3CN) δ 143.5, 142.25, 139.25, 137.8, 136.46, 131.79, 131.05, 130.28, 129.71, 129.12, 128.76, 128.67, 128.63, 127.37

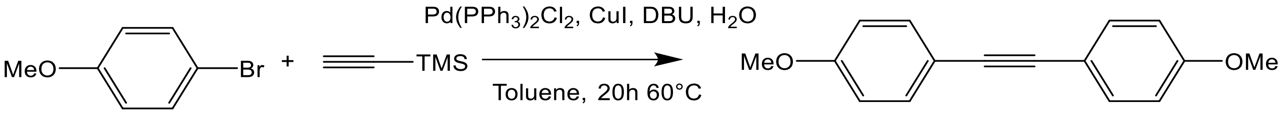
(Z)-(1,2-diphenylvinyl)(phenyl)silane **2Z**



^{1}H-NMR (600MHz, CD_3CN) δ 7.67 (s,1H), 7.53 (m, 2H), 7.43 (m, 4H), 7.27 (m, 2H), 7.40 – 7.30 (m, 8H), 7.25 (m, 1H), 4.77 (s, 2H, Si*H*$_2$)

^{13}C-NMR (MHz, CD_3CN) δ 148.79, 146.12, 139.60, 137.96, 136.23, 132.07, 130.81, 129.65, 129.44, 129.14, 129.12, 129.05, 128.89, 128.26, 127.77

SYNTHESIS OF BIS(4-METHOXY)PHENYLACETYLENE



In a 150 ml Schlenk tube is placed under vacuum and purged with argon then charged with $PdCl_2(PPh_3)_2$ (135 mg, 6 mol%), CuI (60,8 mg, 10 mol%) and 4-bromoanisole (1 equiv, 3,2 mmol). While stirring, dry toluene (16 ml, starting material is 0,20M) is added by syringe. 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) (2,864 mL, 6 equiv) is then added by syringe under argon. Distilled water (22,96 µL, 40 mol%) is added and immediately followed by ice-chilled trimethylsilylethynylene (220 µL, 0.50 equiv). The reaction stirred at 60°C in mineral oil bath for 20 hours covered in aluminium foil protected from light. At the end of the reaction, the mixture is cooled to room temperature and partitioned in ethyl ether and distilled water (100 mL each). The organic layer is washed with 10% HCl (3X 75 mL), saturated aqueous NaCl (1X 75 mL), dried over $MgSO_4$, and the solvent removed in vacuo. The crude dark brown product is purified by silica gel column chromatography using 95:5 exane/ethylacetate eluent mixture. The product was obtained as a crystalline white solid and characterised with ^{1}H-NMR technique.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 4H), 7.63 (d, 4H), 2.62 (s, 6H);

PROCEDURES FOR HYDROSILYLATION OF 1-OCTENE

In a closed Schlenk tube vial were dissolved 1 mmol of 1-octene, 1,10 mmol of phenylsilane and 0,50 mmol of 1,3,5-trimethoxybenzene as internal standard in 0,5 mL of diethyl ether. The catalyst **1** was added in catalytic amount 0,05mmol (5% mol) followed by tBuOK (5% mol). The reaction mixture was stirred overnight at room temperature under inert atmosphere. At the end of the reaction the crude was passed through silica gel and diluted with ethyl ether. Other different temperatures were also tested in this reaction: 80°C, 100°C and 150°C following the same procedure. The conversion of the substrate was monitored by ^{1}H-NMR technique.

