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Synthesis of Manganese Organometallic Complexes

Tesi di laurea sperimentale

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Abstract (It)

Il presente lavoro di tesi si inserisce in un progetto di ricerca volto alla sintesi di nuovi complessi di metalli di transizione per lo sviluppo di catalizzatori da impiegare in reazioni di catalisi omogenea. In particolare il mio progetto si è concentrato sulla sintesi di complessi organometallici di Manganese con leganti carbenici N-eterociclici (NHC). La scelta dei leganti è stata effettuata in modo tale da poter avere leganti chelanti NHC di tipo MIC (mesoionic carbene) sintetizzati tramite cicloaddizione tra un alchino ed un azide catalizzata da rame (CuAAC) e N-alchilazione. Lo studio di questi complessi a base di manganese è ancora tutt'oggi agli albori, leganti NHC vengono molto utilizzati grazie alla possibilità di variarne le proprietà steriche ed elettroniche e alla possibilità di formare legami forti con quasi tutti i metalli. Il manganese è stato scelto poiché un elemento abbondante, poco tossico e poco costoso.

Abstract(En)

The present thesis work is part of a research project aimed at the synthesis of new transition metal complexes to be used in homogeneous catalysis reactions. In particular my project focused on the synthesis of manganese organometallic complexes with N-heterocyclic carbene ligands (NHC). The choice of ligands was carried out to have NHC chelating ligands of the class of MIC (mesoionic carbene). These ligands are synthesized by cycloaddition between alkyl and azide with a copper-catalyzed reaction (CuAAC) and N-alkylation in order to obtain MIC after deprotonation. The study of these manganese-based complexes is still in its infancy today, NHC ligands are widely used thanks to the possibility of varying their steric and electronic properties and the possibility of forming strong bonds with almost all metals. The choice of manganese was made because is an abundant, low-toxic and inexpensive element.

Summary

Introduction

Mn complexes as catalysts

Catalysis plays a key role in the development of modern environmental friendly and atom-economical synthetic methods. Whereas major advances in the area of homogeneous catalysis reside on the use of noble transition metal complexes. The search for new alternatives based on cheap and less toxic first row transition metals has lately received considerable attention from both academic and industrial chemistry communities, and is becoming an emerging trend of the 21th century. In this context, manganese is a particularly attractive candidate because of its natural abundance (the 3rd transition metal in the earth crust after iron and titanium) and biocompatibility, which is particularly valuable for the pharmaceutical industry. Actually, according to a report of the European Medicine Agency, manganese and copper are considered as metals of low safety concern[1]. Manganese coordination compounds bearing porphyrin[2][3], phthalocyanine[4], salen[5], or polyamine[6] ligands have been extensively used in C–H bond oxidation and alkene epoxidation processes. Although organometallic manganese complexes have received much less attention in catalysis, recent intense research efforts in this area are at the point to invert such a tendency. In fact, the number of annual publications on Mn catalysis have significantly grown during the last years, namely in catalytic processes such as direct C–H activation processes[7], hydrosilylation of carbonyl compounds[8], electrochemical CO_2 reduction[9], and hydrogen generation[10].

N-Heterocyclic carbenes (NHCs)

N-heterocyclic carbenes (NHCs) are defined as heterocyclic species containing a carbene carbon and at least one nitrogen atom within the ring structure. The NHCs were introduced by the synthesis and isolation of the complexes with mercury and chromium by Öfele[11] and Wanzlick[12] in 1968. For a long time, carbenes, were considered to be very reactive and short lived molecules that could not be isolated until the publication of a research on stable carbene and its isolation achieved by Arduengo in 1991[13] (Fig.1). Later on studies on this kind of molecule rapidly increased.

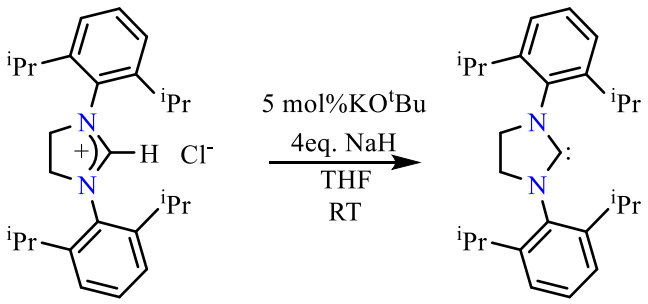


Fig. 1 Synthesis of first N-heterocyclic carbene via deprotonation of an imidazolium salt

The research was focused in particular on the NHCs carbene, especially in organometallic chemistry, because of the ease of synthesis, functionalization, and isolation of NHCs, and the success in metallation with a large variety of hard/soft metals that makes NHCs excellent ligands with similarities to phosphines. NHCs have the ability to coordinate strongly to a wide variety of metals throughout the periodic table with their strong sigma donor ability, which creates highly stable metal NHC complexes. This property also make NHCs bind to both low- and high-oxidation state transition metals. The unusual stability of NHC complexes is in part a result of shielding by sterically demanding substituents on the ring. The most studied NHCs are the five membered ring, but six and seven membered rings are also known. However, much more important is the electronic stabilization

Electronic properties:

- ***Carbenes***

Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons in its valency shell [14][15]. The linear (as an extreme case) and the bent geometries of carbene structure are related to the different possible hybridization of the carbene carbon atom (Fig.2). The sp-hybrid orbitals, coupled with two energetically degenerated p orbitals, and the sp^2-hybrid orbitals (δ orbitals), coupled with a p orbital (pπ orbital), promote the linear or bent geometry, respectively.

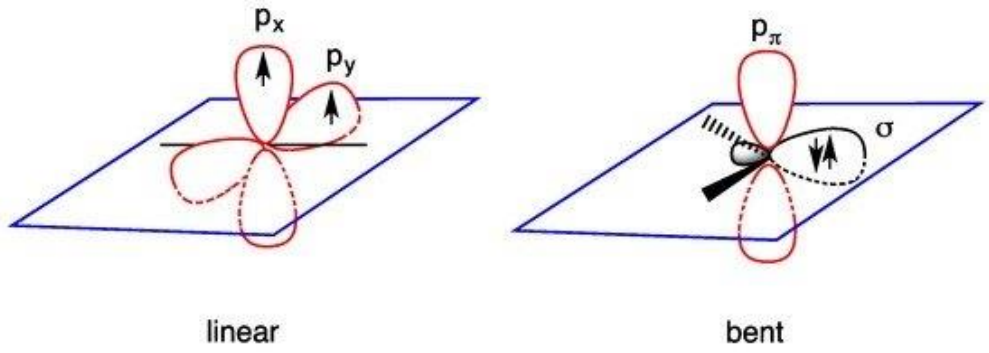


Fig. 2 Geometry at the carbene carbon atom: linear and bent. Arrows: electrons.[16]

The reactivity and the properties of carbenes (with bent geometry) are strongly affected by the arrangement of the two nonbonding electrons (triplet or singlet carbenes). In the triplet ground state, the two nonbonding electrons occupy the two empty orbitals δ and pπ with parallel or antiparallel spin orientation; in the singlet ground state, the two nonbonding electrons occupy only the empty δ orbital as a lone pair, being empty the pπ orbital.

- ***N-Heterocyclic Carbenes (NHCs)***

N-Heterocyclic carbenes (NHCs) are neutral species containing a carbene carbon and at least one adjacent nitrogen atom within a ring structure. In

addition to the nitrogen atom, NHCs could be marked by the presence of other heteroatoms (sulfur and oxygen). As regards the NHC electronic configuration, in contrast to classic carbenes, NHCs such as IAd exhibit a singlet ground-state electronic configuration with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) best described as a formally sp^2-hybridized lone pair and an unoccupied p-orbital at the C^2 carbon, respectively (Fig. 3b). The adjacent electron-withdrawing and p-electron-donating nitrogen atoms stabilize this structure both inductively by lowering the energy of the occupied s-orbital and mesomerically by donating electron density into the empty p-orbital. The cyclic nature of NHCs also helps to favour the singlet state by forcing the carbene carbon into a bent, more sp^2-like arrangement. This ground-state structure is reflected in the C^2-N bond lengths (1.37A˚) observed in IAd, which fall in between those of its corresponding imidazolium salt (IAdH1, 1.33A˚)[13] and its C^2-saturated analogue (IAdH2,1.49A˚)[14], meaning that the C^2-2 nitrogen bonds possess partial double bond character.

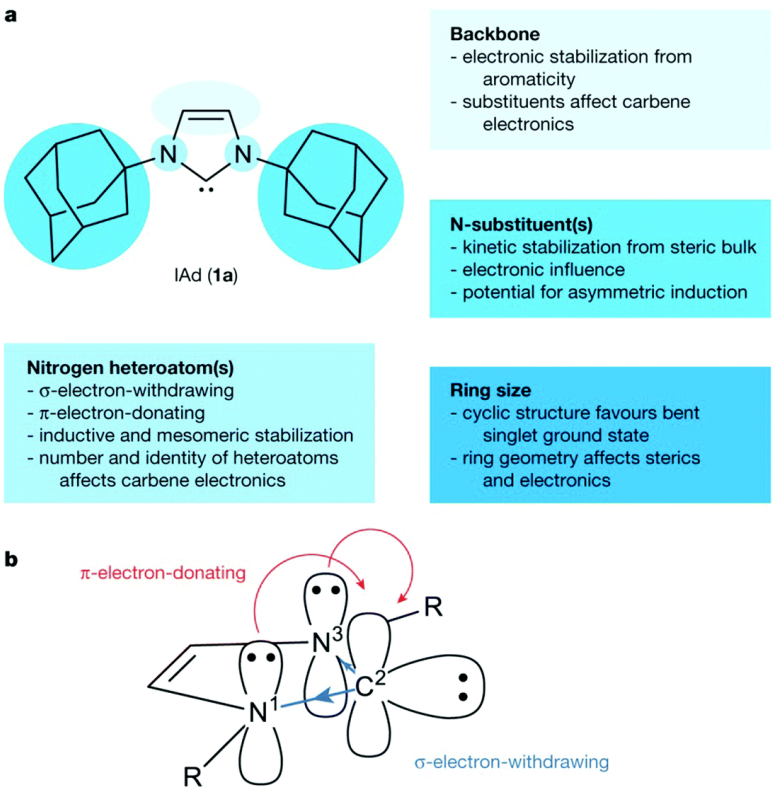


Fig.3 Structural features of NHCs. a, General structural features of IAd b, Ground-state electronic structure of imidazol-2-ylidenes.[17]

NHCs can be modified in different positions to finely tune their steric and electronic properties. For instance, the substituents bound to the nitrogen sterically hinder the dimerization of the carbene species to its corresponding olefin, whereas modifications of the backbone influence the carbene electronics.

NHC coordination with Metals

Initially it was thought that N-heterocyclic carbenes were exclusively σ-donor ligands, then numerous theoretical and experimental studies, have shown a partial π character in the M-NHC bond.

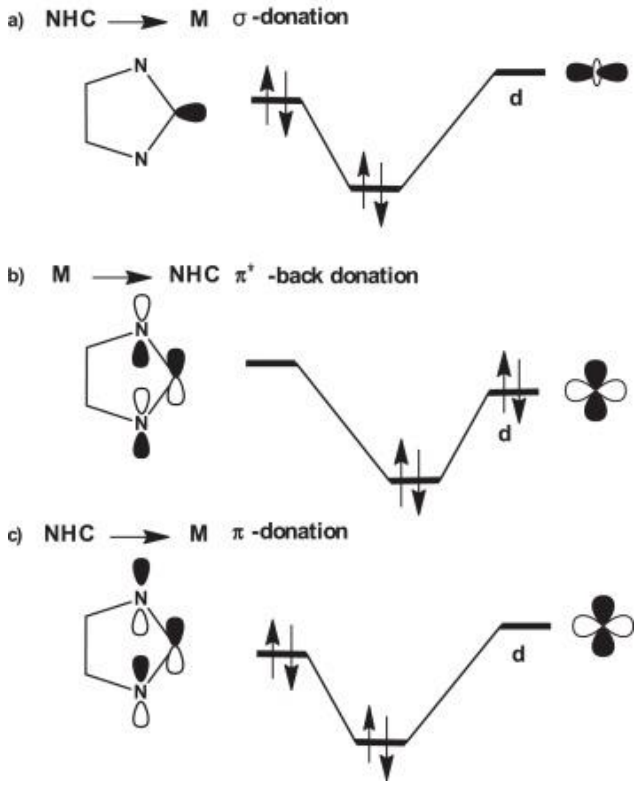


Fig. 4 Interaction M-NHC[158]

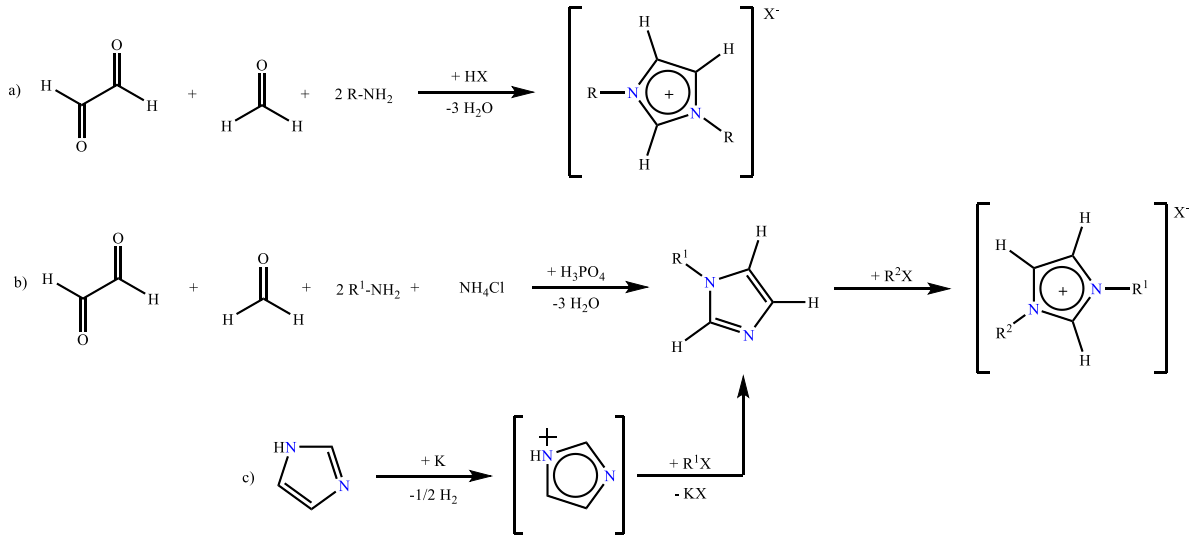
As shown in the figure (Fig.4), in fact, in addition to the donation σ from the sp^2 orbital of the carbene to the empty d orbitals of the metal (a) there is a back donation π from the full d orbitals of the metal to the NHC (b) and a π donation from the NHC to the metal centre (c). The contribution of the π interaction depends on the type of NHC and can be more or less significant, although generally the coordination of the carbene to the metal is indicated with a single bond rather than a double bond, while the π contribution remains limited to delocalization in the heterocyclic ring. This representation best reflects the experimental data concerning the possibility of rotation around the M-NHC bond[18]. The strong σ-donor character of the NHCs allows the establishment of thermodynamically stable interactions with the transition metals, as evidenced by the high dissociation energies of the M-NHC bonds which are higher than the similar phosphine complexes.[19]

In addition to this, the great success of NHCs as ligands is due to the possibility of modulating their steric and electronic properties, simply by changing the substituents on the nitrogen atoms of the ring. The lateral substituents, responsible for the steric hindrance, are not directly linked to the carbene carbon

which coordinates to the metal and therefore have no substantial effects on the electronic density of the complex, which is mainly influenced by the nature of the heterocyclic ring. This allows to independently adjust the electronic and steric properties of the NHC, as opposed to what happens in the case of phosphines, where the substituents are linked to the phosphorus atom coordinated with the metal centre.[20] The (NHC)-metal complexes has boosted catalyst performance in many domains, in particular C–C cross coupling, transfer hydrogenation, oxidation, carbon–heteroatom bond formation and polymerization reactions.

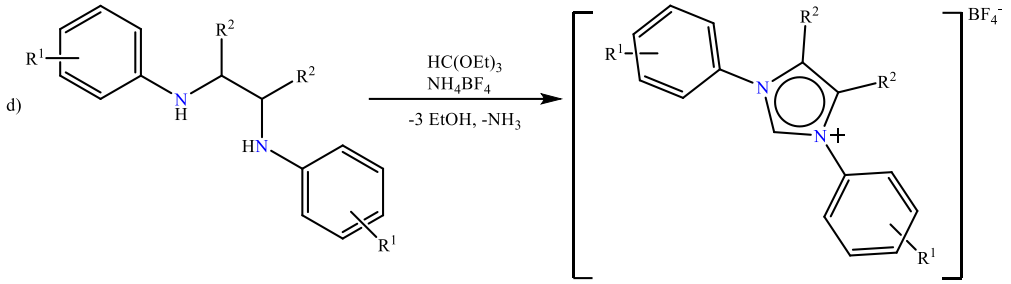
Synthesis of NHCs precursors

Most easily available stable carbenes derived from imidazole, not least because numerous imidazolium precursor compounds can be made along various reliable routes. The one-pot synthesis starting from glyoxal, primary amine, and formaldehyde is straightforward (Scheme 1 a), its variation (Scheme 1 b) allows unsymmetrically N-substituted derivatives to be made, while in another route (Scheme 1 c) the imidazolide anion is alkylated by reactive alkyl-/aryl halides (or -triflate derivatives).



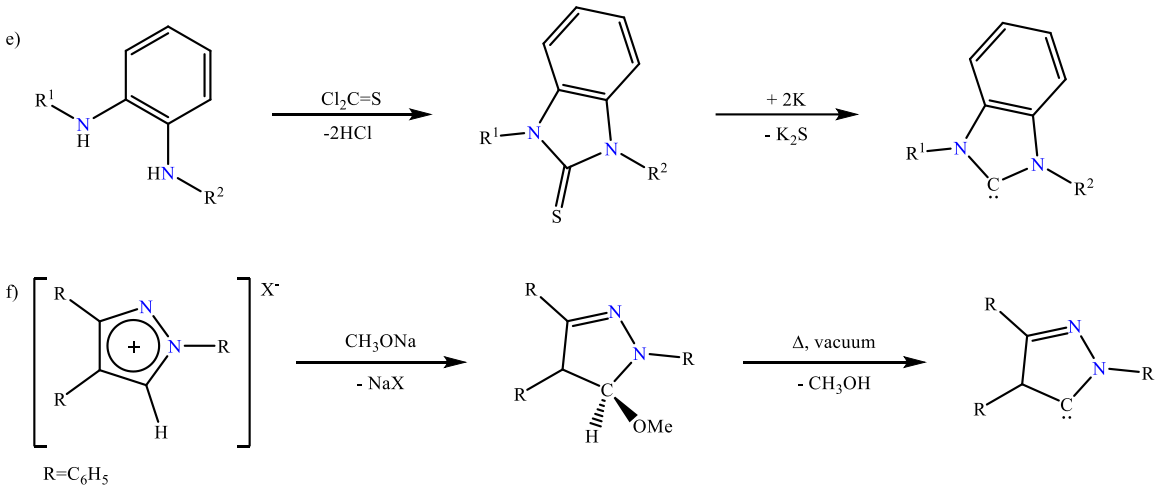
Scheme 1(a,b,c) Convenient synthetic routes to imidazolium salts and imidazolin(2)-ylidenes derived therefrom.

The orthoformiate route (Scheme 2d) converts the easily accessible 1,2-diamines (e.g. from Pd-catalyzed Buchwald coupling) into the aryl-substituted imidazolium salts.



Scheme 2(d) Convenient synthetic routes to imidazolium salts and imidazolin(2)-ylidenes derived therefrom.

The heterocycle synthesis according to Scheme 1a and b was previously mentioned.[21][22][23]. The desulfurization of the cyclic thiourea derivatives (Scheme 3e) depends on relatively drastic conditions but works well in many cases, for example, benzimidazolin-2- ylidenes from the corresponding 2-thiones[24]. Vacuum thermolysis of methoxy derivatives (Scheme 3f) yields carbenes in good yields, as well, for example, 4,5-dihydro-1H-1,2,4- triazol-5-ylidenes.[25]

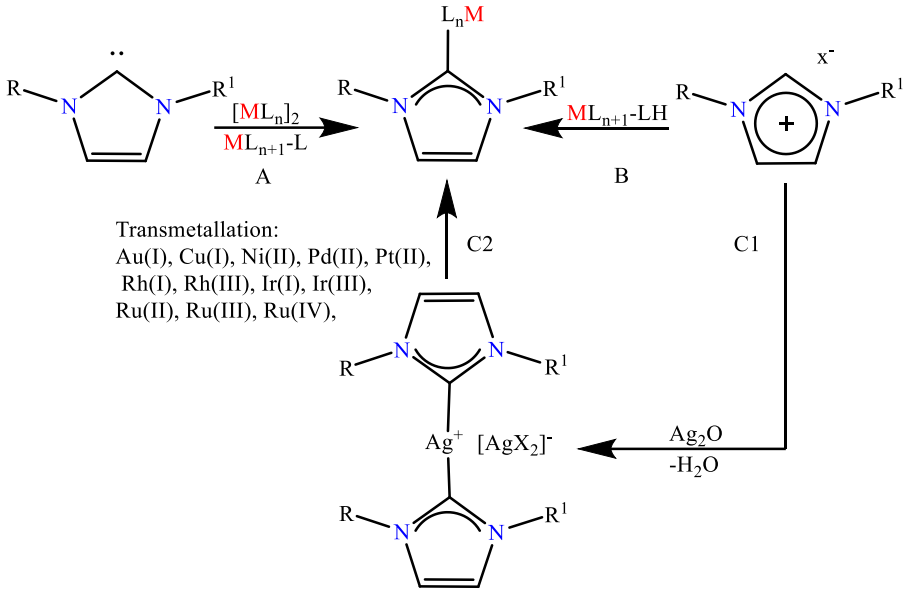


Scheme 3(e,f) Convenient synthetic routes to imidazolium salts and imidazolin(2)-ylidenes derived therefrom.

Alternatively, NHCs can be derived from a large variety of natural molecules that contain an imidazole moiety (biological molecules like histamine, histidine and urocanic acid as imidazolium salts precursors).

Synthesis of NHC complexes

Preparation of complexes between NHCs and metal can be achieved in different ways.(Scheme 4) [26][27]



Scheme 4. Synthetic pathway for NHC complexes

1) Salt is deprotonated by a strong base then free-carbene coordinates to a metal (method **A**)

2) A metal precursor with a basic ligand is used (method **B**). In this case ligand acts as the base of routes A and leaves the complex;

3) Direct reaction of salt with Ag_2O leads to Silver-NHC complexes (method **C1**)

4) Silver-NHC complexes are used as transmetallating agents (method **C2**). Different metal precursor can be used with silver-NHC complexes.[28]

More complex and less used routes are also available.[10]

Mesoionic carbenes (MICs)

Mesoionic carbenes (MICs) are a class of N-heterocyclic carbenes (NHCs). In MICs the canonical resonance structures with the carbene depicted NHCs cannot be drawn without adding additional charges. To differentiate various type of carbene with less heteroatom stabilization new nomenclature has been created. Imidazolylidenes bound via C4/5 rather than C2 were initially termed abnormal carbenes,[29] as they were not binding through their normal position. Later, this definition has been expanded to any N-heterocyclic-carbene that cannot be represented by a neutral uncharged covalent structure[30]. As a common feature, these “abnormal” carbene complexes are represented by a dipolar 5- or 6-membered heterocycles in which the positive and negative charge are at least partially delocalized and which cannot be represented by a single resonance form (Fig.5). These properties are congruent with the IUPAC definition of mesoionic compounds,[31] and therefore, these carbenes should be termed mesoionic carbenes (MICs).

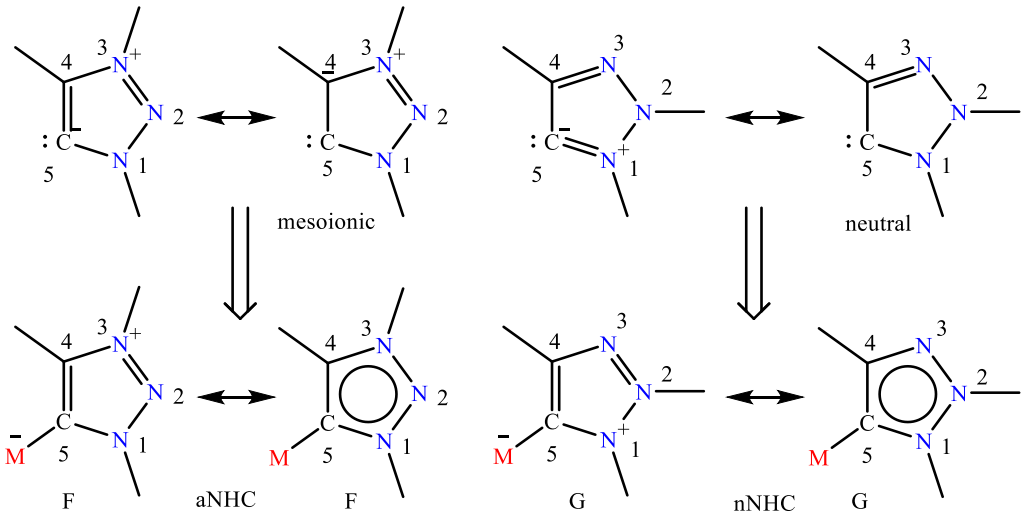


Fig.5 Resonance structure of aNHC and nNHC

Another type of rationalisation on NHCs is focusing on the presence or absence of heteroatoms adjacent to the carbene centre. Thus, N-heterocyclic carbenes without any directly carbene-linked heteroatom are termed remote carbenes. This division of (none) vs remote carbenes is orthogonal to that of (none) vs mesoionic/abnormal carbenes, and there are remote normal as well as remote abnormal NHCs and also non-remote normal and abnormal/mesoionic carbenes (Fig 6).

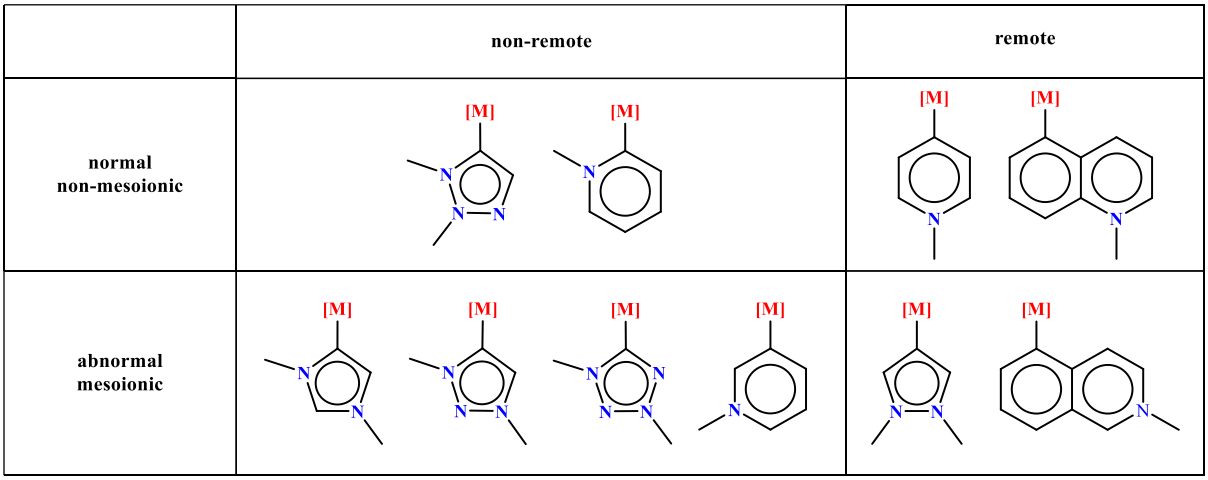


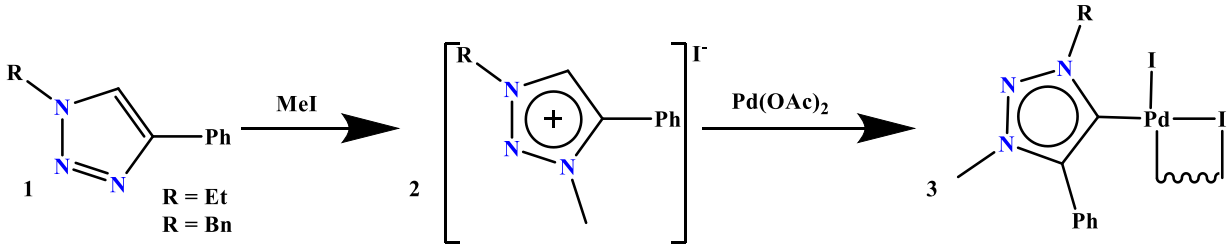
Fig. 6 Classification of different N-heterocyclic carbenes

A variety of free carbenes can be isolated and are stable at room temperature. Most MIC transition metal complexes are less sensitive to air and moisture than phosphine or normal NHC complexes. They are also resistant to oxidation. The robust nature of MIC complexes is due to the ligand's strong σ-donor ability. They are stronger σ-donors than phosphines, as well as normal N-heterocyclic carbenes due to decreased heteroatom stabilization. The strength of carbene ligands is attributed to the electropositive carbon centre that forms strong covalent bonds with the metal[32][33].They have been shown to lower the

frequency of CO stretching vibrations in metal complexes[30][34] and exhibit large trans effect.

1,2,3-triazolylidenes

1,2,3-Triazolylidenes are a recently developed subclass of MICs. The first triazolylidenes were reported by Albrecht in 2008 (Scheme 3).[35] Characteristic for abnormal carbenes, the triazolylidene (trz) ligand displays a small carbene angle (N1-C1-C2, 103°). For example the first complex discovered was the Pd-Trz in which the heterocycle is twisted out of the palladium square plane by ~75°.



Scheme 5 First triazolylidene-Pd complex

These carbenes are typically tri-substituted with alkyl groups in the N1 and N3 positions and an aryl group in the C4 or C5 position. Free carbenes as well as numerous transition metal complexes have been reported because they have tremendous versatility due to the synthetic flexibility of the cycloaddition of alkynes with azides (CuAAC). Free carbenes that are alkylated at N3 tend to undergo decomposition in which the alkyl group participates in a nucleophilic attack at the carbene position. If N3 is substituted with a bulky alkyl group or an aryl group, the stability of the carbene increases significantly. These ligands are strong σ donors, exhibiting stronger donor properties in comparison to classic NHC, yet weaker than “abnormal” imidazol-4-ylidenes.[36] This property, coupled with the electronic flexibility of the mesoionic ligands, makes them a powerful class of ligands for a large variety of catalytic transformations including olefin metathesis, cross coupling, oxidation of water and organic compounds. 1,2,3-triazolylidenes have been underexploited as ligands for first-row transition metals, with only a few examples in the literature (Fig 7).

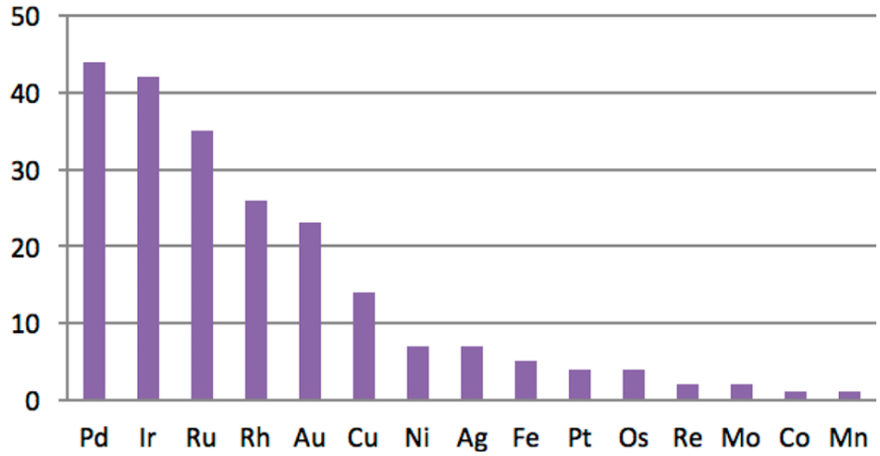
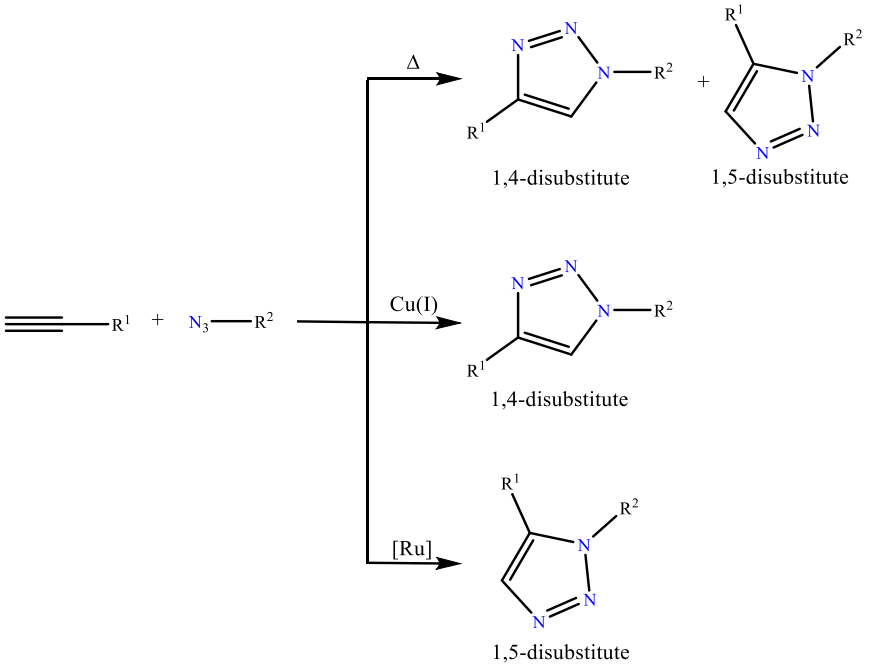


Fig.7 Number of publications of triazolylidene metal complexes per metal (2008−2017) [51].

Synthesis of 1,2,3 triazoles

Various synthetic approaches towards the synthesis of functionalized 1,2,3-triazoles are known as amide surrogates due to the high dipole moment and high H-bonding capabilities. 1,2,3-Triazoles were first synthesized by 1,3-dipolar cycloaddition reaction of azides and alkynes at high temperature (Huisgen cycloaddition) without any selectivity(Scheme 4).[37] This reaction has not been applied widely in organic synthesis due to the high temperature, poor regioselectivity, and low chemical yield. Later, in 2001, Sharpless[38] and Meldal[39] independently introduced a regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles via copper(I)-catalyzed azide-alkyne cycloaddition, which is widely known as the “click reaction”.



Scheme 4 Synthesis of 1,2,3-triazoles via Huisgen and metal catalysed cycloaddition reaction

The Cu(I)-catalyzed azide-alkyne cycloaddition reaction has been broadly accepted as the example of excellence for click chemistry[40] in the chemical community due to the following reasons:

a) copper accelerates the cycloaddition process about 108 times,

b) the reaction can proceed in a broad range of temperatures,

c) it is insensitive to water,

d) the reaction has broad functional group tolerance,

e) the compounds may often be purified by extraction or filtration without any column chromatography,

f) the reaction is insensitive to a pH range from 4 to 12.

Soon after the discovery of the click reaction, another complementary discovery was achieved by the ruthenium catalyzed cycloaddition of alkynes and azides to exclusively form 1,5-disubstituted 1,2,3-triazoles[41].However, high reaction temperature, low yield, and the use of expensive metal catalysts restrict this reaction to become widely applicable. A lot of other methods for the synthesis of 1,2,3,triazoles and its derivates have been studied[42].

Coordination modes of triazole and triazolyl ligand with transition metals

1,2,3-Triazoles bearing several donor sites are potentially versatile ligands for metal coordination[43][44]. Generally, there are mainly three modes with which triazole ligands combine with transition metals (Figs. 8,9 and 10). The first mode is through nitrogen coordination of neutral simple triazoles and chelating triazoles(Fig.8).

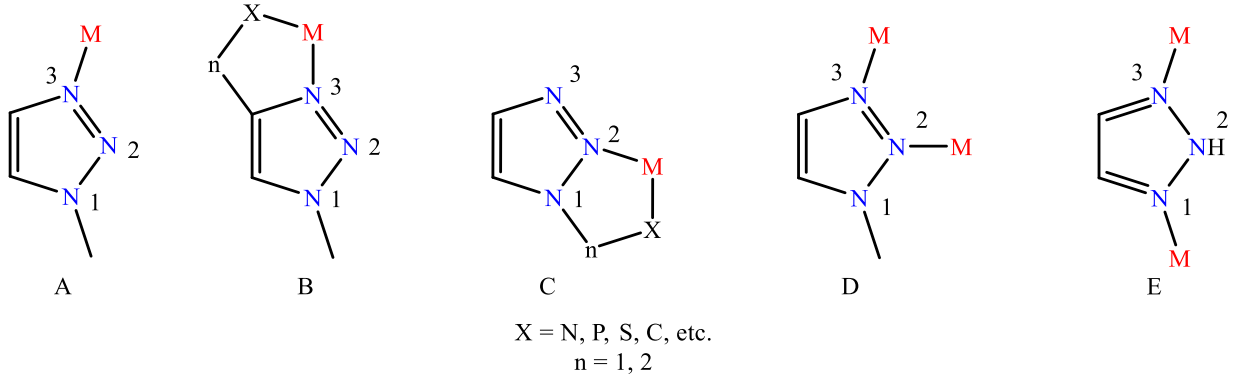


Fig. 8 simple triazoles and chelating triazoles coordinate to transition metal.

DFT calculations have shown that N3 is a better donor compared to N2[45][46]. The triazole ligand coordinates to a metal through the N3 nitrogen atom either as a monodentate ligand (type A) or as part of a bi- or poly-dentate chelate (type B), when there are other donor sites nearby. When the additional donor site is

adjacent to N1, coordination through N2 could form a bi- or poly-dentate chelate (type C)[47]. Thus, for the metal chelates, five- or six-membered cycles are usually formed. Besides, bridging coordination modes with two metals coordinated to two of the nitrogen atoms are possible (types D and E).The second mode is C5 coordination with deprotonated triazolium salts to form N-heterocyclic carbenes (NHCs, Fig. 9).

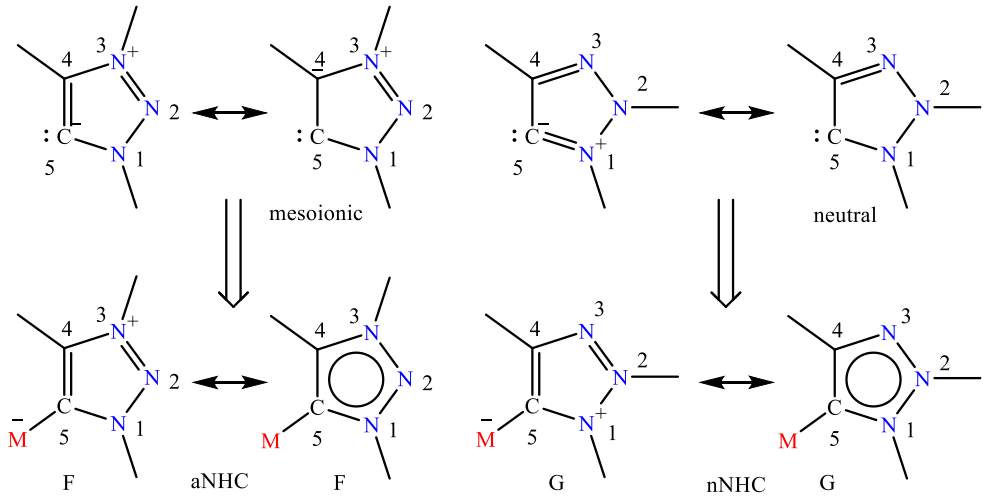


Fig.9 Deprotonated triazolium (NHCs) transition metal complexes.

Albrecht and co-workers used 1,3,4-substituted 1,2,3-triazolium salts as precursors for the synthesis of new aNHCs with various transition metals[48]. These abnormal triazolylidene complexes (type F) are expected to have a great potential for the development of new catalysts with unprecedented reactivities. Recently, an example of normal 1,2,3-triazolylidene carbene with a 1,2,4-substitution pattern was also reported (type G)[49]. Interestingly, owing to its unprecedented substitution pattern, the normal triazolylidenes exhibit even higher donor strength than the abnormal 1,3,4-substituted triazolylidenes [49]. Similarly, metal centers can also chelate to both the carbene carbons and the other adjacent donor sites to form more stable complexes. Additionally, the relatively acidic C-H bond on the 5-position can be directly inserted by transition metal to form a carbon–metal bond. The third coordination mode results from the combination of deprotonated N-H 4,5-di-substituted triazolates as anionic ligands in metal complexes (Fig. 10). The acidic N-H protons can be used to generate anionic ligands. Under basic conditions, benzotriazoles bind to metal via N1 (type H) while 4,5-disubstituted-NH-1,2,3-triazoles bind to metal via N2 (type I). Moreover, additional metal centres can coordinate to the free neutral nitrogen atoms of the metal triazolates forming bridged complexes (types J, K, and L) [50].

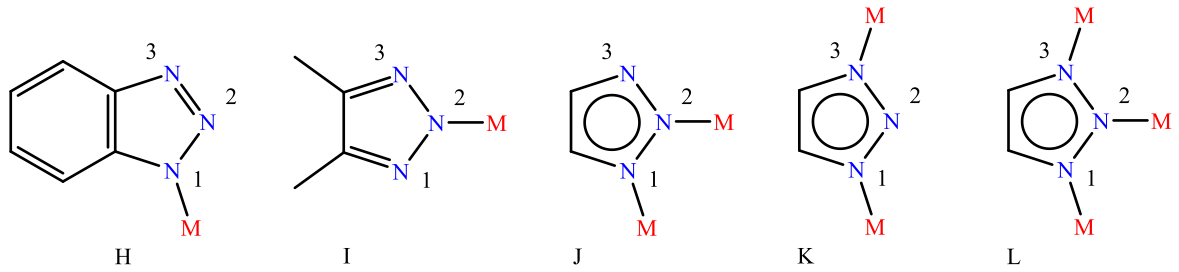
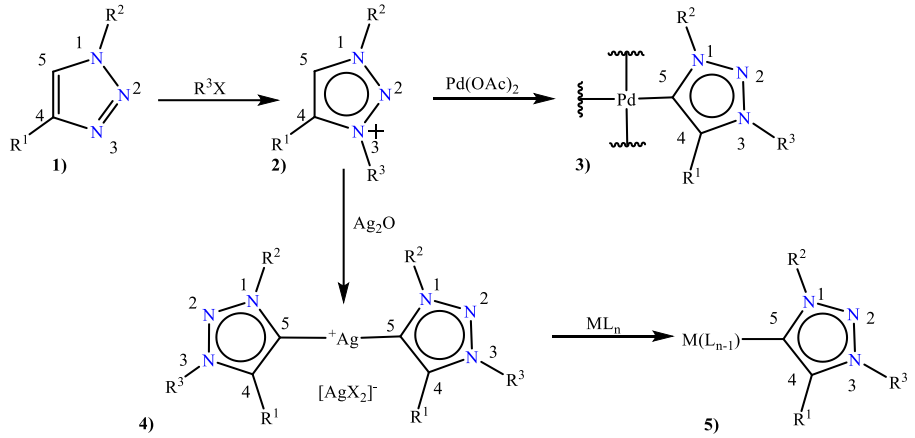


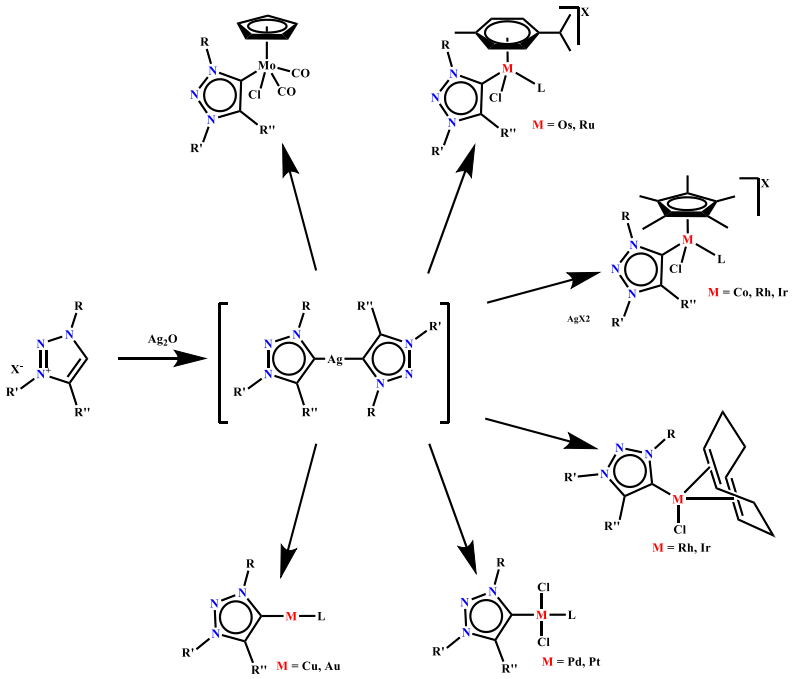
Fig.10 Deprotected NH 4,5-disubstituted triazolates as anionic ligands in transition metal complexes.

The nitrogen-coordinated triazole complexes are easily formed by just combining the triazole with metal complex precursors, resulting in ligand substitution. The C5-coordinated abnormal triazolylidene complexes have been generated by using 1,2,3-triazolium precursors as follows (Scheme 5) [35].



Scheme 5. Metal 1,2,3-triazolium precursors coordination

As already seen above the neutral triazole heterocycles 1) are readily available by “click” reactions of the corresponding alkynes and azides. Selective nitrogen alkylation of the resulting triazoles at the N3-position yields triazolium salts 2) that are precursors of abnormal triazolylidenes. Thus palladium 3) and silver 4) abnormal carbene complexes are obtained by metallation of the triazolium salts 2) via CH bond activation using $Pd(OAc)_2$ or Ag_2O. Other transition metal carbene complexes 5) are also obtained by transmetallation of the resulting silver carbene complexes (scheme 6).[51]



Scheme 6. Transmetallation with various metal precursor to form triazolylidene metal complexes

N-heterocyclic carbene of Manganese

N-heterocyclic carbenes are able to form manganese complexes with several different oxidation states Mn^0 to Mn^V naming Mn(I)NHC as the most common.

The difficulty in preparing low-coordinate low-valent transition-metal complexes likely lies in the proneness of low-coordinate metal species to bind ligands to achieve coordination saturation and the readiness of low-valent metal species to undergo oxidative addition . In this regard 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.

In 2013, Roesky group published a two-coordinate manganese complex supported by a cyclic aminoalkyl carbene (cAAC) ligand [Mn(Me_2-cAAC)$_2$].[52] Its isolation apparently benefits from the strong π-accepting capability of cAAC. Furthermore, the cAAC ligand possesses somewhat radical anion character, and the interaction of [Mn(Me_2-cAAC)$_2$] with H_2 causes the conversion of the cAAC ligands into alkyl ligands.(Fig.11)

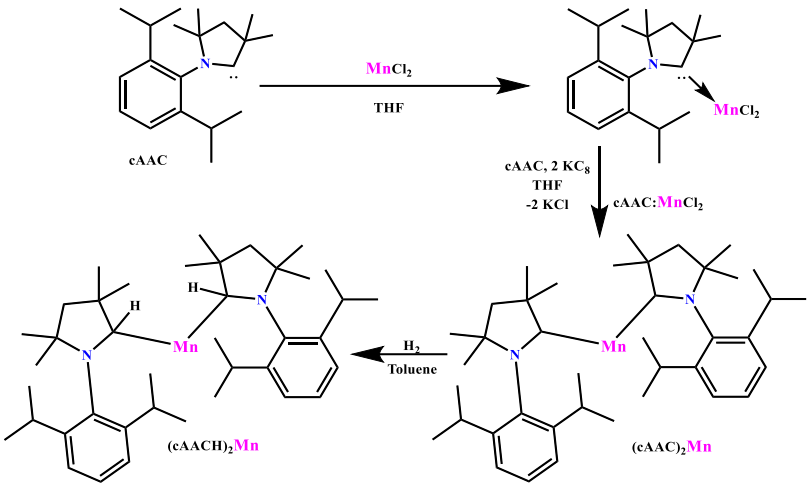


Fig.11 Roesky manganese NHC complexes.

A 2018 study reports that low-coordinate manganese complexes [(NHC)Mn(dvtms)] (dvtms = divinyltetramethyldisiloxane) were readily prepared from the reactions of NHC with $MnCl_2$, dvtms, and KC_8.[53] High covalence of the metal-ligand interaction was reported as so strong π backbonding from the metal centres to the alkene moieties. As a result, [(NHC)Mn(dvtms)] exhibits intriguing reactivity of reductive coupling with alkenes and alkynes to form Mn(II) dialkyl complexes. In addition, [(NHC)Mn(dvtms)] can react with H_2O to give mono-alkene $EtMe_2SiOSiMe_2CH=CH_2$, can be hydrogenated by H_2 to form Mn(II) dialkyl compound, can be oxidized by I_2 to give Mn(II) di-iodide, and can also undergo a ligand-substitution reaction with CO to form a Mn(0) carbonyl complex. (Fig.12)

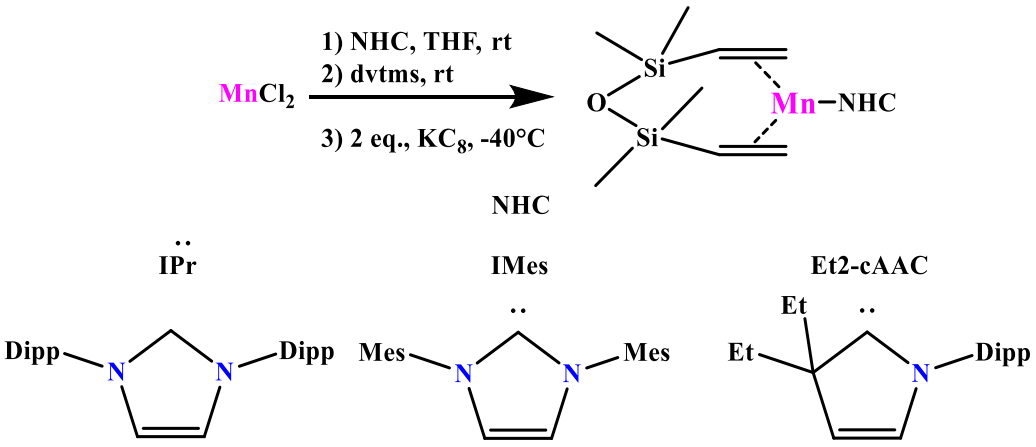


Fig.12 Synthesis of Mn(dvtms)(NHC) complexes

Manganese (I) NHC complexes are the most common and the first to be isolated in 1977 by Lappert and Pye.[53] (Fig.13) They used $CpMn(CO)_3$ as a metal precursor mixed with the NHC in the dimeric form (Fig.13). The harsh conditions of synthesis led to a low yield (180°C for 3 h, yield 1%; 30 min 110°C yield 5%).