PROCEDURES FOR HYDROSILYLATION OF KETONES WITH LIGHT

Hydrosilylation in absence of additives

In a small vial (5 mL), acetophenone (0,117 mL, 1 mmol) was dissolved in 0,4 mL of THF and mixed with phenylsilane (0,153 mL, 1,2 mmol) under nitrogen atmosphere. Complex **1** was then added in catalytic amount (0,01mmol, 1 mol%), the reaction was stirred overnight at room temperature placed under visible light and the conversion was then measured by GC-FID technique. The following GC method was applied for all the tests involving acetophenone, benzaldehyde and methyl benzoate

GC Temperatures

Initial Temperature: 60°C

Initial Hold Time: 2 min

Ramp 1: 20°C/ min

Ramp 1 Final Temperature: 300°C

Final Hold Time: 1 min

Hydrosilylation in presence of Me_3NO as additive

In a Schlenk tube were dissolved 0,117 mL (1 mmol) of acetophenone and 5,57 mg (5% mol) of Me_3NO in 0,4 mL of MeCN. The mixture was then added with 0,153 mL of phenylsilane (1,2 mmol). The catalyst **1** was then added in catalytic amount 0,05mmol (5% mol) . The reaction mixture was placed under visible light and stirred overnight in inert atmosphere. The conversion was then measured by GC-FID technique.

PROCEDURE FOR HYDROSILYLATION OF BENZALDEHYDE WITH LIGHT

In a vial were dissolved 0,102 mL (1 mmol) of benzaldehyde and 5,57 mg (5% mol) of Me_3NO in 0,4 mL of MeCN. The mixture was then added with 0,153 mL of Phenylsilane (1,2 mmol). The catalyst **1** was then added in catalytic amount 0,05mmol (5% mol). The reaction mixture was placed under visible light and stirred overnight in inert atmosphere. The conversion was then measured by GC-FID technique.

PROCEDURE FOR HYDROSILYLATION OF METHYL BENZOATE WITH LIGHT

In a clean Schlenk tube were dissolved 0,125 mL (1 mmol) of methyl benzoate and 5,57 mg (5% mol) of Me3NO in 0,4 mL of MeCN. The mixture was then added with 0,153 mL of phenylsilane (1,2 mmol). The catalyst **1** was then added in catalytic amount 0,05mmol (5% mol). The reaction mixture was placed under visible light and stirred overnight in inert atmosphere. The conversion was then measured by GC-FID technique.

PROCEDURES FOR HYDROBORATION OF ALKYNES

Method A

In a clean vial under nitrogen atmosphere were dissolved 2 mmol of diphenylacetylene, potassium ter-butoxide (1% mol) and 2,2 mmol of pinacol borane in 1 mL of THF. The catalyst **1** was then added in catalytic amount 0,01mmol (1% mol) and the mixture was stirred for 30 minutes at room temperature in absence of light under inert atmosphere. At the end of the reaction the mixture was quenched with 2mL of CH_2Cl_2 and passed through celite. The conversion was then measured by GC-FID technique. The following GC method was applied for all the tests involving the hydroboration of diphenylacetylene:

GC Temperatures

Initial Temperature: 80°C

Initial Hold Time: 2 min

Ramp 1: 15°C/ min

Ramp 1 Final Temperature: 280°C

Final Hold Time: 10 min

Method B

In a clean vial under nitrogen atmosphere were dissolved 2 mmol of diphenylacetylene and 2,2 mmol of pinacol borane in **1** mL of THF. The catalyst 1 was then added in catalytic amount 0,01mmol (1% mol) and the mixture was stirred for 30 minutes at room temperature in total absence of light under inert atmosphere. At the end of the reaction the mixture was quenched with 2mL of CH_2Cl_2 and passed through celite. The conversion was then measured by GC-FID technique.

Method C

In a clean vial under nitrogen atmosphere were dissolved 2 mmol of diphenylacetylene, potassium ter-butoxide (1% mol) and 2,2 mmol of pinacol borane in 1 mL of THF. The catalyst **1** was then added in catalytic amount 0,01mmol (1% mol) and the mixture was stirred for 4 hours at room temperature in total absence of light under inert atmosphere. At the end of the reaction the mixture was quenched with 2mL of CH_2Cl_2 and passed through celite. The conversion was then measured by GC-FID technique.

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