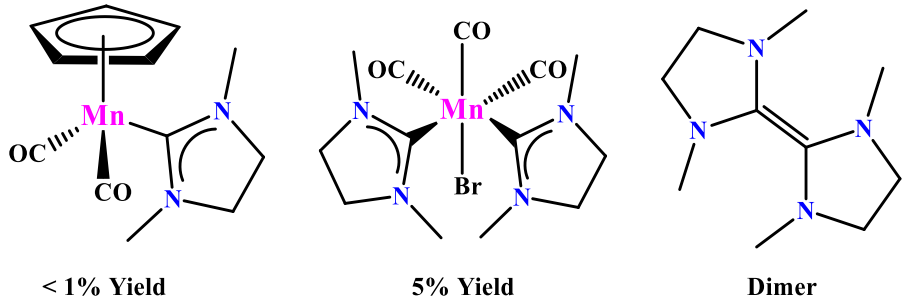


Fig.13. Lappert first isolated Mn-NHC complexes

An alternative synthetic route was reported by Aumann and Heinen, who described the synthesis of NHC Mn complexes via ketenimine manganese intermediates opening a wide possibilities for Mn(I)NHC complexes preparation.[53] (Fig.14)

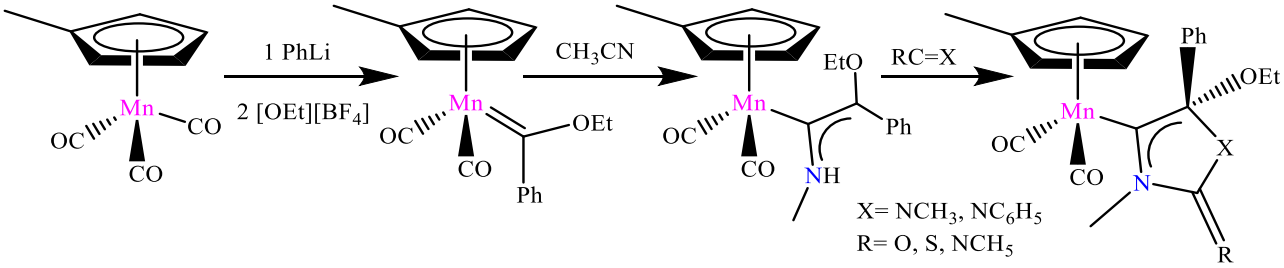


Fig.14 Synthesis of Mn-NHC by ketenimine intermediate

Similar to the three components reaction described by Aumann and Heinen, Fehlhammer group described multicomponent reactions of manganese(I) complexes with the main focus on finding pathways to generate new substitution patterns on heterocycles such as oxazoles and imidazoles.[54], [55] (Fig.15)

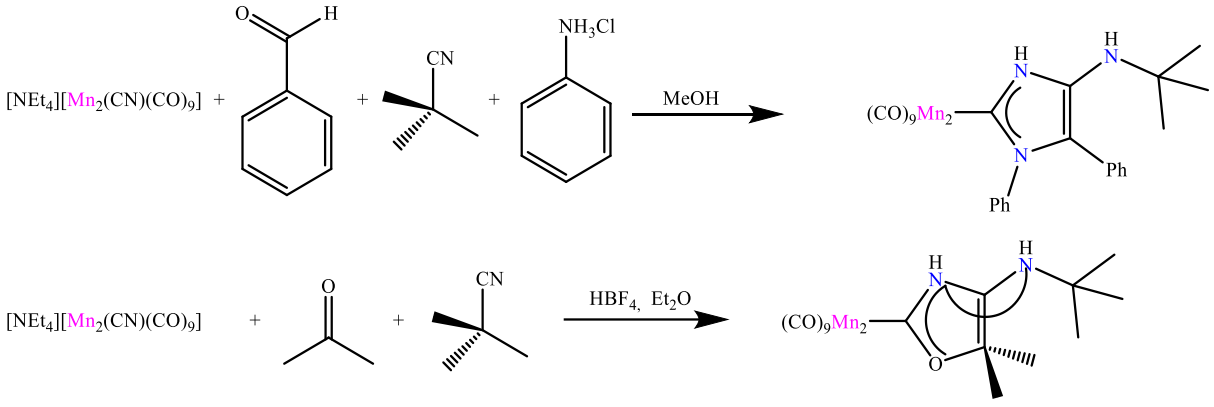


Fig.15 Synthesis of Mn complexes based on oxazoles and imidazoles

Taking inspiration from this work, Ruiz group also reported multicomponent reactions.[56] (Fig.16) They described the application of substituted cyano manganese compounds as starting materials to synthesize Mn(I)NHC. They also generate unsaturated N,O-heterocyclic carbene complexes, prone to be

used as transmetallation agents to transfer NHC ligand to Gold compound and other metals.[56]

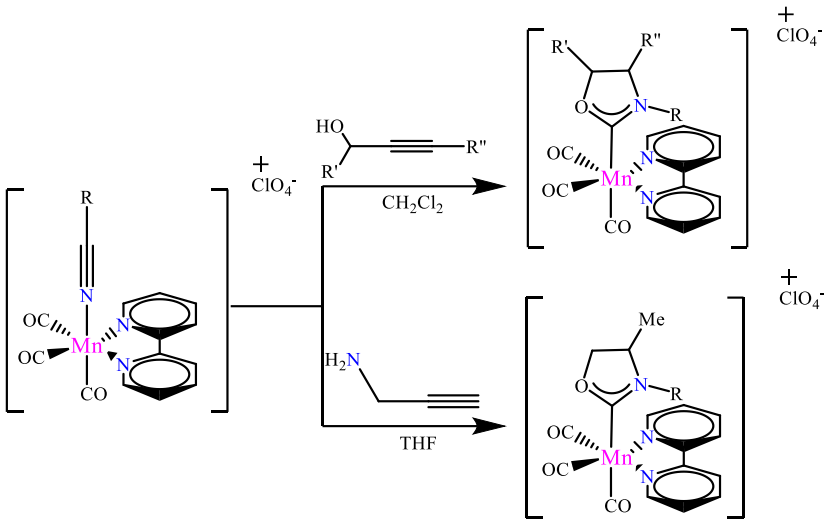


Fig.16 Cyano precursor to Mn-oxazoles and Mn-imidazoles complexes

Another synthetic route, towards N-boranesubstituted Mn(I)NHC complexes, was presented in 1998 by Siebert and co-workers.[56] They used a N-borane ligand with $MnBr(CO)_5$ (Fig.17a) also Edwards, Hahn and co-workers used $MnBr(CO)_5$ with several bis(phosphine), free carbenes and their respective Ag carbenes that deprotonates the coordinated phosphine ligand to form dinuclear compounds b (Fig.17)[57] Hahn and co-workers also treated $MnBr(CO)_5$ with the aminophosphineimine $H_2N(CH_2)_2NQPPh_3$ to produce the corresponding Mn complex c (Fig.17). They also synthetized from c with [11]ane-P2CNHC macrocycle and KO^tBu complex d.[58] (Fig.17d)

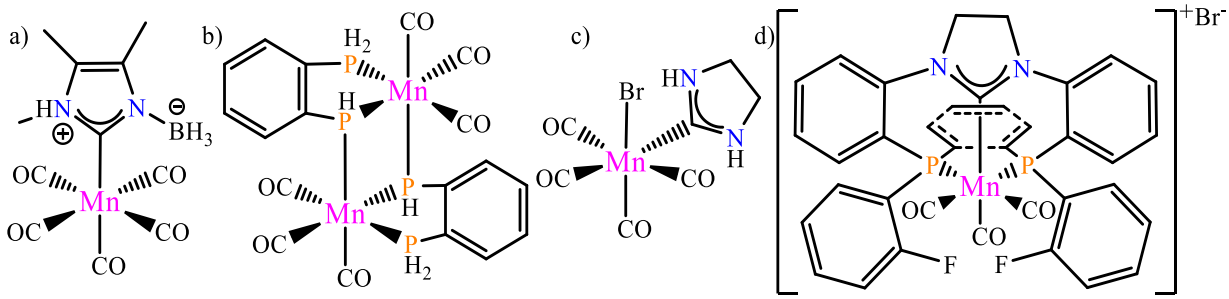


Fig.17 Complexes of Mn(I)NHC derived from $MnBr(CO)_5$

Whittlesey and co-workers treated $MnBr(CO)_5$ with $IiPr_2Me_2$ (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and IPr (1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazole).[59] These resulting complexes were similar to one of the first Mn(I)NHC complexes discovered by Lappert and Pye but with higher yields of about 52%. They also investigated the photochemistry of $Cp'Mn(CO)_2(NHC)$ complexes. By treating precursor $Cp'Mn(CO)_3$ ($Cp' = \eta^5\text{-}C_5H_4Me$) with ligands IPr, IMes(1,3-Dimesitylimidazol-2-ylidene), IEt_2Me_2 (1,3-diethyl-4,5-dimethylimidazol-2-ylidene) and $IiPr_2Me_2$, four new stable Mn(I)NHC

compounds could be synthesized (Yield 40%).[60] Such compounds release one CO ligand when exposed to UV light. The resulting 16-electron complexes are then stabilized by a C–H agostic interaction (Fig. 18).

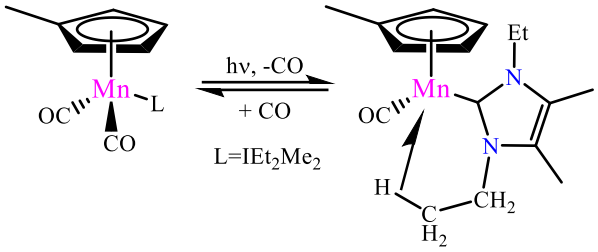


Fig.18 Example of photochemical behaviour in Cp'Mn(CO)2(NHC) complex.

These latter are the first publications in the field, those which have later given way to a large amount of works and projects based on the Mn(I)NHC. New methods of synthesis have been studied up to date, enriching the ways of application. In particular, recently the attention has shifted to the application of these complexes as catalysts.

Complexes of divalent manganese containing metal–carbon bonds are also known, although much less common. The bonding in these high-spin Mn(II) complexes is believed to be much more ionic than that in Mn(I) compounds.[61], [62] Even in those Mn(II) complexes containing strong-field ligands such as cyclopentadienyl, the ionic nature of metal–carbon bond persists due to the large spin-pairing energy of manganese. Thus, high-spin configurations are observed for most Mn(II) organometallics.[63], [64]

Sporadic examples of Mn(II)NHC compounds are present in the literature dating back to Cowley and Jones isolation of a manganocene NHC complex in 2001.[65] (Fig.19)

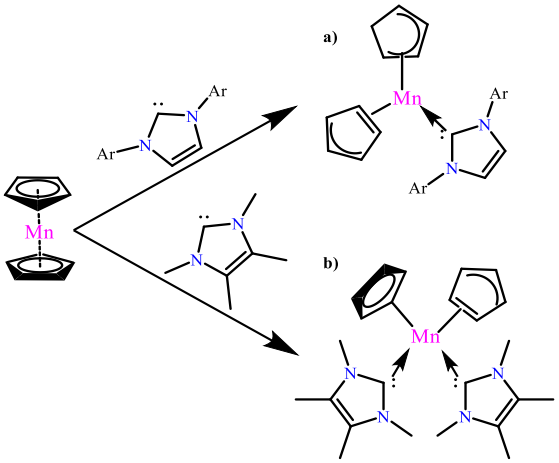


Fig.19 (η2-C5H5)(η4-C5H5)Mn(carbene) (a), (η1-C5H5)- (η2-C5H5)Mn(carbene)2 (b)

Subsequent work by Roesky reported a variety of NHC adducts to Mn(II) salts and Mn(II) β-diketiminate species (Fig.20).[66]–[68]

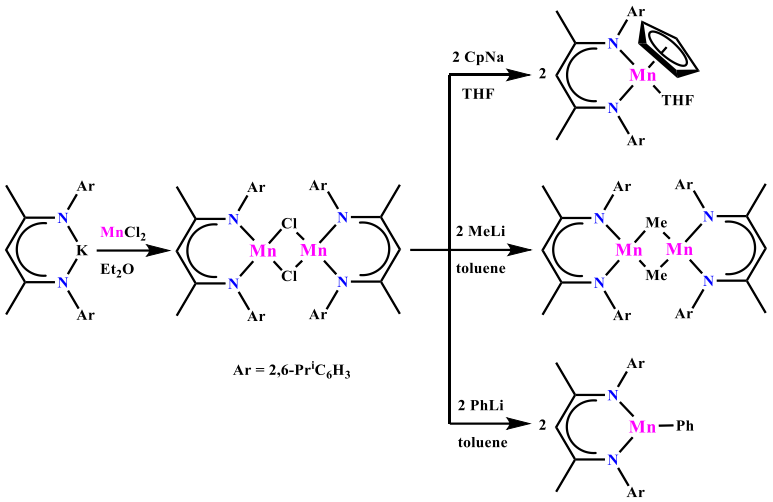


Fig.20 Example of Mn(II) complexes synthetized by Roesky

More recently, both Mulvey and Goicoechea have reported examples of three-coordinate Mn(II)-alkyl species by treatment of manganese hydrocarbyl aggregates, $[MnR_2]_n$ (R = CH_2SiMe_3, $CH(SiMe_3)_2$, or mesityl), with IPr.[69], [70] A variant of the NHC ligand, the cyclic alkyl amino carbene, has also been used to generate low-coordinate Mn species.[52] Danopoulos in 2005 employed chelating variants of NHC ligands to stabilize manganese complexes with pincer dicarbene ligands (Fig.21 a).[71] Al-Afyouni's group studied aryl-substituted NHC complexes of Mn(II) prepared by direct carbene addition to $MnCl_2(THF)_{1.6}$ (Fig.21 b).[72]

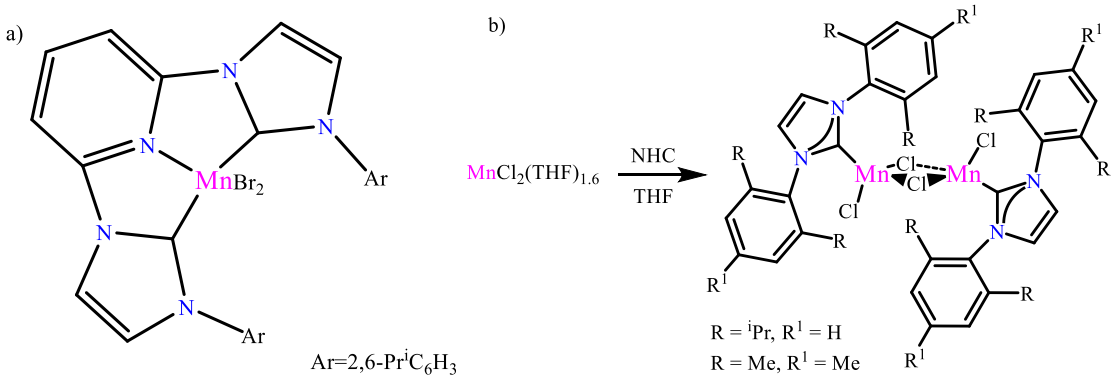


Fig.21 Danopoulos pincer dicarbene complexes (a), Al-Afyouni synthesis of Mn(II)NHC

Stefan Pelties in 2016 reported manganese(II) chloride as a precursor for the synthesis of NHC-stabilized low-coordinate NHC-stabilized manganese(II) compounds.[72] Oliver Hemming in 2018 also reported manganese NHC complexes bearing bulky trimethylsilylamide ligands. He also conduced an interesting study being first in the synthesis of NHC-ligated manganese phosphide complexes (Fig. 22).[72]

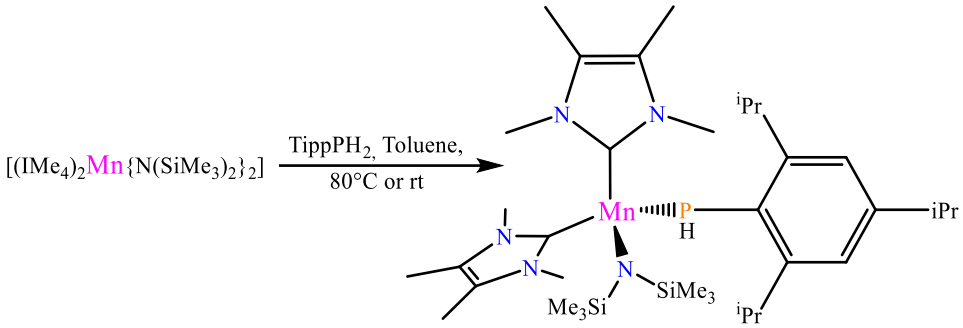


Fig.22 Mn(NHC)-phosphide complexes

Mn(III) and Mn(IV) NHC complexes are rare, due to the harder character of the higher oxidation state of the manganese species. Smith group reported octahedral Mn(III) and Mn(IV) complexes consisting of two tridentate ligands,[73] and Bellemin-Laponnaz reported the first square-pyramidal Mn(III) complex with a tridentate NHC ligand and an acetylacetonate (Fig.23).[74]

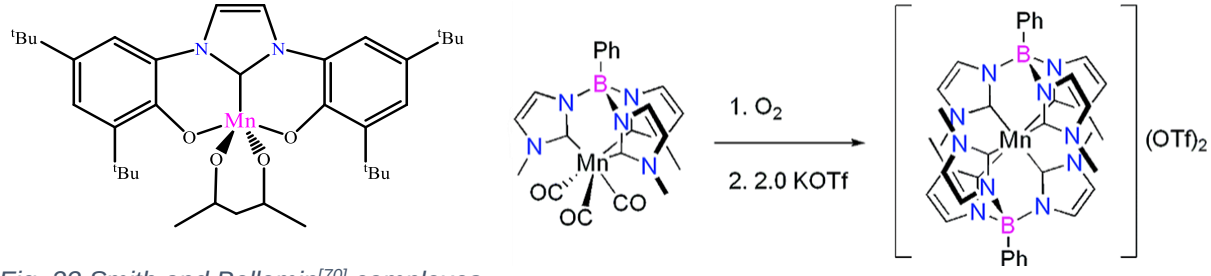


Fig. 23 Smith and Bellemin[70] complexes

The preparation of a new NHC ligand consisting of two carbene carbon atoms and two aryloxy oxygen atoms was reported by Jitsukawa group. The latter acts as a tetradentate ligand for complexation with the hard manganese(III) species. For the development of catalytic activity of the metal complex, they designed a coordinatively unsaturated site or labile ligand around the metal centre. They reported the use of this complex as a catalyst for the oxidation of styrene with PhIO as oxidiser to styrene oxide (Yield 38% 4 h at 40 °C) (Fig.24). [75]

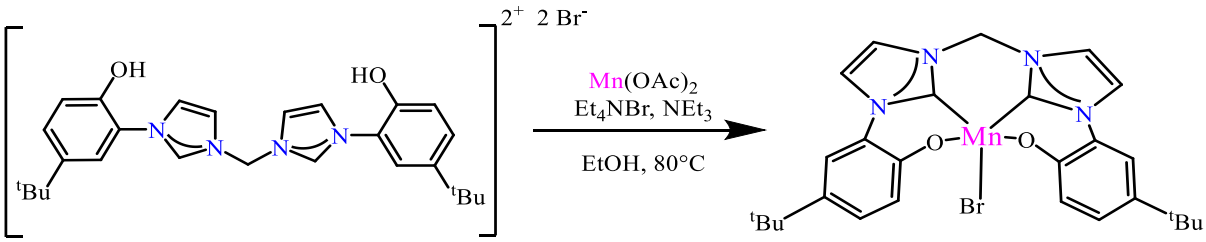


Fig.24 Jitsukawa group synthesis of catalyst

Meyer group, employed the tripodal tris(carbene) ligand framework TIMEN (tris[2-(3-xylylimidazol-2-ylidene)ethyl]-amine) for the synthesis of Mn complexes in +V, +IV, and +III oxidation states. They synthetized the first paramagnetic Mn(V) nitride located in a trigonal ligand field (Fig.25).[76]

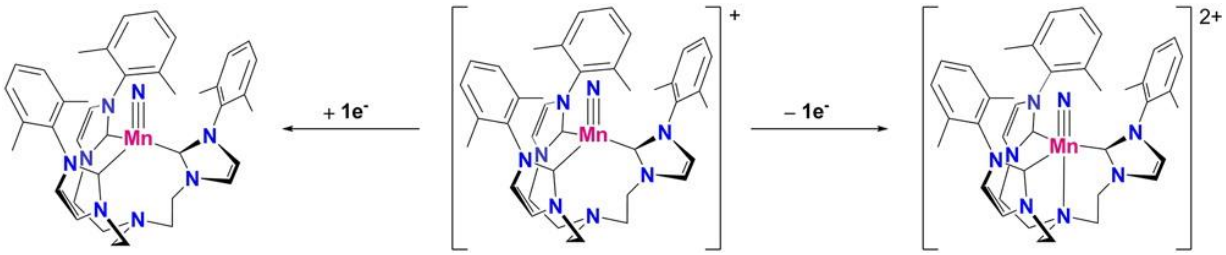


Fig.25 Meyer complexes of Mn(III), Mn(IV) and Mn(V)[76]

Triazolylidene (MICs) Manganese complexes

This subclass of manganese-NHC is only in it's infancy showing few example in literature, the first complex was reported by Smith and co-workers in 2013.[77] They reported a tripodal ligand structured solely from mesoionic carbene.(Fig.26) The donor strength of this ligand is lower than most imidazol-2-ylidene-based tris(carbene)-borate ligands. The attenuated donor strength is proposed to be due to the collective electron-withdrawing effect of the ligand's aryl substituents. In the paper they utilized $[Mn(CO)_3(^tBuCN)Br]_2$ as a precursor for the complex.

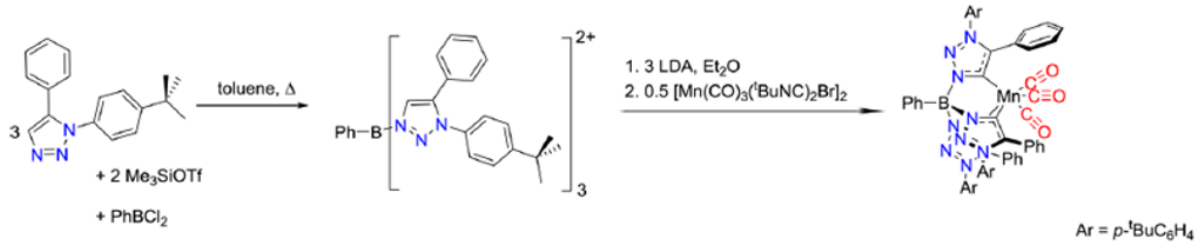


Fig.26 Preparation $Mn(CO)_3$tris(carbene)-borate[77]

Then Royo and co-workers in 2019 described the synthesis of Mn(I) and Mn(II) complexes containing 1,2,3-triazolylidene ligands *vide infra*.

Complexes developed by Royo's group

Royo's group is the group were I started my traineeship; the main interest of the group is the synthesis of organometallic compounds with specific properties for their use in catalytic and biological applications. The group develop new synthetic strategies based on catalytic methods for the functionalization of organic molecules. They are also interested in developing new metal-based drugs for the treatment of human diseases, such as cancer and microbial infections. In line with the interest of the group in developing the organometallic chemistry and catalysis of 3d metals with NHC ligands, they decided to develop a new family of manganese carbonyl complexes bearing bis-NHCs and explore their potential in catalysis.

The first approach to Mn(NHC) type of complexes was in 2018, reporting the synthesis and the catalytic activity of the first purely organometallic *fac*-[$Mn(CO)_3$(bis-NHC^{Me})Br] complex, active in the selective electrocatalytic reduction of CO_2 to CO.[78] For comparative reasons, they have also evaluated the catalytic features of [Mn(CO)3(py-MeNHC)I] (py-MeNHC = *N*-methyl-N'-2-pyridylimidazolium) complex under the same conditions.(Fig.27)

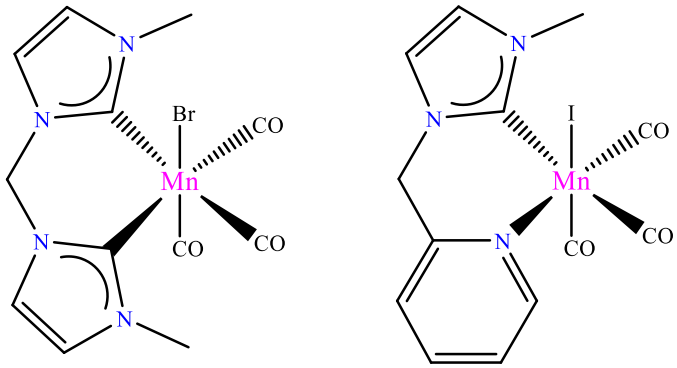


Fig.27 Complexes utilized in the electrochemical reduction of CO_2 to CO

They reported excellent faradaic yields (ηCO~95%) in anhydrous CH_3CN, a maximum turnover frequency (TOF_{max}) of 2100 s^{-1} was measured by CV, clearly higher than the values reported for other Mn based catalysts. Moreover, the addition of water (5%) produces the highest TOF_{max} (~320000 s^{-1}) reported for a Mn based catalyst. The replacement of a pyridine ring with a NHC unit significantly affects the catalytic performance, improving substantially the TOF_{max} and selectivity for CO production of well established C^N ligand-based Mn systems. Complementary FT-IR-SEC measurements and computational data suggest that the strongly nucleophilic character of the Mn atom is likely responsible for the positive ligand effect on catalysis. With the calculation and experimental data was also proposed a mechanism (Fig. 28)

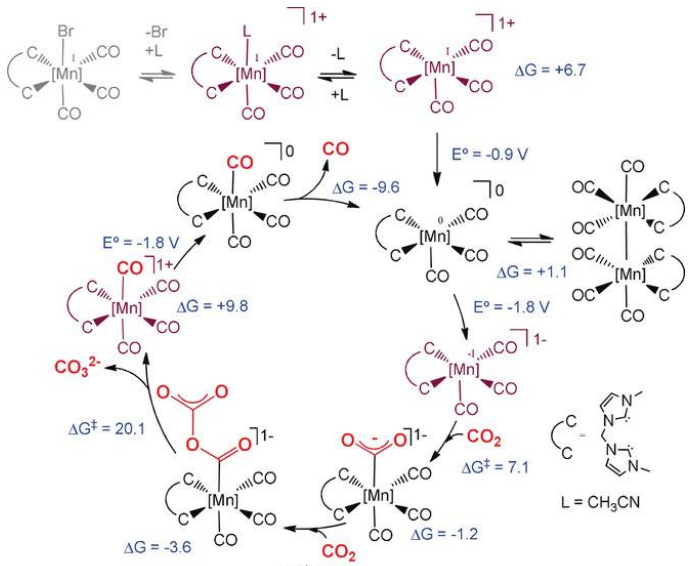


Fig.28 Catalytic cycle for CO_2 reduction

Following this work, the efficiency of these complexes in the reduction of carbonyl groups through hydrosilylation reaction was demonstrated. They reported manganese(I) compounds bearing bis-NHC, mixed NHC-pyridyl, and by-piridyl ligands, aiming to explore the effect of the introduction of NHCs in the first coordination sphere of metal.[79](Fig.29)

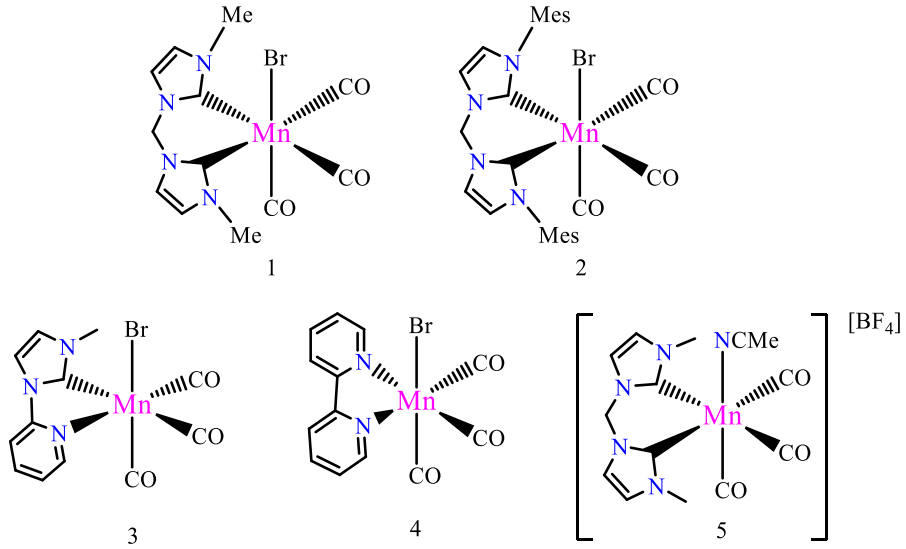


Fig.29 Catalyst tested in the reduction of carbonyl

In particular they studied manganese bis-N-heterocyclic carbene complexes *fac*-[Mn(bis-NHC^{R})(CO)$_3$Br] [R = Me (1), Mes (2)] that efficiently catalyzed the reduction of benzaldehyde, and a wide variety of substituted aryl and alkyl ketones using phenylsilane and polymethylhydrosiloxane (PMHS) as reducing agents, in acetonitrile at 80 °C with 1 mol% of catalyst loading.

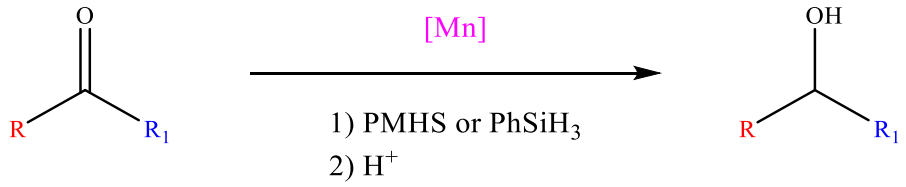


Fig.30 Reduction catalyzed by Mn complex

Notably, α,β-unsaturated ketones and dialkyl ketones were selectively reduced under these conditions. Interestingly, the catalytic efficiency of 1 and 2 was superior than that of fac-[Mn(L2)(CO)$_3$Br] (L2=NHC-py (3), bip (4)) complexes bearing a mixed NHC-pyridyl or bipyridyl ligands, indicating that the presence of the strong donating NHC ligands has a beneficial effect. The related cationic species fac-[Mn(bis-NHC^{Me})(CO)$_3$][BF$_4$] (5) prepared by bromide abstraction with silver tetrafluoroborate displayed even higher activity, reaching TOFs of up 320 h^{-1} (TON of 1000). It is evident that complex 5 is less reactive that the best performing catalysts of Trovitch and Turculet. However, complexes 1, 2, and 5 are air stable compounds, and catalytic experiments are conducted under

atmospheric air, in contrast to the very air sensitive complexes used in other studies. In addition, they constitute the first examples of Mn-based catalysts capable to efficiently reduce carbonyl groups using the readily available and inexpensive PMHS.

They also tested some of these catalyst reporting the first manganese catalyzed reduction of esters to alcohols using the cheap and readily available PMHS as reducing agent. They described an efficient catalytic system for the selective reduction of esters to alcohols using PMHS or phenylsilane in the presence of [Mn(bis-NHC^{Me})(CO)$_3$Br](Fig n), was worth to note that this catalyst don't need an inert atmosphere and any additive despite other catalyst more active that are sensible to air atmosphere (Turculet´s Mn pre-catalyst, [(k2-P,N)Mn (N(SiMe$_3$)$_2$]).[80] Initial experiments were performed using methyl benzoate as a model substrate in the presence of [Mn(bis-NHC)(CO)$_3$Br] (1 mol%) as catalyst and PhSiH$_3$ (1.2 eqv.) as reducing agent, in neat conditions at 100 ºC. Next, the influence of different solvents was evaluated finding THF to be the best solvent. Catalyst was reusable up to 5 cycle reaching an overall TON number of 485 after several days. The tolerance of the catalytic system to functional groups was evaluated by the reduction of a variety of benzoates bearing electron donating and electron withdrawing substituents was investigated. Also catalytic test were performed to explore the utilization of PMHS as a reducing agent. A variety of esters were efficiently reduced with PMHS (3 eqv.) in THF at 100 °C affording the corresponding alcohols in high yields (66-88%).

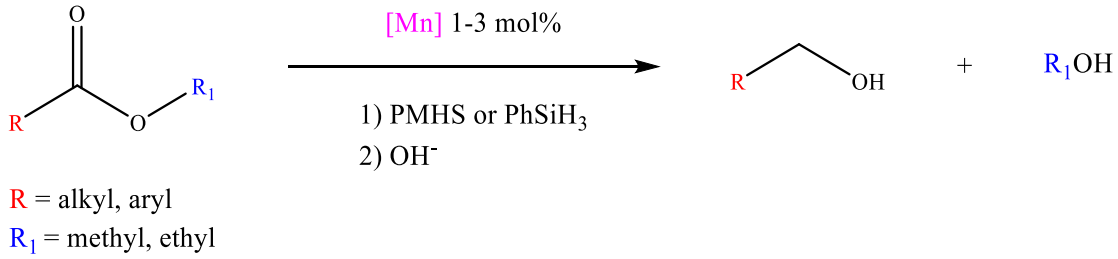


Fig.31 Reduction of ester to alcohol catalyzed by Mn complex

This investigation continued in another article were they reported the first Mn catalysed reduction of sulfoxides to sulfides in 2019 [81] They utilized *fac*-[Mn(bis-NHC^{Me})(CO)$_3$Br] complex as catalyst and silanes as reducing agents. To test catalytic activity they utilize methyl phenyl sulfoxideas a benchmark and phenylsilane as a reductant finding the best condition to be neat conditions without additives, at 100°C with a catalyst loading of 2 mol% (Fig x) A turnover frequency, TOF$_{50}$ of 788 h^{-1} was obtained, which represents the highest TOF value reported so far for a metal-based catalyst, surpassing the activity of its third row counterpart, rhenium, in reduction of sulfoxides with silanes. Also the catalyst could be reused up to 9 times. They test the catalyst for a variety of

sulfoxides and found that in general the reduction to the corresponding sulfide was successfully with a good yield, the only substrate that is susceptible to reduction is the one that contain olefinic group. They also tested the possibility to utilise as a reducing agent TMDS that is a by-product of industry obtaining encouraging result.

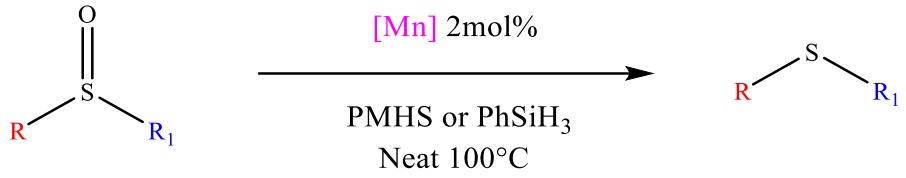


Fig.32 Reduction of sulfoxide to sulfide

Encouraged by the results obtained with *fac*-[Mn(bis-NHC^{R})(CO)$_3$Br] [R = Me (1), Mes (2)] complexes, they extended the work to the coordination chemistry of di(1,2,3-triazolylidenes) to manganese describing the synthesis of Mn(I) and Mn(II) complexes proving their catalytic activity toward the oxidation of alcohols to carbonyl compounds. [77] (Fig. 33)

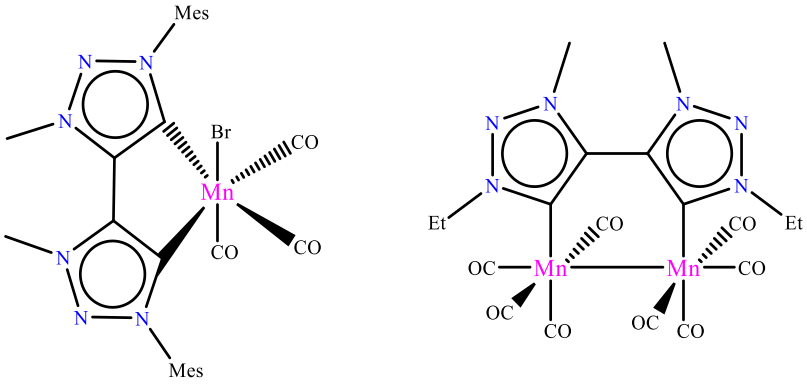


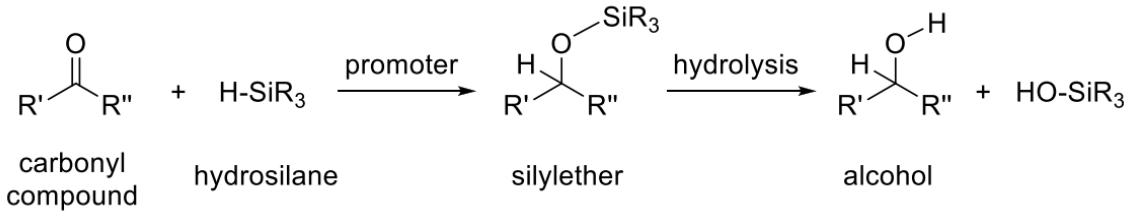
Fig.33 Synthesis of [Mn(CO)3di-trz)Br] and [Mn2(CO)8(μ-di-trz)]

They found the best reaction conditions after screening a variety of conditions, including different solvents, temperature, catalyst loading and percentage of oxidant (MeCN, 40 °C, 1 mol% catalyst, 0.75% oxidant TBHP). The process is applicable to a large variety of alcohols, proceeds under mild condition, is selective and suppresses overoxidation.

Hydrosilylation

Reduction of functional groups containing double or triple bonds in organic molecules is one of the most employed transformations in organic chemistry at any scale. The particular case of the reduction of carbonyl groups into alcohols is of wide interest to agrochemical and pharmaceutical industries as well as for the synthesis of natural products. Hydrogenation is an atom-efficient method in which no reaction side-products are generated and is found very useful in the presence of an heterogeneous catalyst for large-scale synthesis or using more

finely tuned homogeneous catalysts for selective and asymmetric synthesis. However, the high H_2 pressure needed for this process makes it difficult to scale it down to laboratory-sized settings, and the high flammability of hydrogen gas constitutes a real hazard to be regarded. On the other hand, metal hydride compounds, such as $LiAlH_4$, $NaBH_4$ or diisobutylaluminum hydride (DIBAL), employed in stoichiometric amounts are prevalent in medium- and small scale synthesis, their low selectivity and the generation of large amounts of waste being their main disadvantages. Transfer hydrogenation has emerged as an interesting reduction methodology as it avoids the use of high pressure of H_2 gas and utilizes readily available hydrogen donors (frequently 2-propanol) instead, in the presence of a catalyst. As an alternative to the before mentioned methods, hydrosilylation operates under mild conditions and it does not require high hydrogen pressure nor stoichiometric amounts of moisture sensitive reactants as $LiAlH_4$ or borohydrides. Hydrosilylation consists of the addition of a primary, secondary or tertiary substituted silane across a double bond (C = X) in which new H−C and X−Si single bonds are formed. Hydrolysis of the silylated intermediate affords the final reduced product. A general reaction scheme for the particular case of carbonyl hydrosilylation is depicted in scheme 7.



Scheme 7. Main step in carbon-oxygen reduction by hydrosilylation

As a further utility of this reaction, the silylether intermediate can also be used as a protecting group in synthesis[82]. The difference in the electronegativity values of Si (1.9) and H (2.2) atoms makes the Si-H bond slightly polarized in a way that it tends to produce hydrides. This feature, along with the strength of the Si-O bond, renders the reduction of C=O bounds via hydrosilylation a thermodynamically favoured process. Nevertheless, the reaction needs a promoter to proceed, which activates either the carbonyl substrate (acid catalysts) or the silane (transition-metal catalysts or bases). As a consequence, catalytic hydrosilylation combines an exceptional reducing capability with a high selectivity that can be finely tuned by the hydrosilane choice and ligand design. Silanes used in hydrosilylation processes are usually air-stable liquids and therefore easy to handle; likewise, the silicon by-products can be readily removed from the reaction crude by means of common laboratory methods as vacuum pump, extraction with organic solvents or column chromatography. At the same time, the need for stoichiometric hydrosilanes as reductants and subsequent generation of organosilicon by-products represents the main drawback of this reduction method, despite such waste are essentially not toxic nor hazardous. Many hydrosilanes are commercially available and their

reactivity and price can vary substantially among them, which can considerably compromise the viability of a hydrosilylation process. Some hydrosiloxanes, such as polymethylhydrosiloxane (PMHS) and 1,1,3,3-tetramethyldisiloxane (TMDS), are produced as intermediates or byproducts in the silicone industry and are therefore inexpensive. Unfortunately, these di- or polysiloxanes usually show poor activity toward hydrosilylation when compared to other monomeric silanes as phenylsilanes ($Ph_nSiH(4-n)$; n = 1−3), triethoxysilane ($(EtO)_3SiH$) or methyldiethoxysilane ($(EtO)_2MeSiH$). Among the most active hydrosilanes, phenylsilane ($PhSiH_3$), which actually contains 3 equiv of hydride, is frequently employed for the reduction of carbonyls due to its high activity, but its market price prevents its implementation on large-scale synthesis. The electronic properties of alkoxysilanes are favorable for some catalytic processes, and therefore are a common choice. The first hydrosilylation of a double bond, in which $HSiCl_3$ was added to 1-octene, was reported in 1947[83].This reaction was catalyzed by diacetyl peroxide and was proposed to follow a free-radical mechanism. The use of a peroxide (tert-butyl perbenzoate) as a catalyst was also reported by Speier and co-workers in 1956,[84] and it was Speier's team as well who first reported during following years the use of precious metal salts ($RuCl_2$, $IrCl_3$, $H_2PtCl_6{\cdot}6H_2O$, among others) as catalysts for the hydrosilylation of terminal[85] and internal[86] olefins. It was in 1972 that Ojima published the first catalytic hydrosilylation of carbonyl compounds, using $RhCl(PPh_3)_3$ as a catalyst (Wilkinson's catalyst) and Et_3SiH as a hydride source.[87] The hydrosilylation of cyclohexanone under such conditions proceeded quantitatively at room temperature in very short times, though the reaction of aromatic ketones needed to be heated at 60 °C. Shortly thereafter, the use of chiral ligands to induce asymmetry was implemented by the groups of Kumada,Kagan and Ojima. Since these early reports, an explosive development in transition-metal-catalyzed hydrosilylation took place. The advances reported during the first decades of intense research, until the late 2000s have been discussed in a number of books and reviews. In the last decades, however, there has been a growing interest in the replacement of second- and third-row transition metals (such as ruthenium, rhodium, palladium, iridium or platinum), by more economically available first-row transition metals such as manganese, iron, cobalt, nickel or copper. Although the electronic properties of second/third row transition metals have permitted the development of highly efficient homogeneous catalytic systems based on coordination compounds of such metals, their increasing market prices and concern about environmental impact have prompted many researchers to direct their efforts to the design of new catalytic systems based on cheap and environmentally friendly first-row transition metals. In the last ten years the best complexes were reported by Du's group whit a MnN(salen-3,5- $^tBu_2$) complex in 2013, the system achieved 98% conversion within 2 hours at 0.5 mol% catalyst loading with $PhSiH_3$ at 80 ºC .[88]

In 2014, Trovitch reported a pentadentate Mn(II) complex promote hydrosilylation. The catalyst promote a broad range of ketones at 1 mol% loading in benzene-d6. Then under neat conditions, the catalyst loading was lowered to 0.1 mol% where acetophenone was reacted to form the corresponding silylated product within 4 minutes. In addition, the catalyst loading was further lowered to 0.01 mol%, aliphatic ketone was successfully reduced within 5 minutes achieving 99% conversion.[89] (a) Du's MnN(salen-3,5- $^{t}Bu_2$) complex. (b) Trovitch's ($Ph_2PPrPDI$)Mn complex (Fig.33).

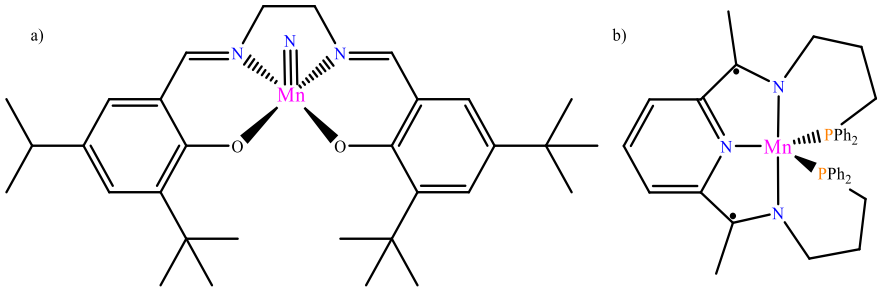
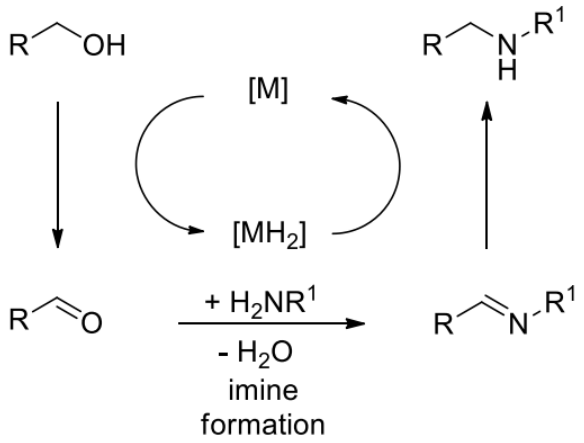


Fig.33.Manganese complexes for hydrosilylation

N-alkylation

The chemistry of amines, amides and other nitrogen-containing compounds plays a central role in organic synthesis. A great number of natural, pharmaceutical and agrochemical compounds have a C-N bond and for this reason, several methods have been developed to prepare them. Particularly, we focus our attention on the synthesis of amines. There are numerous reactions which give amines as products, including reductive amination processes from carbonyl groups and amination of aryl halides. Among all the reactions to make amines that are carried out efficaciously in the pharmaceutical industry, N-alkylation processes using alkyl halides or tosylates are the most used (36%), followed by reductive amination (20%) and N-alkylation of amides and reduction (10%).[90] Nucleophilic substitutions (SN2) are still widely used, even though alkylating reagents are often genotoxic. The reduction of amines and amides is often carried out using flammable or toxic reducing reagents, such as lithium aluminium hydride, borane or sodium cyanoborohydride, which also lead to complex work-up procedures and to the generation of a high level of waste. In the last few years, the rise of green chemistry has highlighted the need to develop strategies that increase the sustainability of such processes.[91] One of these strategies replaces highly reactive reagents such as alkyl halides or tosylates with less reactive reagents such as alcohols, ROH. Effectively, the use of alcohols as alkylating agents is beneficial as these reagents are readily available, highly stable, low in toxicity, easily stored, low in cost and relatively high in atom efficiency.[92] Generally, alcohols are not used as alkylating reagents because the hydroxyl group is not a good leaving group. However, they can be activated by catalytic dehydrogenative oxidation to generate in situ

a more reactive carbonyl species, which can react as an electrophilic or a nucleophilic species. If the carbonyl compound or its derivative is subsequently reduced under the reaction conditions, this protocol is known as a hydrogen auto-transfer process or borrowing hydrogen.[93] The additional reactivity of the ketone is exploited by imine formation and reduction to an amine, alkene formation and reduction to a C-C bond and enolisation, electrophilic trapping and reduction to a functionalised alcohol.[94] The general mechanism for the first pathway, which leads to carbon-nitrogen bond-formation reactions.(scheme 8)



Scheme 8. Main step in carbon-nitrogen bond formation

The first step is the abstraction of hydrogen from the starting alcohol by a catalyst to form the corresponding carbonyl compound. The following step is a condensation reaction between the new carbonyl compound and the amine, which leads to imine or iminium formation. Finally, the abstracted hydrogen is returned and incorporated into the final product. The atom efficiency of such process is really high as the only by-product is water. The first examples of homogeneous amine alkylation with alcohols were developed by Grigg[95] and Watanabe[96][97][98][99] in 1981 using rhodium and ruthenium-based catalysts, respectively. Temperatures as high as 180 °C were required for these transformations. More recent developments have led to more active catalysts and relatively milder reaction conditions. Fujita, Yamaguchi, [100][10]–[16] and co-workers successfully used Cp*Ir complexes for the alkylation of amines and sulfonamides. The Williams[107][108][109][110][94][111][112] group has also been very successful in using ruthenium- and iridium-based catalysts for such alkylation reactions. Also noteworthy is the Yus group,[10][11][115] who have been successful in using simple palladium and copper salts for the alkylation of amines, amides, and sulfonamides. Using $Ru_3(CO)_{12}$ combined with various ligands, the Beller group[111][116][117][118] has been able to carry out alkylation reactions with great success. Other iridium catalysts have also been used by the Kempe[119][120][121][122] group and have shown good results. Significantly, they were the first to report reaction temperatures as low as 70

°C.[120][122] Martin-Matute and co-workers also reported an iridium catalyst capable of amine alkylation with alcohols at 50 °C.[123] Recently, alkylation at 50 °C and room temperature was reported by the Andersson group[124] using an iridium catalyst. This is the first time amine alkylation using alcohols has been performed at room temperature, though it was limited only to alkylation of anilines.

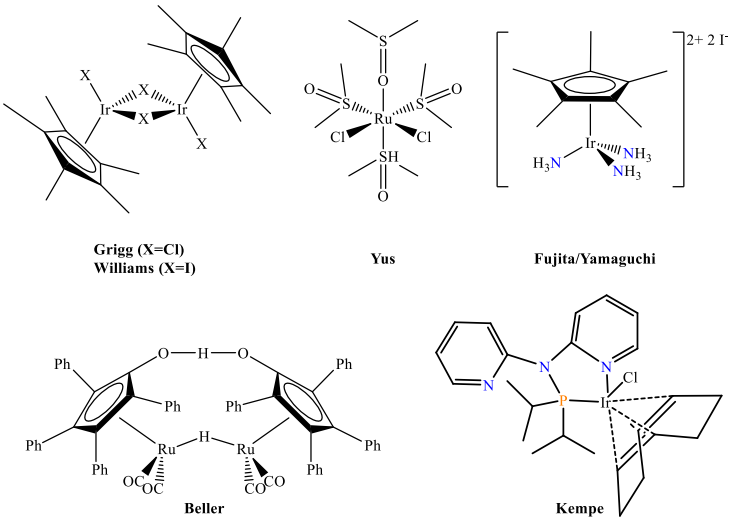


Fig. 34. Catalyst employed in the N-alkylation

First row transition metal catalyst has been reported[125][126] and in particular Mn-based catalysts for hydrogen transfer and borrowing hydrogen processes, including N-alkylation of amines, have attracted attention only very recently (Fig.35). [127][128][129]. Since 2016, various Mn(I) pincer complexes have been reported from Milstein[130]–[135],Beller[48], [56]–[57],kempe[138][130], kirchner[59][60], Hultzsch[129] and others.

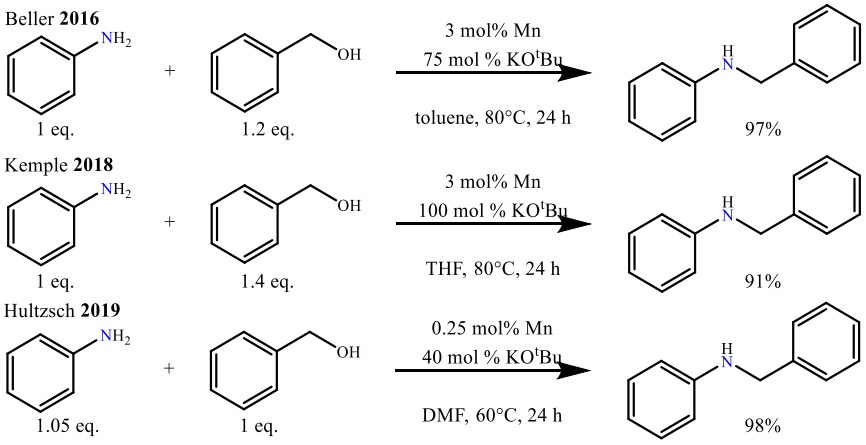


Fig.35 Manganese complexes catalyze N-alkylation of aniline

Preparation of Royo's ligands and complexes

The bidentate NHC pro-ligands were prepared similarly by heating dibromomethane with the appropriate molar ratios of 1-methylimidazole or 1-mesitylimidazole in acetonitrile. This is the classical reaction for the synthesis of bidentate bis-NHC ligands bearing two imidazole rings and a methylene bridge.[141]

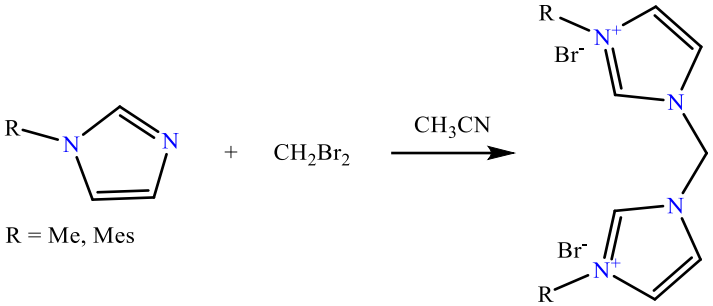


Fig.36 Synthesis of bis-imidazolium salts

The synthesis of the manganese bis-NHC complexes *fac*-[Mn(bis-NHCR)$(CO)_3$Br] [R = Me; Mes] was achieved by treatment of $Mn(CO)_5$Br with the corresponding imidazolium salts in the presence of potassium tert-butoxide in excess. [142](Fig. 37)

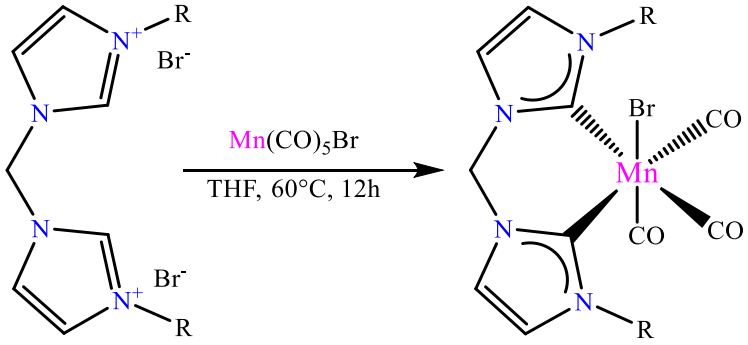


Fig.37 Synthesis of fac-[Mn(bis-NHCR)(CO)3Br] [R = Me; Mes]

The bidentate NHC-pyridyl pro-ligands were prepared via an Ullmann-type Cu(I) coupling reaction between 2-bromopyridine and imidazole. The reaction proceed by ligand promoted Cu-catalyzed chemistry developed but not yet general for the N-arylation of imidazoles. Coordination capability of benzotriazole, which is favourable for stabilizing catalytic species and assisting catalytic cycles.[143]

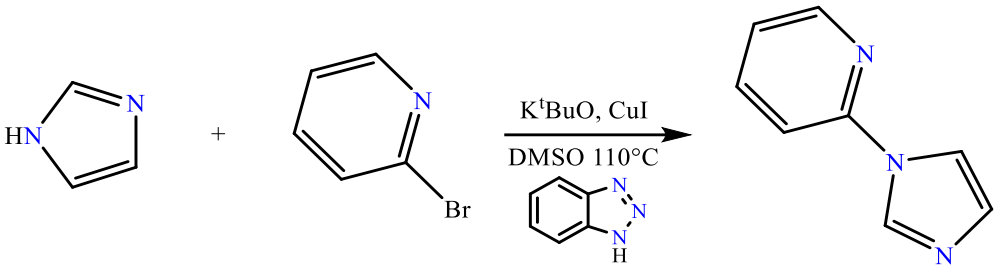


Fig.38 Synthesis of 1-(2-pyridyl)imidazole

Formation of the desired imidazolium salts was achieved by heating the 1-(2-pyridyl)imidazoles with the appropriate alkyl halide (methyl iodide or methyl bromide) in acetonitrile.

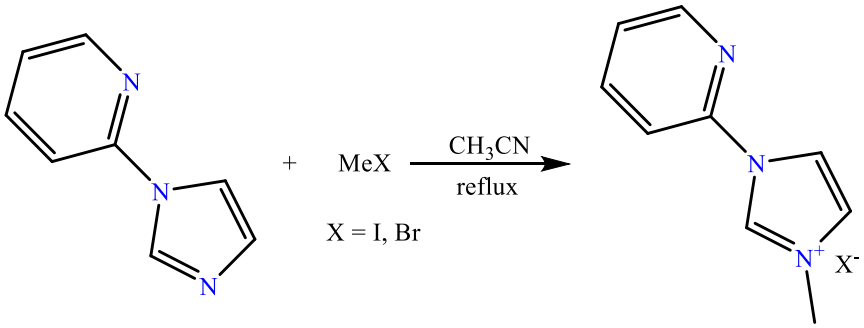


Fig.39 Synthesis of imidazolium salt (NHC-pyridyl pro-ligand)

The ligand was chelated to pentacarbonylbromomanganese [MnBr(CO)$_5$] with excess KO^{t}Bu. This reaction yields [Mn(CO)$_3$(NHC-pyridyl)X], which was isolated as a crystalline yellow-orange solid.[144] (Fig.40)

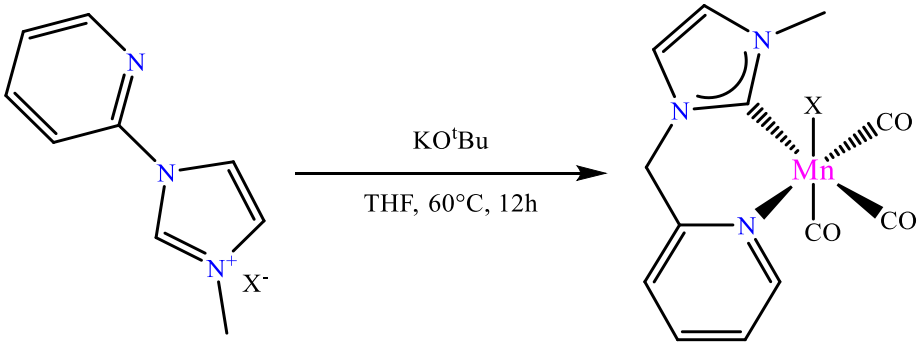


Fig.40 Synthesis of [Mn(CO)3(NHC-pyridyl)X]

The bidentate triazoles salt were prepared following a straight forward path: starting from the desire azide (ethyl azide or mesityl azide) and the di-alkyne via a copper catalysed cycloaddition the triazole ring was formed. Methylation with methyltriflete (MeOTf) produced the triazole salt. At this point was performed an ion exchange to obtain the di-triazolium bromide salt.[145] (Fig.41)

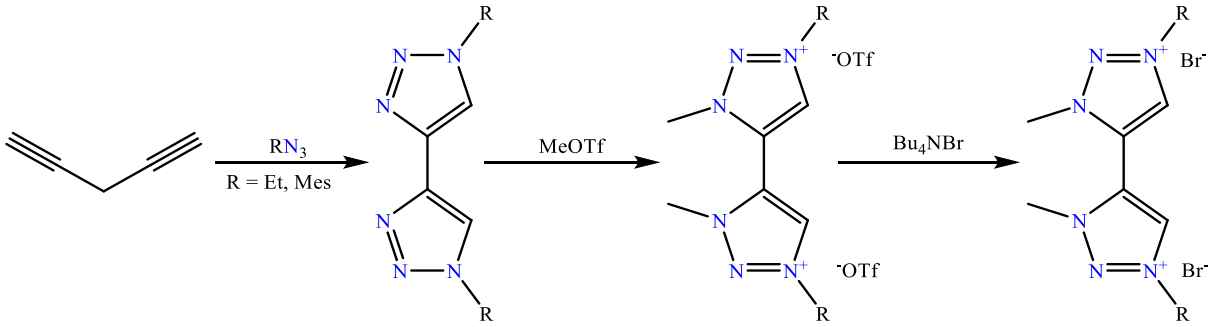


Fig.41 Synthesis of di-triazolium bromide.

The monometallic Mn(I) complex [$Mn(CO)_3$di-trz)Br] containing a bidentate chelating di-(triazolylidene) ligand was prepared from di-triazolium bromide salt by treatment with $Mn(CO)_5Br$ in the presence of 2 eq. of KO^tBu (Fig 42). Surprisingly, when the same reaction protocol was applied to the di-triazolium triflate salt bearing an ethyl group on N1 rather than the mesityl group, the bimetallic Mn(0) complex [$Mn_2(CO)_8$(μ-di-trz)] with the two metal centres bridged by the di-(triazolylidene) ligand was isolated with indication of concomitant bromine formation.

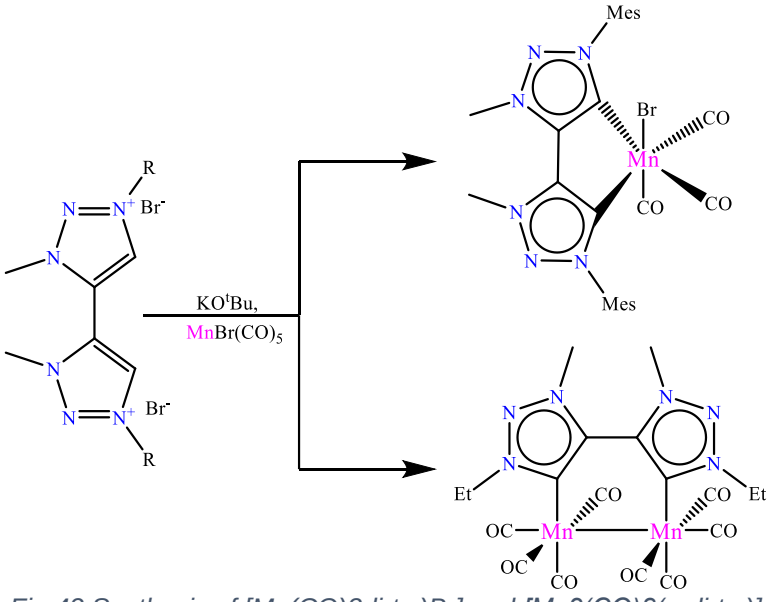


Fig.42 Synthesis of [Mn(CO)3di-trz)Br] and [Mn2(CO)8(μ-di-trz)]

Aim of the Thesis work

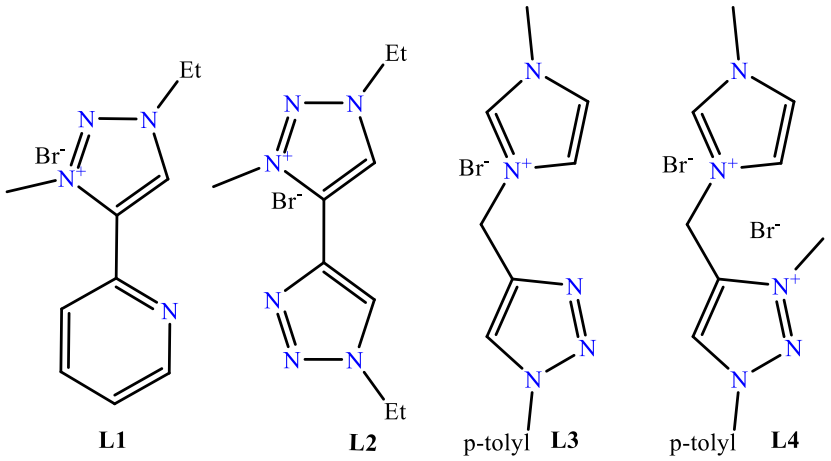
My master thesis was developed in the group of Prof. Beatriz Royo at the Instituto de Tecnologia Química e Biológica Antonio Xavier from Universidade Nova de Lisboa. The aim of my work was the preparation of a new family of manganese tricarbonyl complexes bearing chelating mixed NHC-triazolylidene ligands containing a CH_2 bridge, and the investigation of their catalytic activities in hydrosilylation reactions. I was involved in:

1) Preparation of imidazolium and triazolium salts that are used as precursors for the synthesis of NHCs.
2) Coordination of the NHC ligands to manganese.
3) Characterisation of the organometallic compounds by NMR and FT-IR.
4) Complex should have been tested in reaction of hydrosililation and N-alkylation.

Due to the global pandemic, I was forced to come back to Italy, and likely I was able to continue the plan of work in the group of Prof. Rita Mazzoni.

Results and Discussion

Ligands precursors reported in Scheme 9 were prepared following the procedures reported in the literature[142] and employed for the preparation of the corresponding Mn complexes the most of which were already developed in the group of Beatriz Royo (Scheme 9 L1, L2). with the principal aim of varying electronic, steric effect stability and catalytic activity of Mn complexes. Ligands 1 and 2 present similar substituent on triazolium ring, but they bear a pyridine or a triazole respectively as the C_4 substituents. Comparison between ligand 3 and 4 are focused on the characteristic of carbene interactions as L3 will coordinate through the carbene of imidazole and the nitrogen of triazole ring, instead L4 will coordinate with two carbene deriving from imidazolium and triazolium salts. Another interesting difference can be found between L1, L2 and L3, L4 in the CH_2 bridge.



Scheme 9. Ligand under investigation.

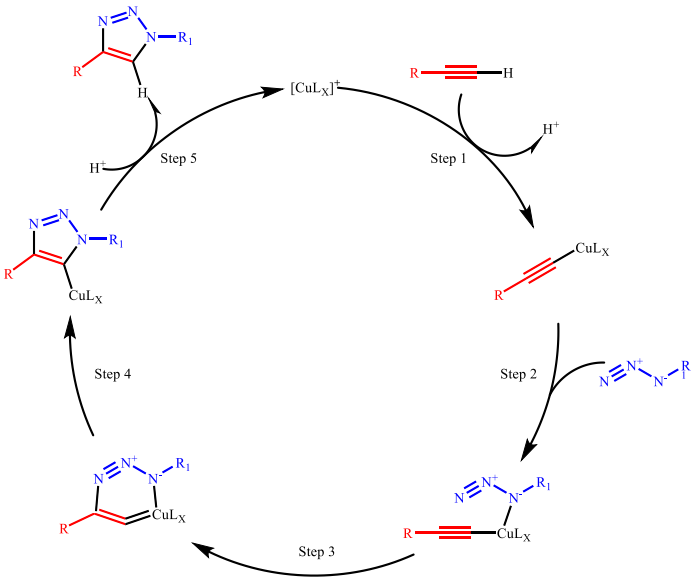
As previously stated, the first two ligands have been already synthesized and fully characterized in Royo´s group.[146] The other two ligands (L3, L4) were synthetized utilising as a guideline an article of Arnab Rit and co-workers. [147] This work was focused on the synthesis and catalytic application of Ru(II) and Ir(III)–NHC. We prepared a similar ligand but instead of having a phenyl group attached on the triazole ring, we introduced a p-toluene group..

General method for synthesis of ligand

In general the synthesis of ligands were performed as following :

1) Preparation of the azide. This reaction is an SN2 azidation of alkyl halides utilizing nucleophilic azides, in particular sodium azide (NaN_3)[148]. The reaction proceeds under mild conditions. [148]
2) Azide-alkyne Huisgen cycloaddition that is a 1,3-dipolar cycloaddition between an azide and a terminal or internal alkyne to give a 1,2,3-triazole

in particular this reaction is the copper(I) catalysed variant that produce only the 1,4-regioisomers.(Scheme 10)



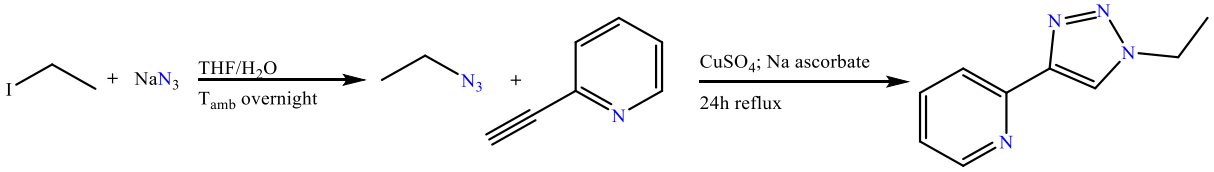
Scheme10. Catalytic cycle of CuAAC

3) Methylation reaction achieved by an excess of trimethyloxonium tetrafluoroborate (Me_3OBF_4). Trimethyloxonium tetrafluoroborate is generally ranked as the strongest commercially available reagent for electrophilic methylation.
4) Anion exchange from BF_4^- to Br- using tetra-n-butylammonium bromide (TBAB). The exchange is possible because the product is less soluble in acetone than the reagents. For these reaction was used at least two fold excess of TBAB to increment precipitation.

Synthesis of ligands

Ligand 1

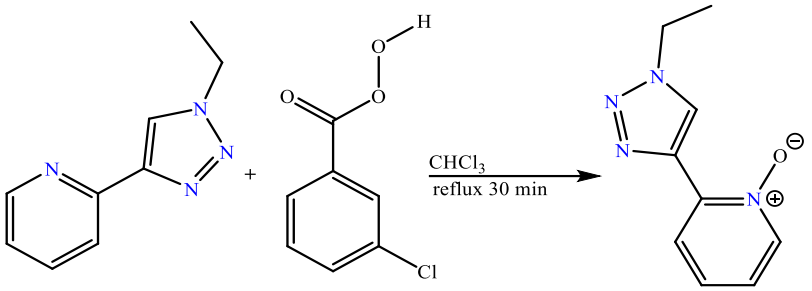
Synthesis of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine



Scheme11. Synthesis of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine

The synthesis was already reported in literature [149]. The product was isolated as a yellow oil (yield 98%) and identified as 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine by comparison with the literature ^{1}H-NMR characterization.

Synthesis of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine 1-oxide



Scheme12. Synthesis of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine 1-oxide

In order to methylate the nitrogen in the triazol ring was necessary to protect the nitrogen in the pyridine and the way to do this was the oxidation with meta-chloroperoxybenzoic acid (m-CPBA) to form the n-oxide. The reaction itself happens through a “concerted” transition state. That is, the bond between the oxygen and the nitrogen is being formed at the same time that the O-O bond is breaking and the proton is transferred from the OH to the carbonyl oxygen.(Fig.43)

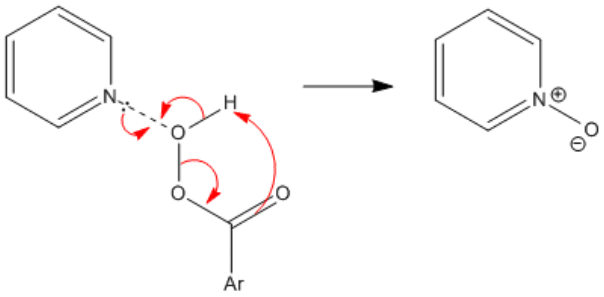
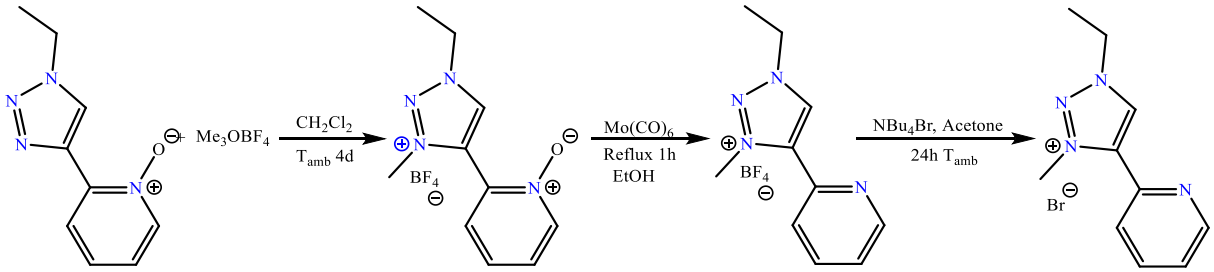


Fig.43 Reaction mechanism of nitrogen oxidation with m-CPBA

The product was isolated as a white powder in 96% yield, and identified by comparison with the literature ^{1}H-NMR characterization[150].

Synthesis 1-ethyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium bromide



Scheme 13. Synthesis of 1-ethyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium bromide

Once the nitrogen is protected the methylation is achieved by an excess of Me_3OBF_4 (4eq.). The product obtained was used in the next step without further purification.

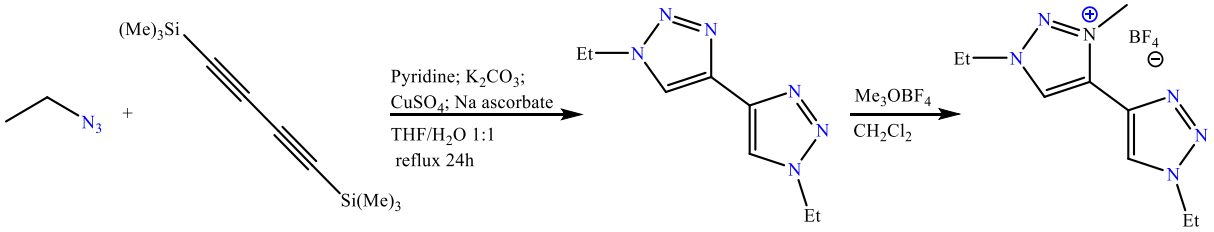
In the preparation of ligand were utilized two different approaches, the first one consisted in performing the reaction at low temperature reaction for a prolonged period of time, and the second one consisted on heating at 80°C the reaction mixture in a pressured tube. The second approach allowed to diminish the reaction time by 1/3.

Deprotection is achieved by the utilization of molybdenumhexacarbonyl. This is a robust method and offer mild conditions for the deprotection reaction.[151][152]. The product was isolated in 61% yield and identified by comparison with the literature ^{1}H-NMR characterization. [153]

The last step in the synthesis of ligand 1 was the anion exchange from BF_4^- to Br^- using TBAB. For the reaction was used 2 eq. of TBAB, the product was obtained as a white precipitate and identified by comparison with the literature ^{1}H-NMR characterization. Yield 88%.

Ligand 2

Synthesis of 1,1'-diethyl-3-methyl-1H,1'H-[4,4'-bi(1,2,3-triazol)]-3-ium tetrafluoroborate

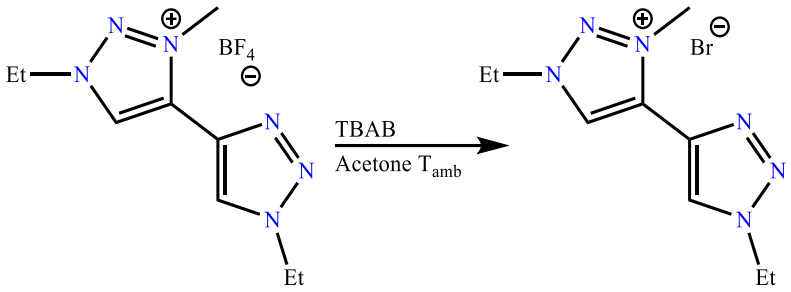


Scheme14. Synthesis of 1,1'-diethyl-3-methyl-1H,1'H-[4,4'-bi(1,2,3-triazol)]-3-ium tetrafluoroborate

Synthesis of ethyl azide was performed as previous step, without further purification the azide was reacted with the alkene producing the desire bis-triazole. In this case was performed a variation of click reaction that involve a tandem trimethylsilyl-deprotection/click reaction, which improves the synthetic efficiency of preparation of a bis(triazole) bidentate chelator directly from commercially available 1,4-bis(trimethylsilyl)butadiyne. With the goal of establishing a multistep one-pot approach for preparing 1,2,3-triazole, it was found in literature that simple addition of K_2CO_3 to standard aqueous click reaction conditions led to the formation of desired products from trimethylsilyl-protected butadiyne reactants. This tandem deprotection/click transformation utilizes the commonly employed H_2O/THF solvent system and requires no special exclusion of oxygen. As arylalkynes are commonly prepared from their trimethylsilyl-protected precursors, this method circumvents the need to isolate intermediate alkyne products.[154] Yield 88%.The product was identified by comparison with the literature ^{1}H-NMR characterization.

The followed step was hard to get because the desired product was the monomethylated and to do so sub-stoichiometric amount of methylating agent was utilized. In the preparation of ligand were utilized two methods, the first one consisted of a low temperature reaction for a prolonged period of time, and the second one was experimented successfully and consisted of heating at 80°C the reaction mixture in a pressure tube this diminished reaction time by 1/3. The product resulted from the fast method is a mixture of non methylated, mono methylated and di methylated and the slow method produced only the non methylated and mono methylated. The di methylated product was easily removed because is the only product not soluble in dichloromethane. Yield 88%. The product was identified by comparison with the literature ^{1}H-NMR characterization.

Synthesis 1,1'-diethyl-3-methyl-1H,1'H-[4,4'-bi(1,2,3-triazol)]-3-ium bromide

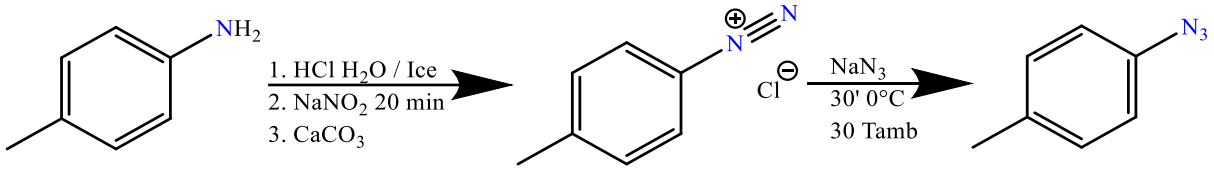


Scheme15. 1,1'-diethyl-3-methyl-1H,1'H-[4,4'-bi(1,2,3-triazol)]-3-ium bromide

The last step in the synthesis of ligand 2 is the anion exchange. The second time I performed this reaction no precipitate was formed so I had to find another way to separate the compound, I performed an solvent-solvent extraction and the two solvent chosen were CH_2Cl_2 and H_2O, to understand which mixture of solvents were able to separate the two compound a small amount of substance was putted in the mixture of solvent under test and a small amount of both solvent were putted in a tlc and eluted whit EtOH, the ligand is uv active but to see the reagent left is necessary to stain the tlc with a solution of $KMnO_4$, the product was found to be more soluble in water. With the extraction was also possible to obtain better yield. Yield 70%. The product was identified by comparison with the literature ^{1}H-NMR characterization.

Ligand 3

Synthesis of p-tolyl azide

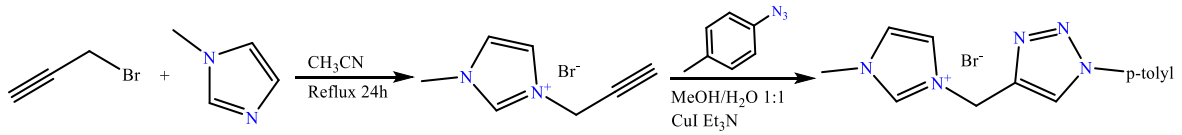


Scheme 16. Synthesis of p-tolyl azide

The first step is an diazotatium reaction performed creating a diazonium salt immediately reacted with NaN_3 to form the azide.

To obtain the desired product the diazo group N_2^+ can be substituted in a process called dediazotation, which liberates nitrogen N_2 and an aryl carbocation or more commonly in combination with single electron transfer and an aryl radical. Arildiazone cations undergo several reactions in which the N_2 group is replaced by another group. The process is an aromatic nucleophilic substitution reaction. In this case the diazo group is substitute with azide to give 1-azido-4-methylbenzene a yellow liquid. Yield 74%. The product was identified by comparison with the literature ^{1}H-NMR characterization. [155]

Synthesis of 1-methyl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide



Scheme17. Synthesis of 1-methyl-3-(prop-2-yn-1-yl)-1H-imidazol-3-ium bromide

The second step require the formation of imidazolium salt; the reaction is an alkylation of a mono functionalized imidazole, easily available from a condensation reaction, with excess of alkylating agent (2eq.). Yield 87% The product was identified by comparison with the literature ^{1}H-NMR characterization.[156]

To obtain ligand 3 cycloaddition was performed. NMR experiment were performed in particular ^{1}H-NMR,^{13}C-NMR, HSQC, it's possible to attribute with the help of these spectrum almost all the peaks. (Fig.44) Yield 44%

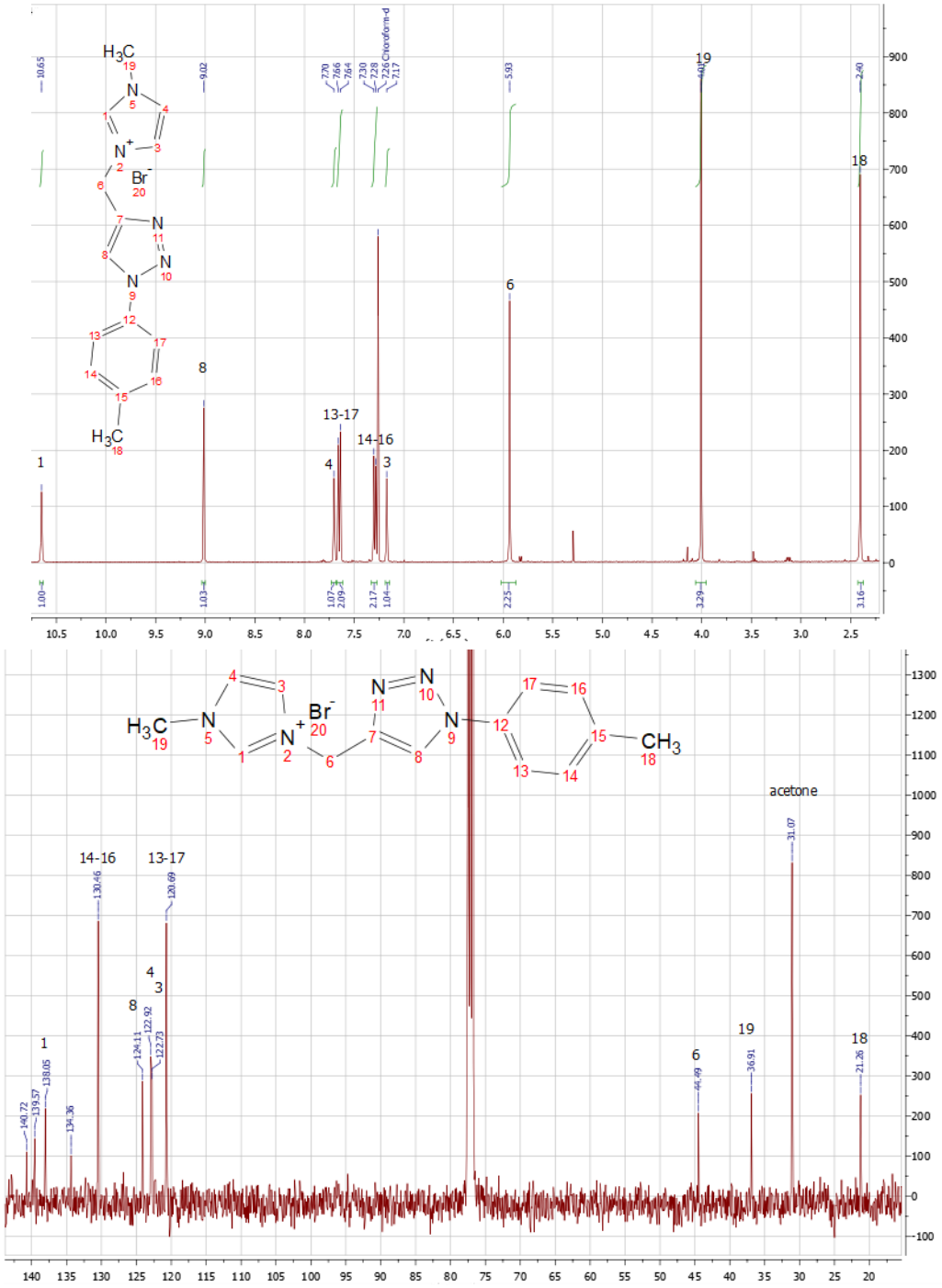
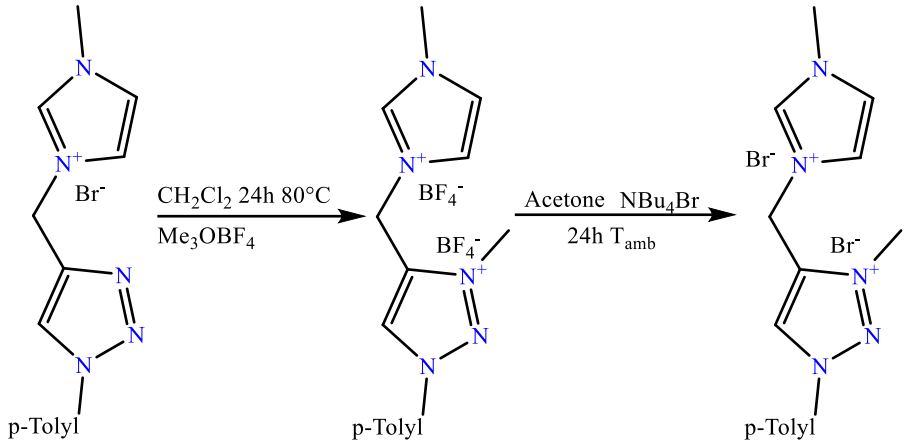


Fig.44 ^{1}H-NMR and ^{13}C-NMR spectrum of 1-methyl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide

Ligand 4

Synthesis of 3-methyl-4-((1-methyl-1H-imidazol-3-ium-3-yl)methyl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium dibromide



Scheme18. Synthesis of 3-methyl-4-((1-methyl-1H-imidazol-3-ium-3-yl)methyl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium dibromide

Methylation makes the triazole proton relatively more acidic, suitable for deprotonation to generate carbene centre, as evident from the downfield shift of the proton signal to 9.24 ppm, in comparison to that observed in the non methylated compound (9.02ppm). The product was obtained as a white solid. Yield 96% After ion exchange was obtained a white hygroscopic powder. Yield 67 %. The characterization was achieved by ^{1}H-NMR. (Fig.45)

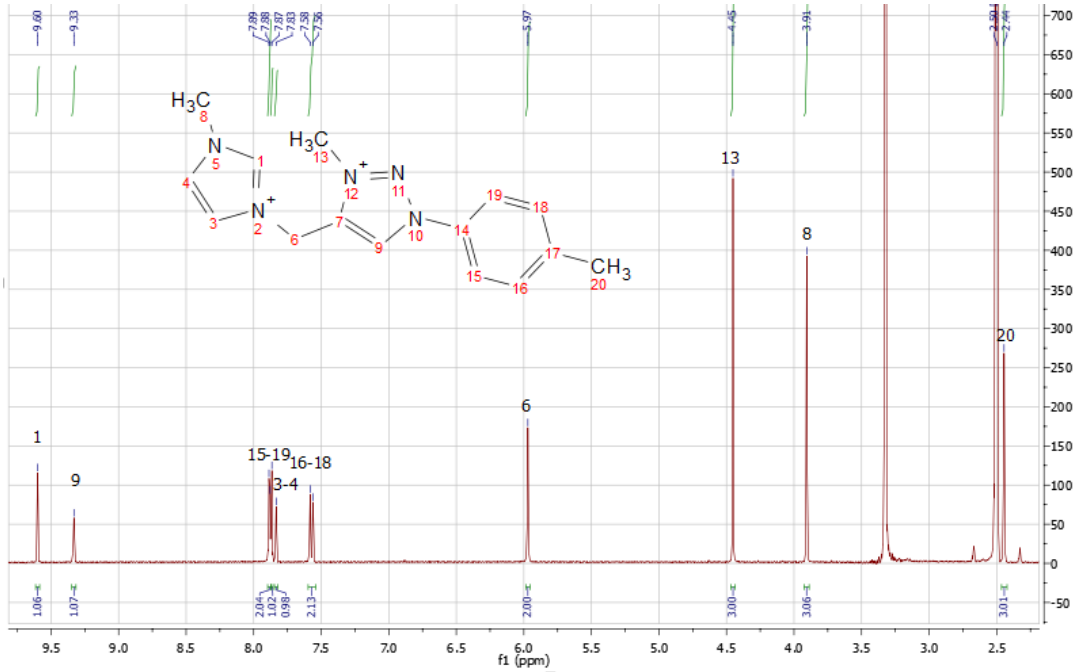
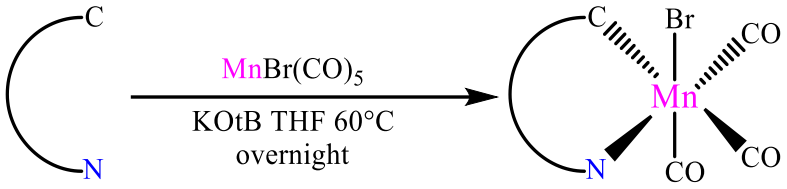


Fig.45 ^{1}H-NMR spectrum of 3-methyl-4-((1-methyl-1H-imidazol-3-ium-3-yl)methyl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium dibromide

Coordination synthesis

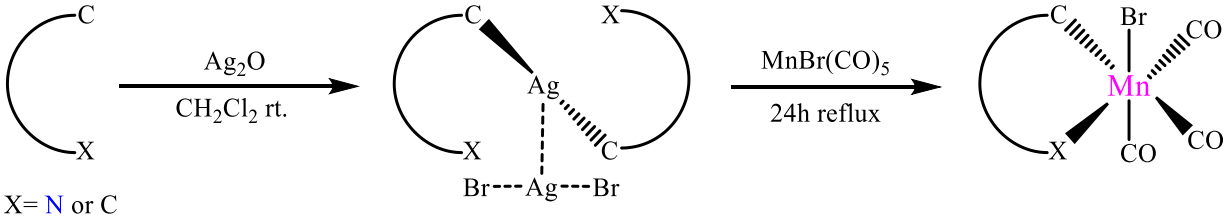
The synthesis of the manganese complexes 1-4 was attempted following two different synthetic approaches:

1) Treatment of $Mn(CO)_5Br$ with the appropriate ligand in the presence of potassium tert-butoxide[144] (Scheme 19)



Scheme19. Synthesis of organometallic complex

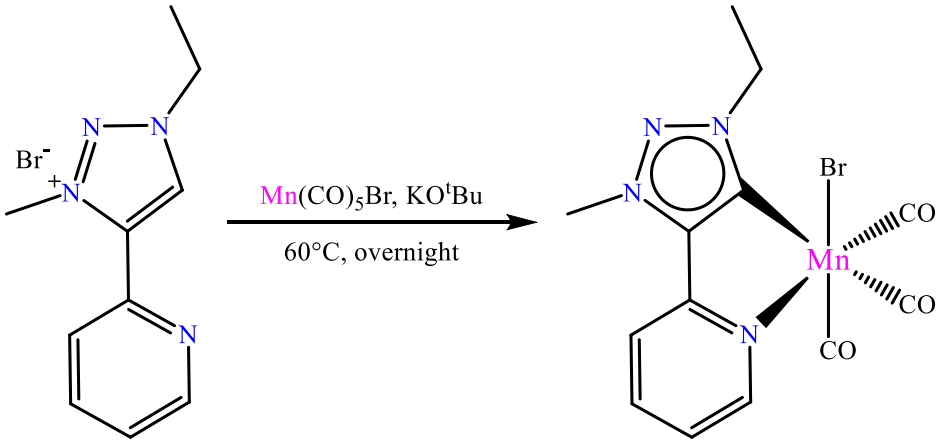
2) Treatment of ligand 2, 4 with silver oxide followed by trans-metallation reaction to $Mn(CO)_5Br$. (Scheme 20) [157]



Scheme 20 Synthesis of organometallic complex by transmetallation

Complex 1

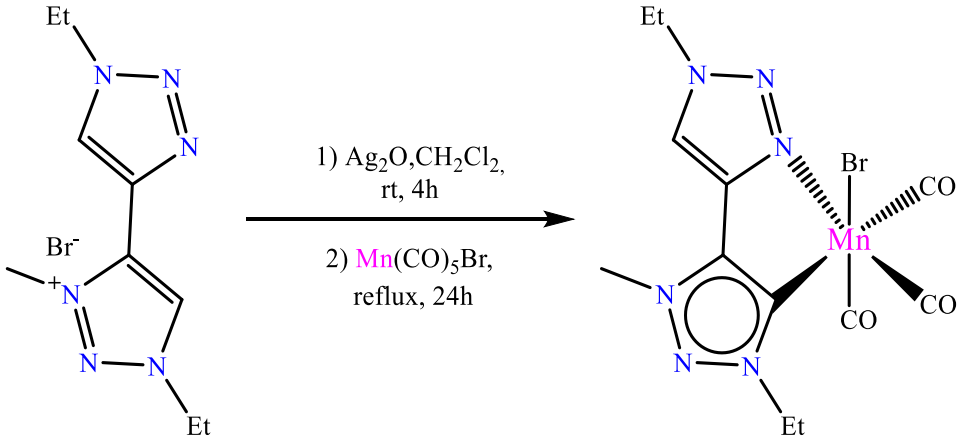
The synthesis of complex 1 was performed following the method described in the literature by Royo and co-workers .[146]



Scheme 21 Synthesis of complex 1

Complex 2

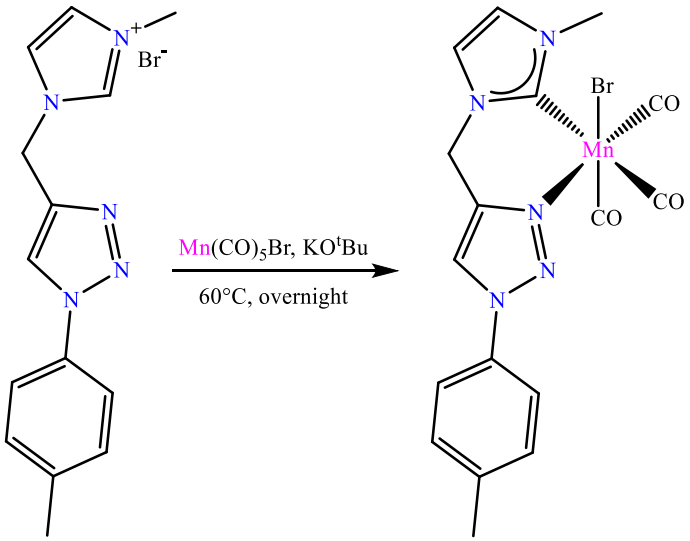
The synthesis of complex 2 was performed following the method described in the literature by Royo and co-workers.[146]



Scheme 22 Synthesis of complex 2

Complex 3

Attempts to synthesise complex 3 were made following similar methods as those described for the synthesis of complexes 1 and 2.



Scheme 23 Attempt to synthesize complex 3

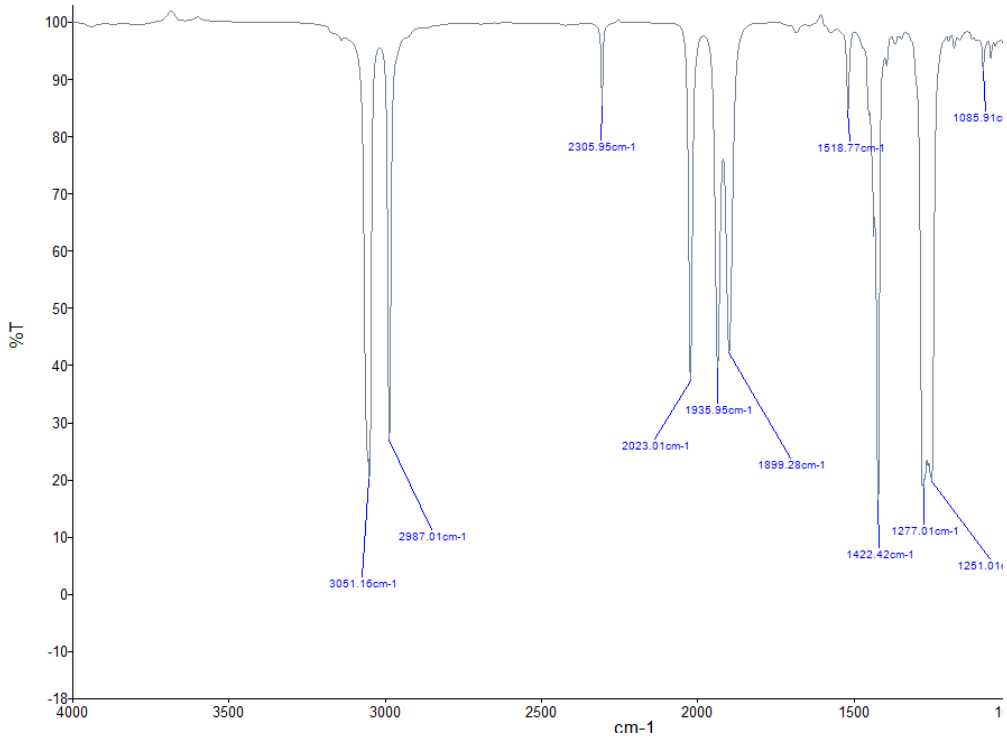


Fig.46 FT-IR of Complex 3 in CH_2Cl_2

The analysis FT-IR was accomplished in CH_2Cl_2, the peaks at 2023 cm^{-1},1935 cm^{-1},1899 cm^{-1} are characteristic of carbonyl group of the complex. Thanks to the symmetry of the complex was possible to correlate the number of peaks observe and the number of carbonyl. This suggest a coordination of ligand as planned in the synthesis.

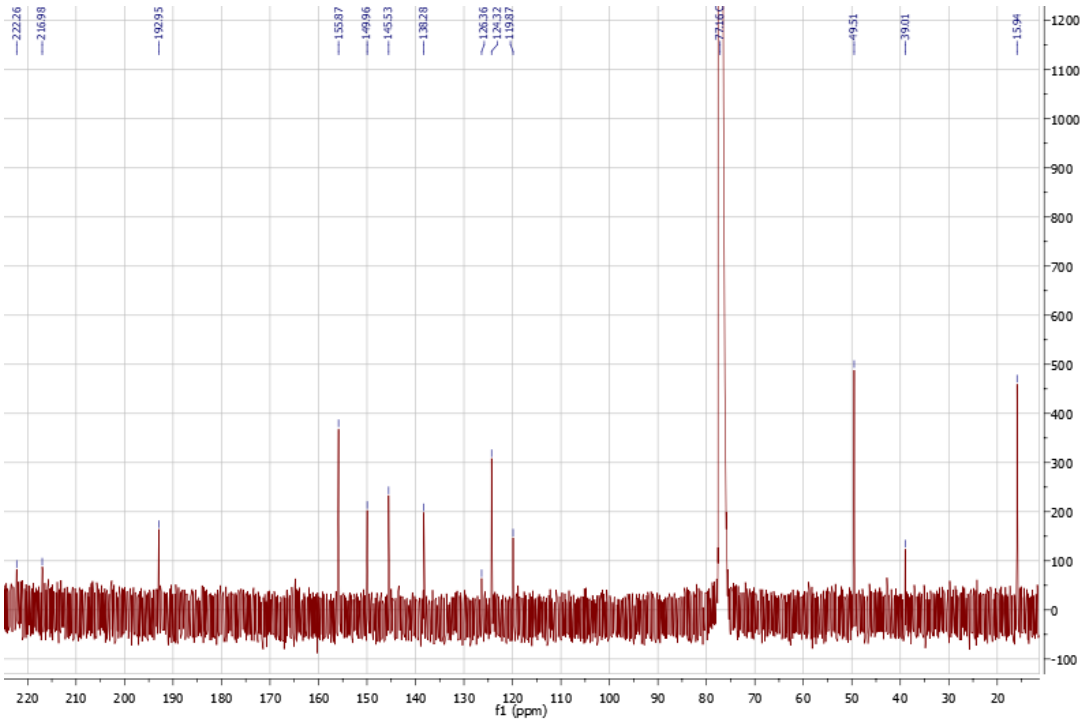


Fig.47 ^{13}C-NMR spectrum of complex 3

The signal at 192.95 suggests the presence of a Mn-carbene and signals at 216.98 and 222.26 suggest the presence of carbonyls, as displayed in similar complexes.[77][78][79] Comparing this spectrum to the spectrum of L3 is possible to find some similarity, the number and the disposition of methyl and CH_2 bridge carbon are similar, the other carbon are shifted presumably due to the coordination.

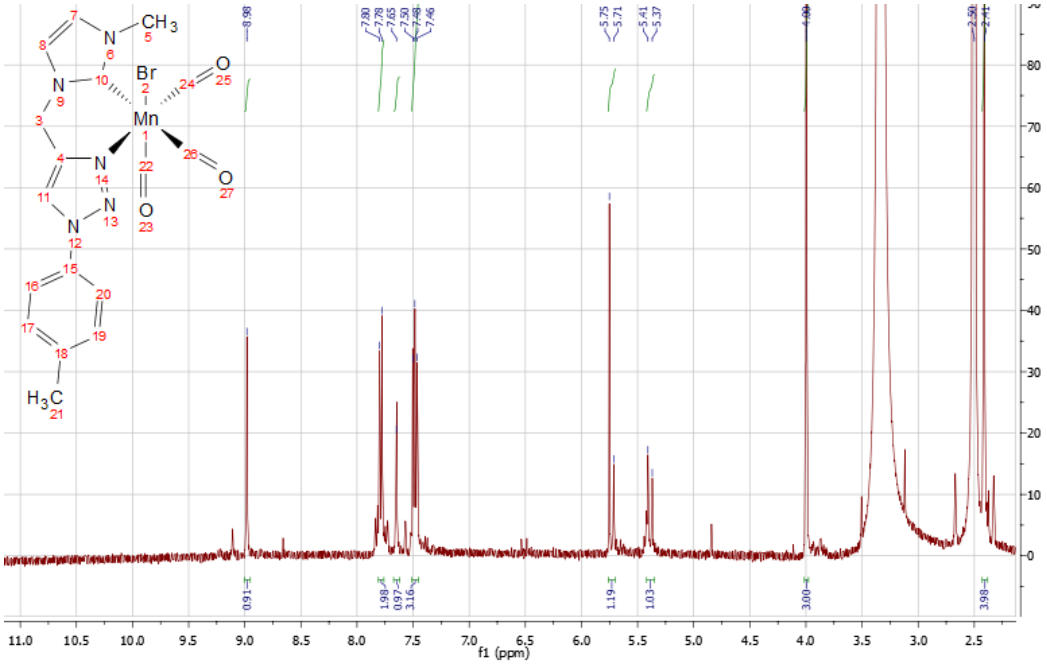


Fig.48 ^{1}H-NMR spectrum of complex 3

The ^{1}H-NMR spectrum suggests the presence of a H-Trz at 8.98ppm that is in line with the coordination by N, the absence of H-imid could be due to the coordination. Also the peak of triazole is almost unchanged, the other peaks are a bit shifted.

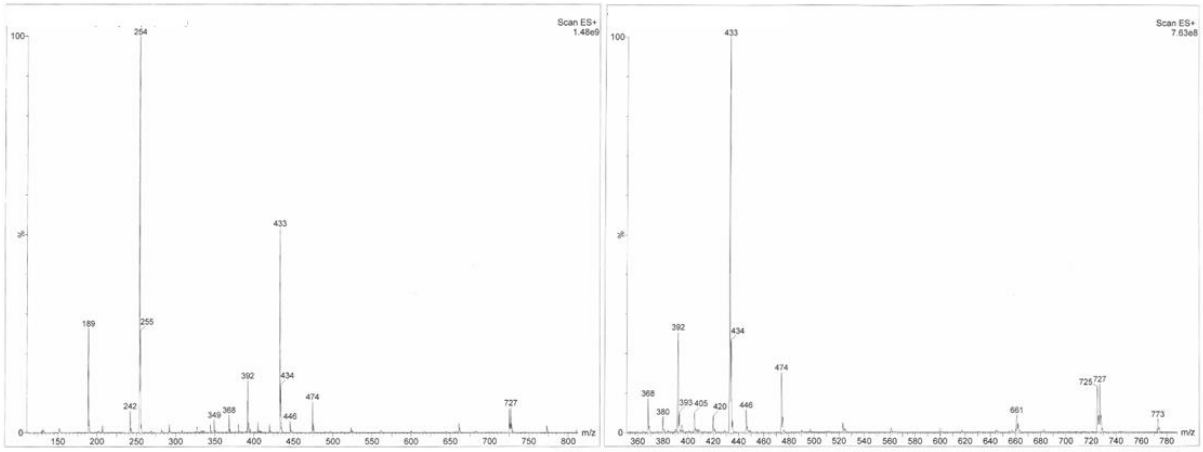


Fig.49 ESI$^+$-MS spectrum of complex 3

From the ESI-MS experiment several peaks can be identified as following described: 725 m/z [M+$C_{14}H_{17}N_5$], 254 m/z [$C_{14}H_{17}N_5$], 392 m/z [M-Br], 433 m/z [M-Br+CH_3CN], 474m/z [M-Br+2CH_3CN]

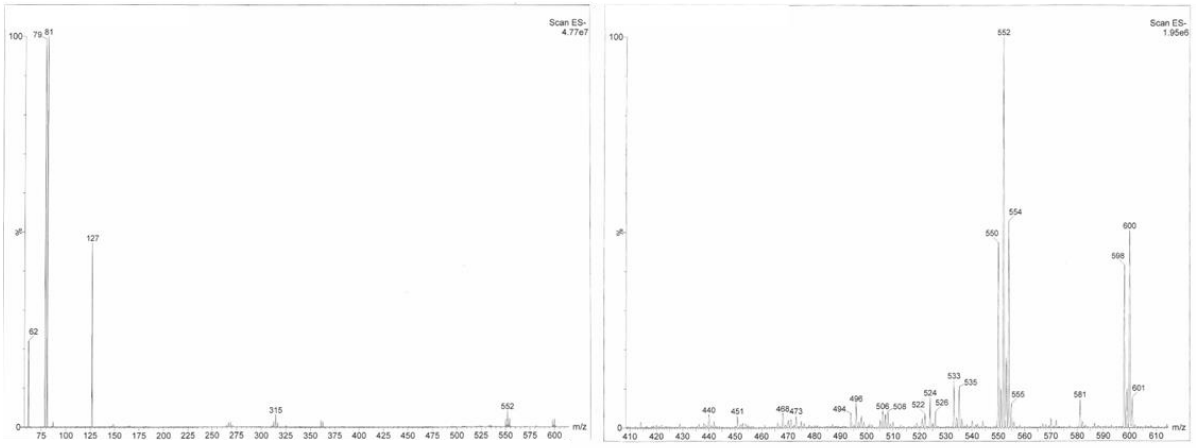


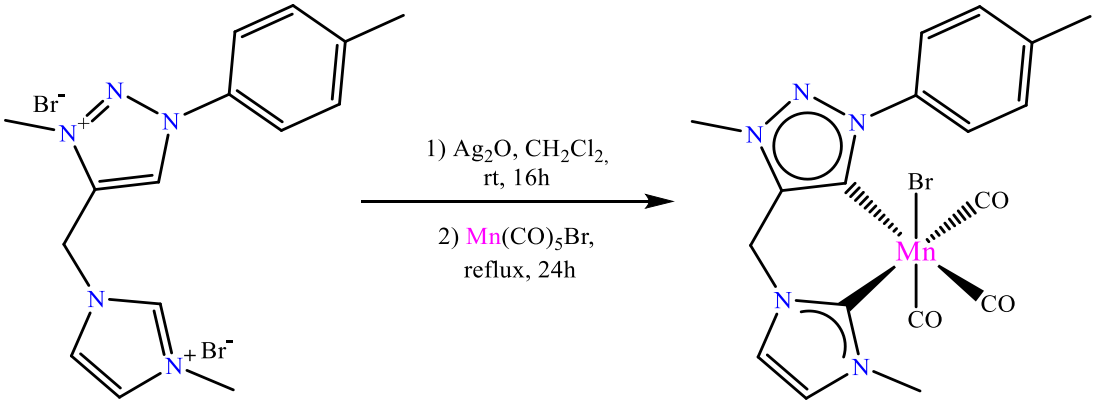
Fig. Fig.50 ESI$^-$-MS spectrum of complex 3

550 m/z [M+Br], 522 m/z [M+Br-CO], 494 m/z [M+Br-2CO], 598 m/z [M+I]

The ESI-MS analysis suggests that some rearrangement occurred during the ionization. As an example in positive mode the peak at 725 m/z is a combination of complex plus a molecule of ligand and also at 392 m/z the peak of complex minus bromine, in this analysis was not possible detect the peak of molecular ion of complex maybe because the condition during the ionization were to harsh for the complex to resist unaltered. Even in the negative mode there is not the peak of complex but there are peaks of complex plus bromine and with losses of carbonyls. Taking in consideration all spectra is likely possible to confirm that the complex was obtained as expected.

Complex 4

Attempts to synthesise complex 4 were made following similar methods as those described for the synthesis of complexes 1 and 2



Scheme 23 Attempt to synthesize complex 4

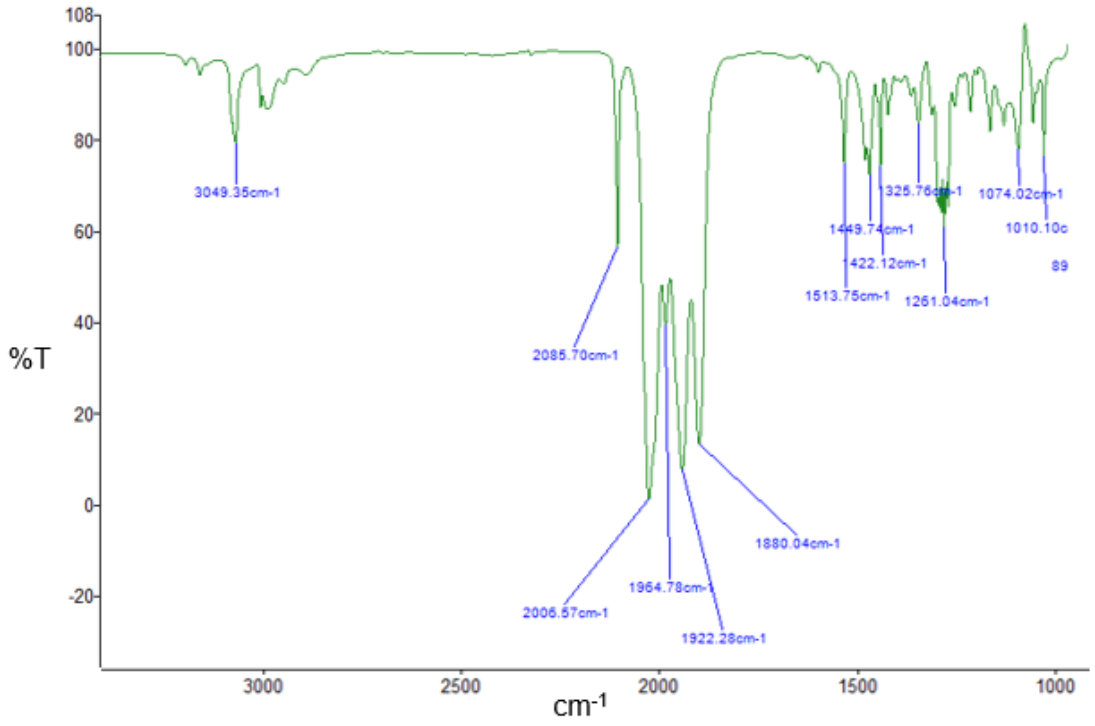


Fig.51 FT-IR of Complex 4 in CH_2Cl_2

The analysis FT-IR was accomplished in CH_2Cl_2, the peaks at 2006 cm^{-1},1922 cm^{-1},1880 cm^{-1} are characteristic of carbonyl group of the complex, the peaks at 2085, 1964 are most likely some impurity containing carbonyl group.

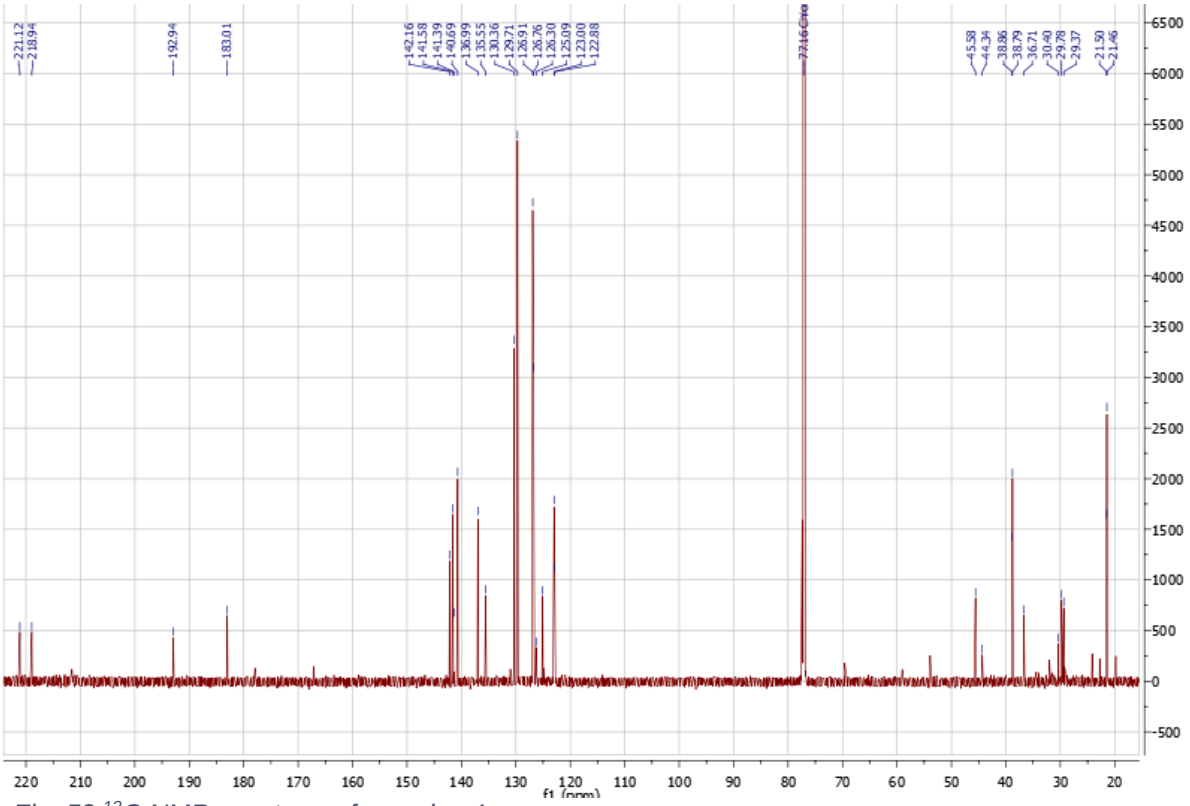


Fig. 52 ^{13}C NMR spectrum of complex 4

In the ^{13}C-NMR spectrum the presence of signals at 183.01 and 192.94 suggest presence of Mn-carbene this could evaluate the coordination of metal with ligand and also signal at 221.12 and 218.94 suggest the presence of carbonyl as showed in similar complexes.[77][78][79] The presence of all these peaks could be due to some ligand left.

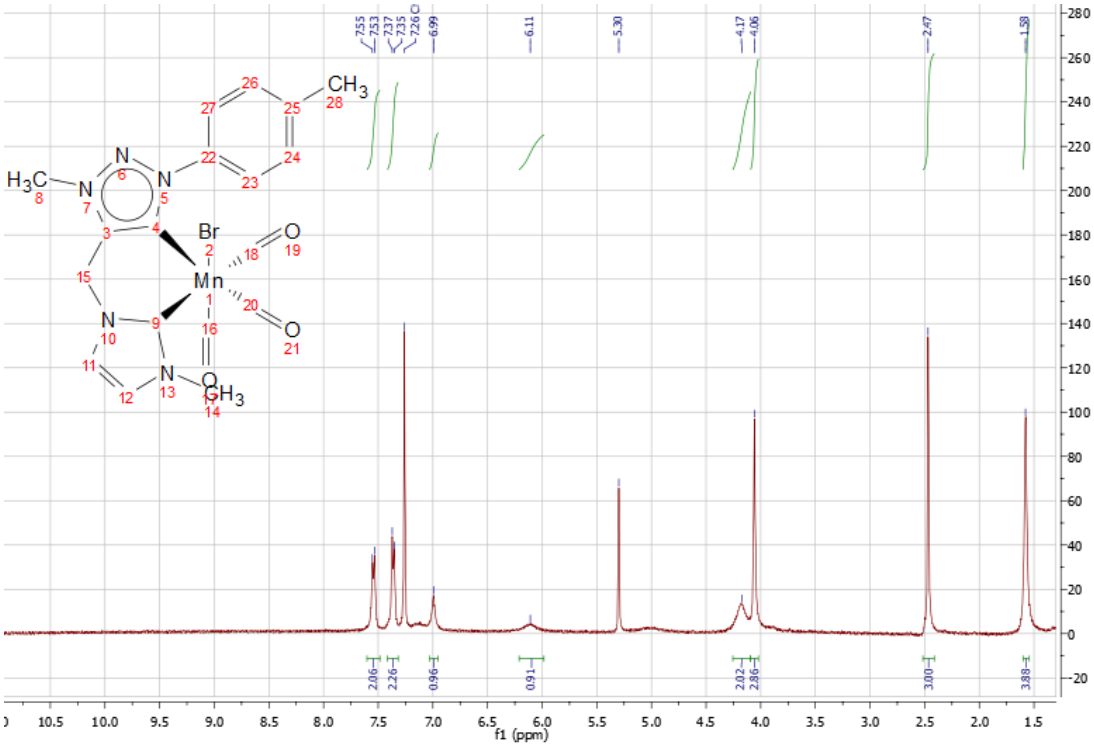


Fig.53 ^{1}H-NMR spectrum of complex 4

In the ^{1}H-NMR spectrum is possible to observe the absence of proton after aromatic zone, that in L4 correspond to the C-H of triazole and N(CH)N in imidazole, and the shift of the other proton is most likely due to the coordination.

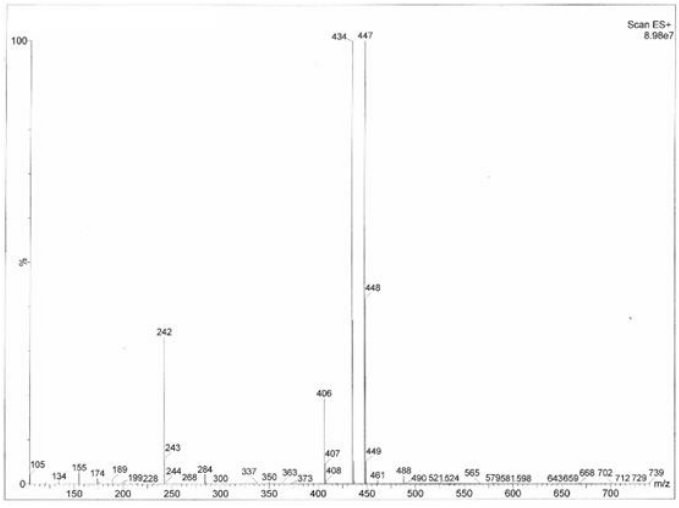


Fig.54 ESI-MS spectrum of complex 4

From the ESI-MS experiment several peaks can be identified as following described: 406 m/z [M-Br], 434 m/z [M-Br+CO], 447 m/z [M-Br+ CH_3CN].

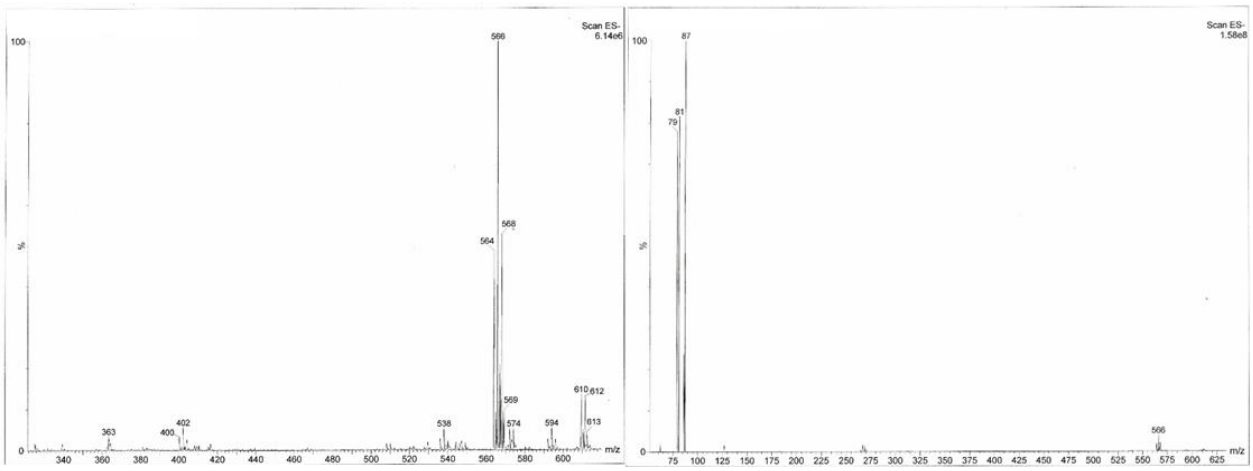


Fig.55 ESI-MS spectrum of complex 4

564 m/z [M+Br], 538 m/z [M+Br-CO], 592 m/z [M+Br+CO]

Characterization of complex 4 suggest the presence of the desired product but is likely the co-presence of small amount of contaminant. In the FT-IR are visible three characteristic signals of carbonyl but there are also other two peaks in the same region, this displays the possibility to have the desired product plus some impurity containing carbonyl groups The ^{13}C-NMR of the crude shows signals of carbonyl and Mn-carbene as expected, there are also some peaks of impurities most likely attributable to some ligand left (doubled peaks in ligand zone), there are not discreet peaks of carbonyl impurity, shown in FT-IR. Comparing ^{1}H-NMR of ligand and complex is possible to determinate the coordination, of triazole and imidazole ring. From ESI-MS analysing is not possible to detect the molecular ion. Anyway, there are peaks corresponding to the molecular ion minus an atom of bromine and addition of other groups like CO and solvent (406 m/z [M-Br], 434 m/z [M-Br+CO], 447 m/z [M-Br+ CH_3CN]). With the negative mode vice versa is possible to notate un inverse behaviour, the main peaks are composed of molecular ion plus an atom of bromine an loss or gain of CO (564 m/z [M+Br], 538 m/z [M+Br-CO], 592 m/z [M+Br+CO]). These peaks display that some rearrangement happened during the ionization of the molecule. In conclusion is likely to have the desired compound with some impurities, probable ligand left and an unknown carbonyl compound, the separation and eventually the characterization of them will be attempted in future studies.

Conclusion

In this thesis, work was focused on the synthesis and characterization of Mn-NHC complexes. The synthesis of the complexes depicted in Fig 56 was accomplished. Complexes 1 and 2 were already synthetized in the group of Royo, and complexes 3 and 4 are new complexes. All complexes 1-4 were characterized by ^{1}HNMR, ^{13}CNMR, FT-IR and ESI-MS.

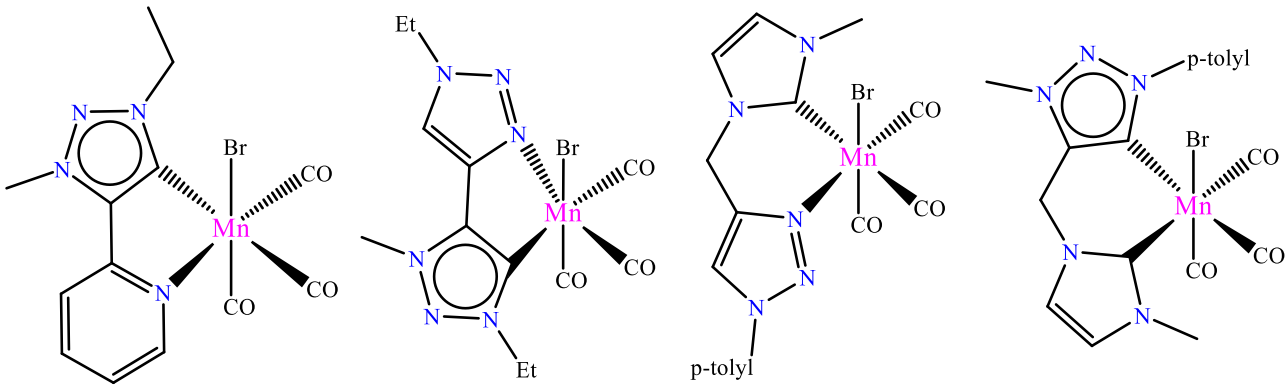


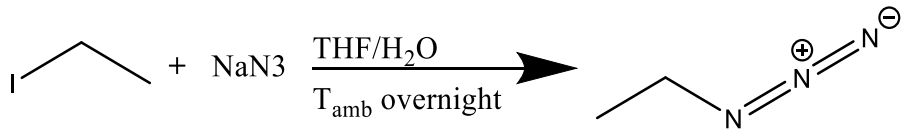
Fig.56 Manganese-NHC complexes

Experimental section

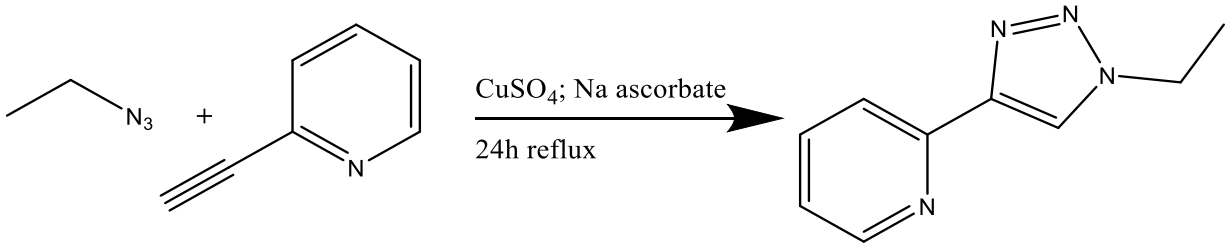
General information

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. 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 Agilent Technologies 7890A Gas Chromatograph provided with a capillary column Agilent 19091J-413 HP-5, 30 m x 0.320 mm x 0.25 µm. 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.

Synthesis of 1-ethyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium bromide

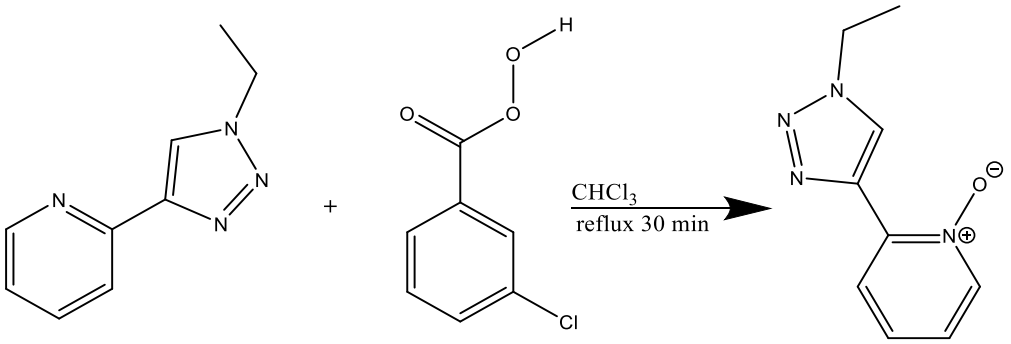


In a schlenk tube was added 1.75 g of NaN_3 (3.5eq), 60 mL of a mixture of THF/H2O (1/1) and then add 0.62 mL EtI (1eq) after the reaction was left react overnight at room temperature.



At the mixture was added 36 mg CuSO4; 444 mg sodium ascorbate; 0.56 mL 2-ethynylpyridine (0.7 eq) after the addictions was left react for 24h at reflux. At completed reaction the solution was left cool down to room temperature with a flux of N_2 and THF was removed by the vacuum line. To separate the compound was execute an extraction with 3X50 CH_2Cl_2 ; the organic phase was collected and washed with a solution of NH_3 10% 2X50, water 2X50 and brine 2X50. The organic solution was dried with Na_2SO_4, filtered and the solvent was removed with the use of rotavapor. Obtaining 1.0785 g of product (Yield 91.07% based on ethynylpyridine). The characterization was achieved by NMR.

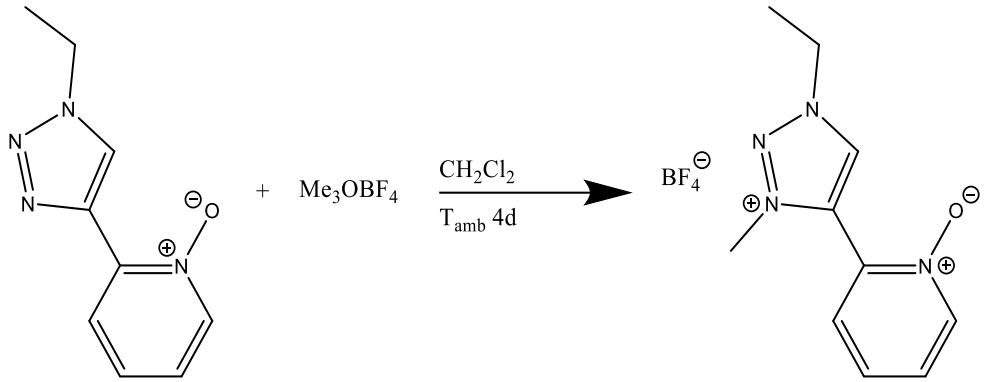
^{1}H-NMR (399.9 MHz, $CDCl_3$, 25°C): δ ppm 8.47 (d,1H,CH_{ar}), 8.09(s,1H,CH_{trz}), 8.06(d,1H,CH_{ar}), 7.68(t,1H,CH_{ar}), 7.12(t,1H,CH_{ar}), 4.37(q,2H,CH_2), 1.49(t,3H,Me).



In a schlenk tube were placed 1g of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine (1eq); 40 mL CHCl3; 2 g 3-chlorobenzoperoxoic acid (2eq) and refluxed for 30 min past this time the flask was cooled to room temperature end added 250 mL CH_2Cl_2, washed 3X125 NaOH 1M, dried with Na_2SO_4, filtered, the solvent was removed by rotavapor and to eliminate the last trace of solvent the product was leaved under vacuum. The product obtained is 0.9417 g (Yield 86.3%). The characterization was achieved by NMR.

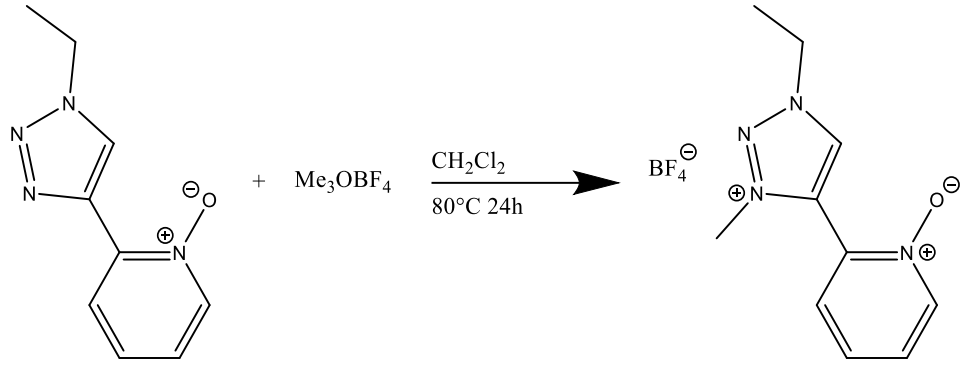
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.14 (s,1H,CHtrz), 8.39 (d,1H,CHar), 8.35 (d,1H,CHar), 7.48 (t,1H,CHar), 7.40 (t,1H,CHar), 4.51 (q,2H,CH2), 1.48(t,3H,Me)

Method 1

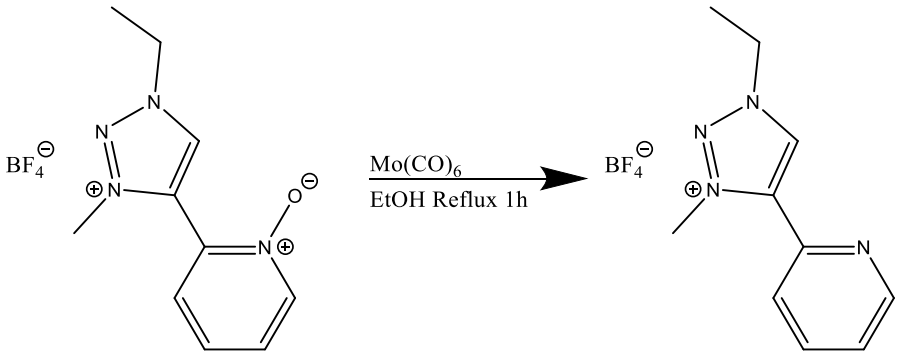


In a schlenck tube were placed 0.9400 g of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine 1-oxide (1eq) was dissolved in 25 mL of dry CH_2Cl_2 and was added 2.805 g of Me_3OBF_4 (4eq) and was leave under stirring for 4d at room temperature under N_2 atm. The solvent was removed under vacuum. The product wasn't isolated but was used row in the followed step.

Method 2

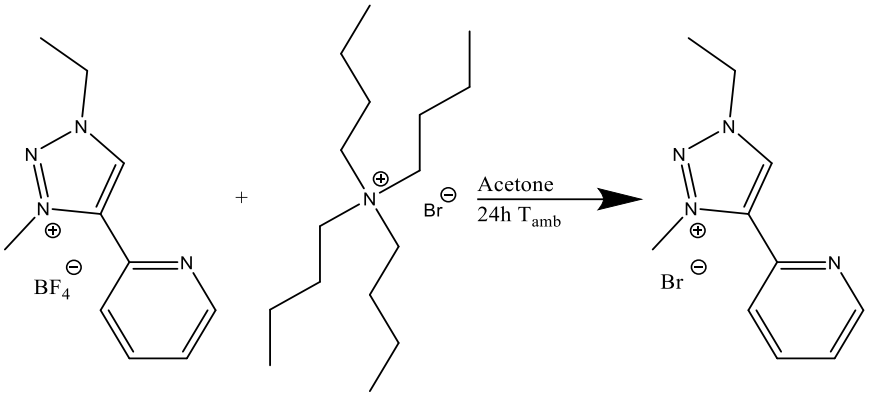


In a pressure tube were placed 1 g of 2-(1-ethyl-1H-1,2,3-triazol-4-yl)pyridine 1-oxide (1eq) was dissolved in 25 mL of dry CH_2Cl_2 and was added 3 g of Me_3OBF_4 (4eq) and was left under stirring for 24h at 80°C under Ar atm. The solvent was removed under vacuum. The product wasn't isolated but was used row in the followed step.



The product was dissolved in 100 mL of anhydrous EtOH, was added 1.517g (1eq.) of $Mo(CO)_6$ and was putted under reflux for 1h. The solvent was removed and the separation was carried by column chromatography with a mixture of solvent CH_2Cl_2/MeOH in rapport 10/1 obtaining 0.8297 g (Yield 60.8% method 2 55.57%). The characterization was achieved by NMR.

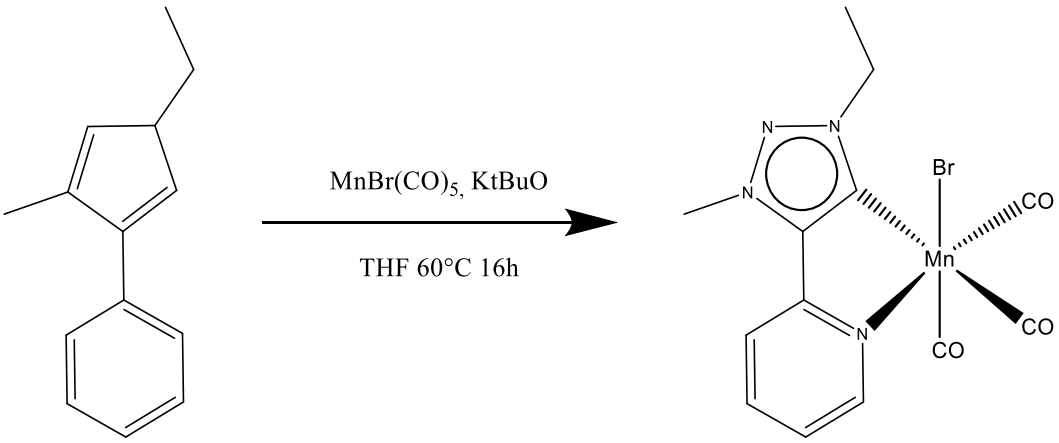
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.51 (s,1H,CHtrz), 8.86 (d,1H,CHar), 8.15 (t,1H,CHar), 8.04 (d,1H,CHar), 7.67 (t,1H,CHar), 4.70 (q,2H,CH2), 4.56 (s,3H,Me), 1.60 (t,3H,Me)



The product from the previous step was dissolved in the minimum amount of acetone possible and was added 1.8312 g of TBAB (2eq.). the reaction mixture was left at room temperature for 2h and the white precipitate was filtered and was washed with 10 mL of acetone and 2x10 of ethyl ether obtaining 0.5085g (Yield 62.9%). The characterization was achieved by NMR.

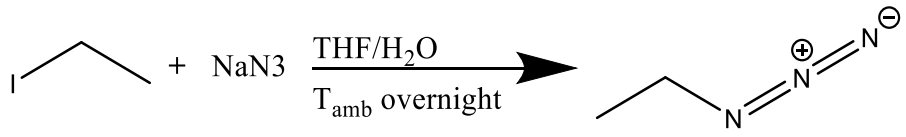
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.58 (s,1H,CHtrz), 8.86 (d,1H,CHar), 8.16 (t,1H,CHar), 8.07 (d,1H,CHar), 7.70 (t,1H,CHar), 4.70 (q,2H,CH2), 4.57 (s,3H,Me), 1.61 (t,3H,Me)

Synthesis of complex 1

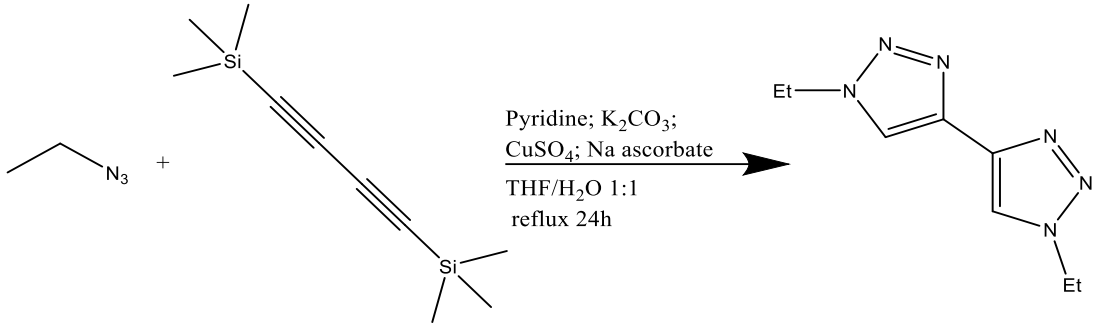


$MnBr(CO)_5$ 0.3983 g (1.3eq) was suspended in THF 25 mL and KtBuO 0.1626 g (1.3eq) was first added, followed by slow addiction of 1-ethyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium 0.3 g (1eq). the resulting suspension was heated at 60°C overnight under stirring. All volatile were removed under vacuum and the resulting residue was washed with Et_2O 4x20 mL and dissolved in CH_2Cl_2 100 mL . The CH_2Cl_2 solution was washed with water 100 mL, and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow crystalline powder.(Yield 88.4%) The characterization was achieved by NMR,ESI-MS and FT-IR.

Synthesis of 1,1'-diethyl-3-methyl-1H,1'H-[4,4'-bi(1,2,3-triazol)]-3-ium



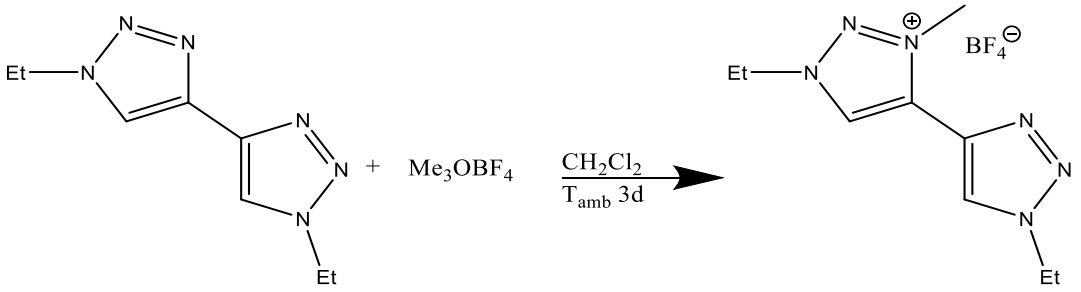
In a schlenk tube was added 0.87 g (3eq) of NaN_3, 30 mL of a mixture of THF/H_2O (1/1) and then add 0.36 mL (1eq) EtI after the reaction was left react overnight at room temperature.



At the mixture(0.95eq EtN_3) was added 0.411 g (1eq) 1,4-Bis(trimethylsilyl)butadiyne, 0.196 mL of pyridine, 0.582 g K_2CO_2, 73 mg $CuSO_4$, 0.582 g sodium ascorbate after the addictions was heated and left react for 24h. At completed reaction the solution was left cool down to room temperature with a flux of N_2 and THF was removed by the vacuum line. To separate the compound was execute an extraction with 3X50 mL CH_2Cl_2 ; the organic phase was collected and washed with a solution of NH_3 10% 2X50, water 2X50 and brine 2X50. The organic solution was dried with Na_2SO_4, filtered and the solvent was removed with the use of rotavapor. Obtaining 0.3526 g of product (Yield 87.4 based of alkyne). The characterization was achieved by NMR.

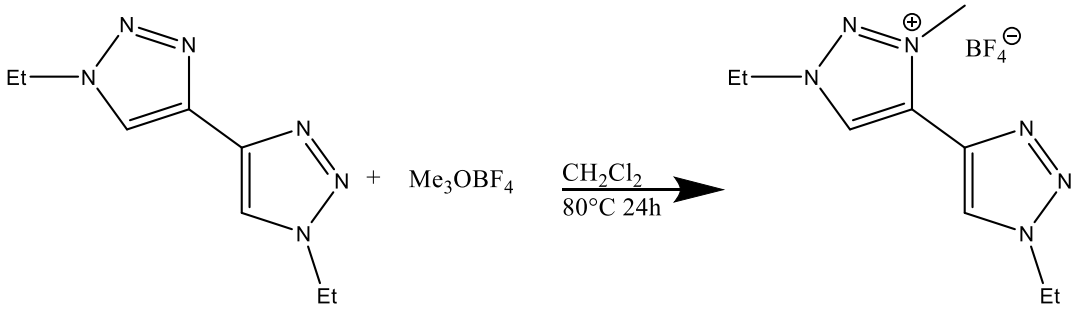
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 8.49 (s,2H,CHtrz), 4.44 (q,4H,CH2), 1.48 (t,6H,Me)

Method 1



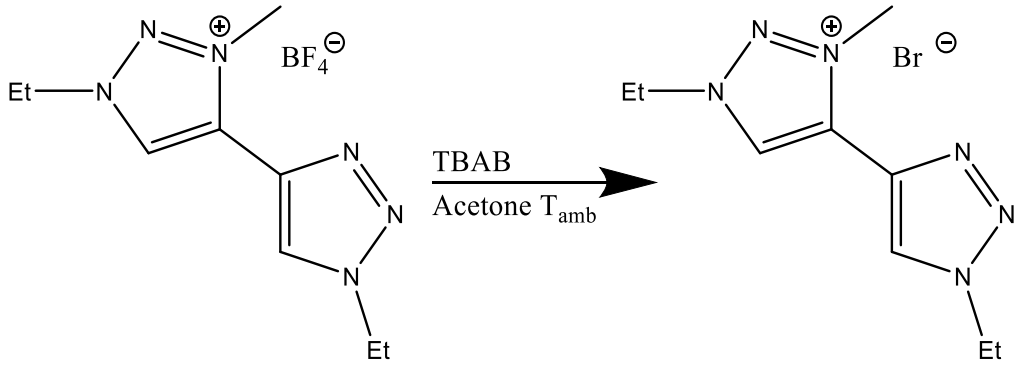
In a schlenck tube were placed 0.313 (1eq) of 1,1'-diethyl-1H,1'H-4,4'-bi(1,2,3-triazole) was dissolved in 45 mL of dry CH_2Cl_2, was added 0.2 g (0.8eq) of Me_3OBF_4 and was left under stirring for 3d at room temperature under N_2 atm. The solution was putted in 200 mL of hexene and the precipitate was filtered and the remaining solvent was removed under vacuum obtaining 0.335g (Yield 87.5%). The characterization was achieved by NMR.

Method 2



In a pressure tube were placed 0.685 (1eq) of 1,1'-diethyl-1H,1'H-4,4'-bi(1,2,3-triazole) was dissolved in 90 mL of dry CH_2Cl_2, was added 0.5 g (0.95eq) of Me_3OBF_4 and was leave under stirring for 24 at 80°C under Ar atm. The solution was putted in 300 mL of hexene and the precipitate was filtered and the remaining solvent was removed under vacuum the solid was washed with 50mL of CH_2Cl_2 and dried under vacuum obtaining 0.831g (Yield 79.30%). The characterization was achieved by NMR

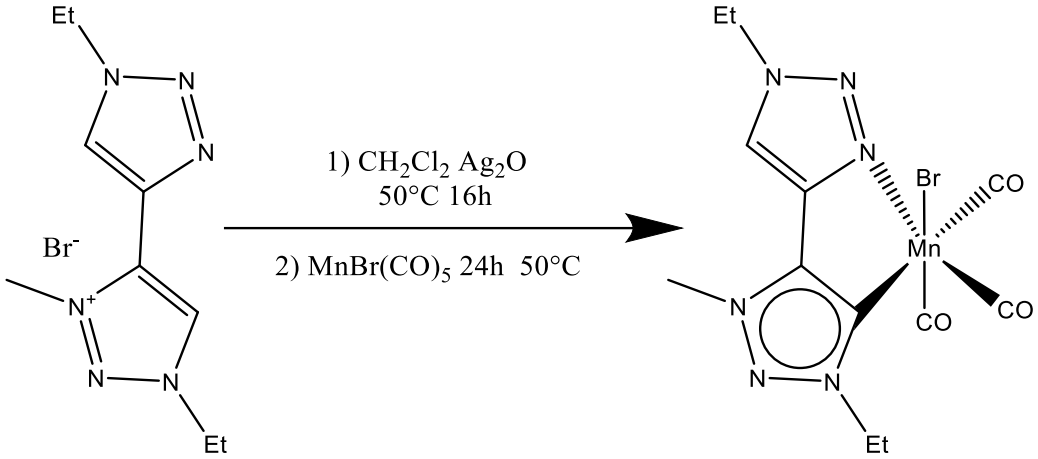
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.34 (s,1H,CHtrz), 8.97 (s,1H,CHtrz), 4.69 (q,2H,CH2), 4.56 (q,2H,CH2), 4.46 (s,3H,Me), 1.58 (t,3H,Me), 1.52 (t,3H,Me)



The previous product was putted in a schlenck tube and dissolved with the minimum amount of dry acetone possible and was added 0.749 g (2eq) of TBAB and the mixture was left react overnight. The resulting precipitate was filtered and washed with acetone and ether. The remaining solvent was eliminated by vacuum obtaining 0.1366g (Yield 41.7%). The characterization was achieved by NMR.

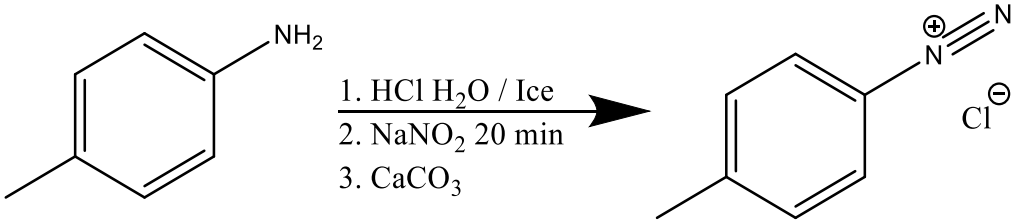
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.40 (s,1H,CHtrz), 9.03 (s,1H,CHtrz), 4.70 (q,2H,CH2), 4.57 (q,2H,CH2), 4.47 (s,3H,Me), 1.58 (t,3H,Me), 1.52 (t,3H,Me)

Synthesis of complex 2

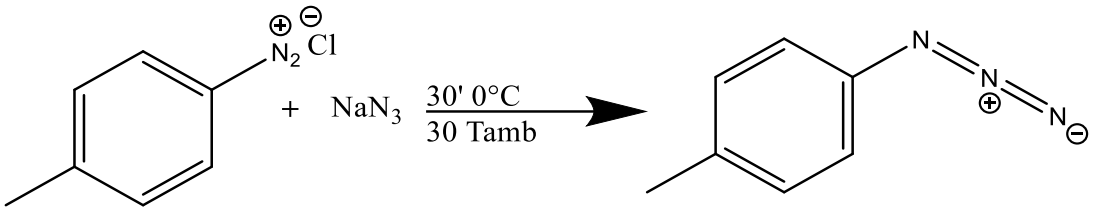


The complex was formed dissolving 136.6 mg (1eq) of the ligand in 15 mL of dry CH_2Cl_2, at this mixture was added 55.12 mg (0.5eq) of Ag_2O and was left react protected from the light at room temperature for 4h. The precursor $MnBr(CO)_5$ (1eq) 130.8 mg was added and was left 24h at 50°C . After cooling to room temperature the mixture was filtered two time through a pad of celite, the mixture was washed two times with water, dried with $MgSO_4$, the solvent was removed and the solid remained was washed with 3x15 mL of Et_2O and dried under vacuum to yield the desired complex a yellow powder 157.8 mg (Yield 78.0%). The characterization was achieved by NMR, ESI-MS and FT-IR.

Synthesis of p-Tolyl azide



In a round bottom flask was first added 5.15 g of p-toluidine, followed by slow addiction of 10 mL of HCl(concentrate), 30 mL of H_2O and 30 mL of ice. In the same time was prepared a solution of $NaNO_2$ (3.69 g in 15 mL of H_2O). The $NaNO_2$ solution was added dropwise and the mixture was left react for 20 min, after that was added 6 g of $CaCO_3$.



At the mixture was added slowly a solution of NaN_3 (3.77 g and 15 ml H_2O). Completed the addiction the mixture was left for 30 min in an ice bath and 30 min at room temperature. The mixture was extracted with pentene and filtered on a plug of silica. The solvent was removed in the rotavapor at low temperature to yield a yellow liquid 3.175g.(Yield 49.61%) The characterization was achieved by NMR.

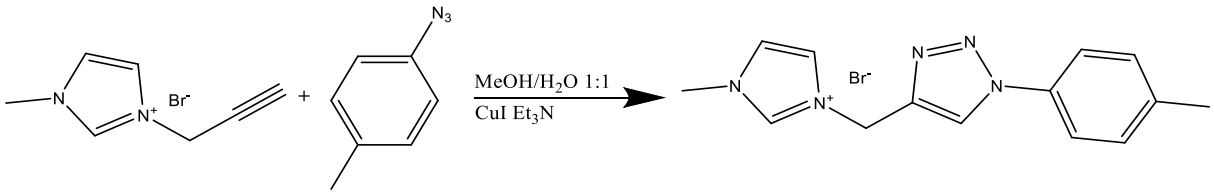
^{1}H-NMR (399.9 MHz, $CDCl_3$, 25°C): δ ppm 7.16 (d,2H,CHar), 6.93 (d,2H,CHar), 2.34 (s,3H,Me)

Synthesis of 1-methyl-3-(prop-2-yn-1-yl)-1H-imidazol-3-ium bromide

In a 100 mL round-bottomed flask was added 2 g (24.36mmol) followed by 25 mL of acetonitrile. To this mixture, was slowly added approximately 2-fold excess of a solution 80 wt% in toluene of propargyl bromide (7.30 g 61.38 mmol). The solution was refluxed for 24h, after which it was cooled to room temperature. All the volatile were removed under vacuum, and the resulting product was washed with Et_2O 2x20 mL. the compound was then dried under vacuum. Obtained 5.2528 g. The characterization was achieved by NMR.

^{1}H-NMR (399.9 MHz, $CDCl_3$, 25°C): δ ppm 10.51 (s,1H,CHimid), 7.59 (s,1H,CH-CH-N), 7.43 (s,1H,CH-CH-N),5.42(s,2H,CH2), 4.12 (s,3H,Me),2.74 (s,1H,CH)

Synthesis of 1-methyl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide

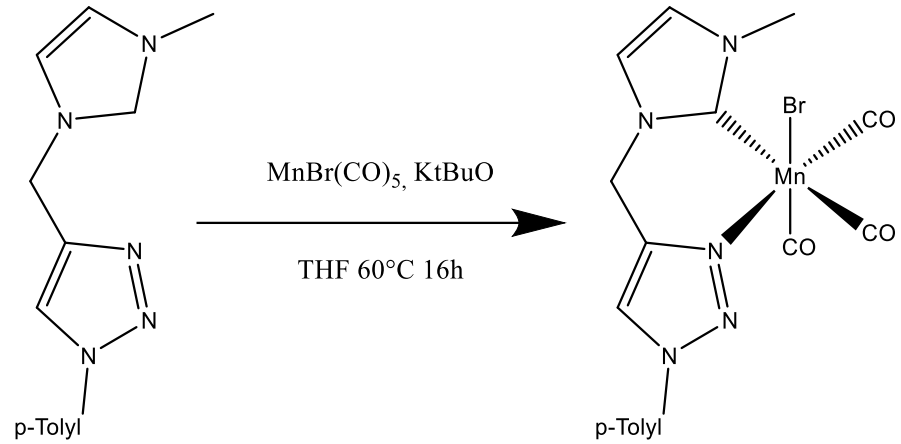


A 50 mL portion of MeOH and H_2O (1:1) was added to a flask containing p-Tolyl azide 0.903g (6.79 mmol) and 1.5 g (7.47mmol) of 1-methyl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide. The resulting solution was stirred for 10 min to make it homogeneous, and 65 mg (0.34 mmol) of CuI and 1.37 g (13.58 mmol) NEt_3 were added to it. The solution was then stirred overnight at room temperature, and the reaction mixture was extracted with CH_2Cl2. The organic layer was dried with Na_2SO_4 and filtered, and the solvent was removed by vacuum. The obtained residue was washed with Et_2O 3x10 mL and dried under vacuum to yield the compound as a cream-colored hygroscopic solid 0.9713 g (Yield 28.6). The characterization was achieved by NMR.

^{1}H-NMR (399.9 MHz, $CDCl_3$, 25°C): δ ppm 10.65 (s,1H,CHimid), 9.02 (s,1H,CHtrz), 7.70 (s,1H,CH-CH-N), 7.65 (d,2H,CHar), 7.30 (d,2H,CHar), 7.17 (s,1H,CH-CH-N), 5.93 (s,2H,CH2), 4.01 (s,3H,Me),2.40 (s,3H,Me).

13C-NMR (150.8 MHz, CDCl3, 25°C): δ ppm 140.72, 139.57, 138.05 (N-CHimid-N),134.36, 130.46(CHar), 124.11 (CHtrz), 122.92 (N-CHimid-CH), 120.69 (CHar), 44.99 (CH2), 36.91(Me), 21.26 (Me)

Synthesis of complex 3



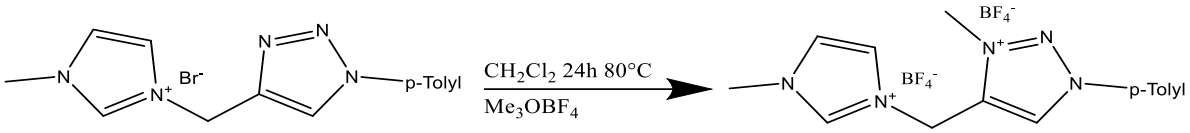
$MnBr(CO)_5$ 0.21 g (1.3eq) was suspended in THF 20 mL and K^{t}BuO 88 mg (1.3eq) was first added, followed by slow addiction of 1-methyl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide 0.2 g (1eq). The resulting suspension was heated at 60°C overnight under stirring. All volatile were removed under vacuum and the resulting residue was washed with Et_2O 4x20 mL and dissolved in CH_2Cl_2 100 mL . The CH_2Cl_2 solution was washed with water 100 mL and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow powder 0.2444 g (Yield 86.3%). The characterization was achieved by NMR, ESI-MS and FT-IR.

^{1}H-NMR (399.9 MHz, $CDCl_3$, 25°C): δ ppm 7.58(s,2H,CHar), 7.32 (s,2H,CH), 7.08 (s,1H,CH), 4.09 (s,3H,Me), 2.43 (s,3H,Me)

^{13}C-NMR (150.8 MHz, $CDCl_3$, 25°C): δ ppm 192.10(C-Mn),155.784,149.876, 145.441,137.37, 124.230, 118.70, 49.414 (CH2), 37.96(Me), 15.838 (Me)

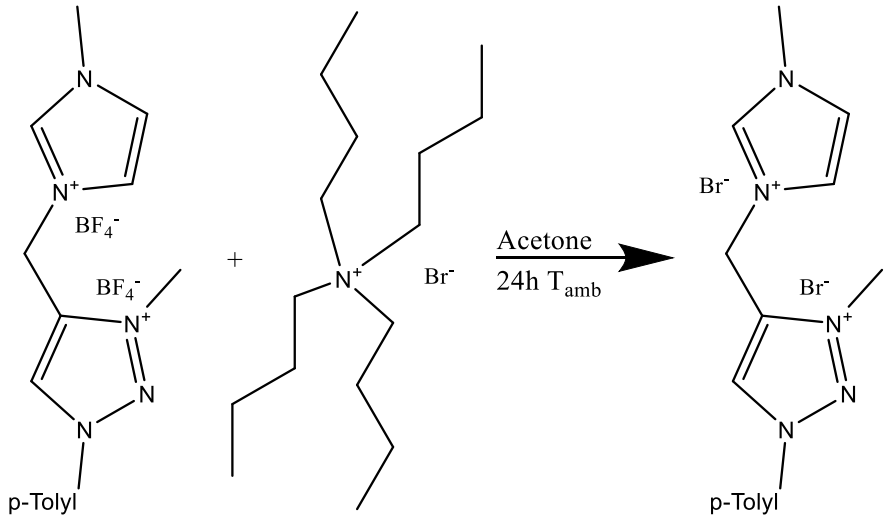
FT-IR CO stretching signal 2023 cm^{-1}, 1935 cm^{-1}, 1899 cm^{-1}

Synthesis of mono(3-methyl-4-((1-methyl-1H-imidazol-3-ium-3-yl)methyl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium) dibromid



0.25g (1eq) of 1-methyl-3-((1-(p-tolyl)-1H-1,2,3-triazol-4-yl)methyl)-1H-imidazol-3-ium bromide, 0.2766 g (2eq) of Me_3OBF_4 and 10 mL of dry CH_2Cl_2 were mixed in 50 mL pressure tube. The tube was closed, and the reaction mixture was heated at 80°C for 24h. all the volatile were removed by vacuum and 10 mL of MeOH and the resulting mixture was stirred for 30min at room temperature in air to decompose the excess of oxonium salt. All the volatile were then removed in vacuo and after washing the residue with Et_2O 3x5 mL and the minimal amount of CH_2Cl_2. The product was obtained as a white solid 0.3166 g (Yield 95%) . The characterization was achieved by NMR.

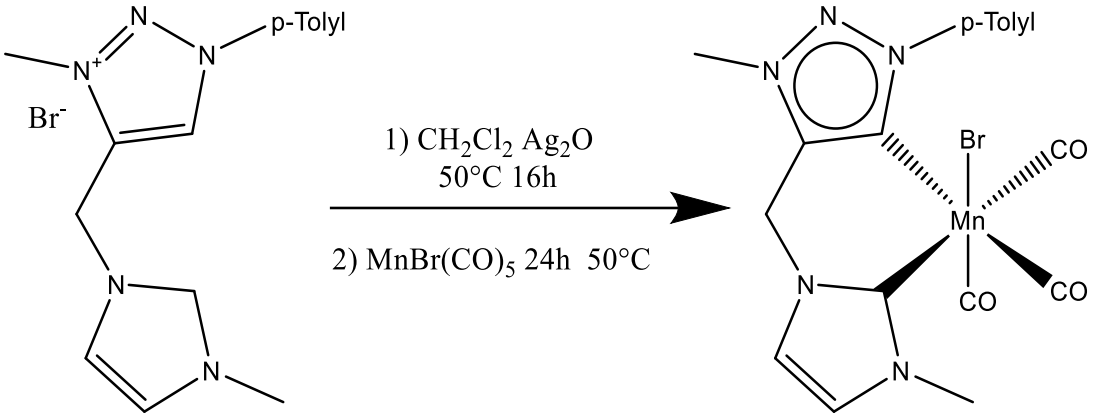
^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.51 (s,1H,CHimid), 9.24 (s,1H,CHimid), 7.85 (d,2H,CHar), 7.83 (s,2H,CH-CH-N), 7.57 (d,2H,CHar), 5.93 (s,2H,CH2), 4.43 (s,3H,Me), 3.90 (s,3H,Me),2.44 (s,3H,Me)



The product from the previous step 0.3166 g was dissolved in the minimum amount of acetone possible and was added 0.9217 g of TBAB (4eq.). The reaction mixture was left at room temperature overnight and the white precipitate was filtered and was washed with 10 mL of acetone and 2x10 of ethyl ether obtaining 0.1878 g (yield 61.23%). The characterization was achieved by NMR.

^{1}H-NMR (399.9 MHz, DMSO-d_6, 25°C): δ ppm 9.60 (s,1H,CHimid), 9.33 (s,1H,CHimid), 7.89 (d,2H,CHar), 7.83 (s,2H,CH-CH-N), 7.57 (d,2H,CHar), 5.97 (s,2H,CH2), 4.45 (s,3H,Me), 3.91 (s,3H,Me), 2.44 (s,3H,Me)

Synthesis of complex 4



The complex was formed dissolving 187.8 mg (1eq) of the ligand in 15 mL of dry CH_2Cl_2, at this mixture was added 101.4 mg (0.5eq) of Ag_2O and was left react protected from the light overnight at 50°C. The precursor $MnBr(CO)_5$ (1eq) 120.3 mg was added and was left 24h at 50°C . After cooling to room temperature the mixture was filtered two time through a pad of celite, the mixture was washed two times with water, dried with $MgSO_4$, washed with 3x15 mL of Et_2O and dried under vacuum to yield the desired complex a yellowish powder 154.8 mg (Yield 72.6%). The characterization was achieved by NMR, ESI-MS and FT-IR.

^{1}H-NMR (399.9 MHz, $CDCl_3$, 25°C): δ ppm 7.54 (d,2H,CHar), 7.36 (d,2H,CHar), 6.99 (s,1H,CH-CH-N), 4.18 (s,2H,CH2), 4.06 (s,3H,Me), 2.47 (s,3H,Me)

^{13}C-NMR (150.8 MHz, CDCl3, 25°C): δ ppm 221.003 (CO), 218.816 (CO), 192.822 (Cimid-Mn), 182.892 (Ctrz-Mn),142.038, 141.458, 141.269,140.562, 136.870, 135.430, 130.233, 129.581, 126.783, 126.632, 124.962,122.874, 122.750, 45.448 (CH2), 38.723, 38.653, 36.576, 29.643, 29.236, 21.365, 21.325

FT-IR CO stretching signal 2005cm^{-1}, 1922cm^{-1}, 1880cm^{-1}

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