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SYNTHETIC STRATEGIES FOR MOLECULAR GOLD CLUSTERS STABILIZED BY N-HETEROCYCLIC CARBENES

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Chapter 1: Introduction

Carbenes, N-heterocyclic carbenes and their organometallic chemistry

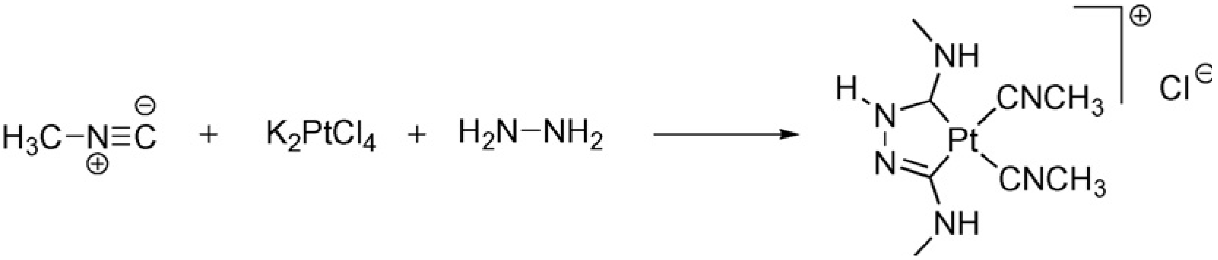
General introduction to carbenes

A carbene is defined as a neutral species containing a divalent carbon atom with a six electron valence shell. The incomplete octet and coordinative unsaturation render free carbenes inherently unstable and they have traditionally been seen only as reactive transient intermediates in chemical transformations, for example cyclopropanation. The carbene carbon can act as a nucleophile and as an electrophile, and this explains their generally very high reactivity and instability. For these reasons the isolation of an uncoordinated carbene remained unachievable for a long time.[1][2]

The first postulation of the existence of carbenes was made in 1855 by Geuther and Hermann: dichlorocarbene was supposed being the fundamental reaction intermediate in the alkaline hydrolisis of chloroform. The same compound was later proposed as an intermediate in the Riemer-Tiemann reaction. Prior to the First World War, Staudinger and Kupfer studied the formation of methylene derivatives and diazomethane as reaction intermediates. Thanks to the recognition given to free radicals, between the 1920s and the 1930s carbenes were regarded as diradical species, for example methylene was seen as a linear species with two degenerate p orbitals, leading to a triplet state. In the 1950s there was a resurgence of the interest in carbenes, that led to the identification of dibromomethylene as the intermediate in the first cyclopropanation, performed in 1954 by Doering et al.[2][3]
Between the 1950s and the 1980s a great number of studies on the electronic configuration of carbenes were performed. Most importantly, two different ground states were hypothesized, a singlet state with a trigonal planar geometry and a triplet state with a linear geometry. In 1964, however, after the synthesis and attempted isolation of dimesithylmethylene, the analysis of the decomposition products led to the assumption of a triplet state with a non-linear geometry.[2][4] In the following years the energy difference between the two ground states of several carbenes was studied, and this allowed to understand the importance of inductive and mesomeric effects (mesomeric effect = electronic delocalization) of the substituents on the

dilvalent carbon on the separation between these states. In particular σ-electron withdrawing groups stabilize the filled non-bonding orbital and favour the singlet state, and electronic delocalizations determine the geometry and the thermodynamic stabilization of the carbene. In particular π-electron-donating groups tend to confer a bent geometry, while π-electron-withdrawing groups a linear geometry. [2]

The history of carbenes in coordination chemistry begun in 1915, when Chugaev synthesized the first metal-carbene complex reacting hydrazine with isocyanide complexes of Pt(II). Due to the lack of adequate characterization techniques, the product was hypothesized being an hydrazine bridged Pt complex, and the correct structure was determined only in 1973 (Scheme 1). [2][5][6]



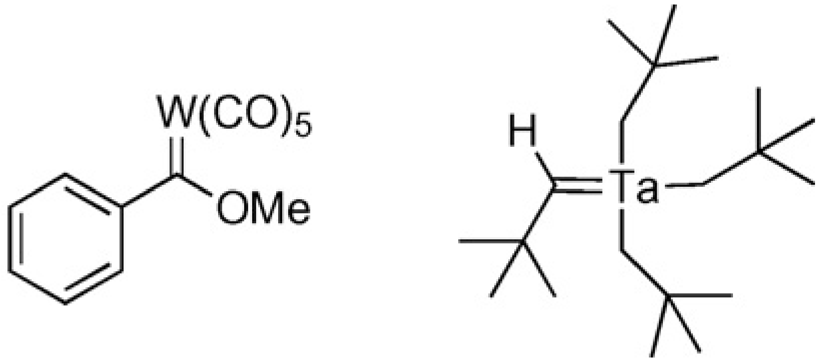
Scheme 1: synthesis of Chugaev's salt. [2]

The first unanbigously characterized metal-carbene complex was synthesized by Fischer in 1964 (methoxyphenylmethylene tungsten(0) pentacarbonyl) (see scheme 2)[7]. In the same period Wanzlick was interested in carbene isolation, and was convinced that diamino carbenes would be stable. His work didn't bring to the isolation of a carbene, but allowed to obtain the first NHC-metal complex in 1968[8]. Őfele obtained another metal-NHC complex at the same time and indipendently, and also reported in the same year a complex with a carbene without α-heteroatoms[9][10]. In 1974 Schrock reported the first synthesis of a metal-alkylidene complex with the metal in high oxidation state (see scheme 2). [11]

Fischer and Schrock carbene complexes are very important species, not only in an historical fashion, but also because they can be used as a basis to understand the extremes in the behaviour of a carbene bound to a metal center.

- In Fischer carbene complexes the carbene fragments are stabilized by the presence of a π-electron-donating heteroatom adjacent to the carbene carbon, and the metal-carbon bond can be described as mutual donor-acceptor interactions of two singlet state fragments. The bonding is due to σ C-->M donation and to π M-->C back-donation,with π electrons polarized towards the metal. The back donation is hampered by the fact that the carbene is already stabilized by its heteroatoms, and in some cases, for example diaminocarbenes (ex: NHCs), this effect is so strong that the M-C bond is represented as single. Fischer carbene complexes are electrophilic and prone to nucleophilic attack at the divalent carbon.

- Schrock carbene complexes possess carbene fragments that are poorly stabilized (ex. alkyl substituents) and that form a bond with the metal that can be described as covalent, originated from the interaction of two triplet state fragments. The π electrons are almost equally distributed between the two fragments and the bond is seen as a true double bond. These species are nucleophilic and prone to react with electrophiles at the divalent carbon, in a process similar to a Wittig reaction. These complexes can be obtained only with early transition metals in high oxidation states (d^0). [2]



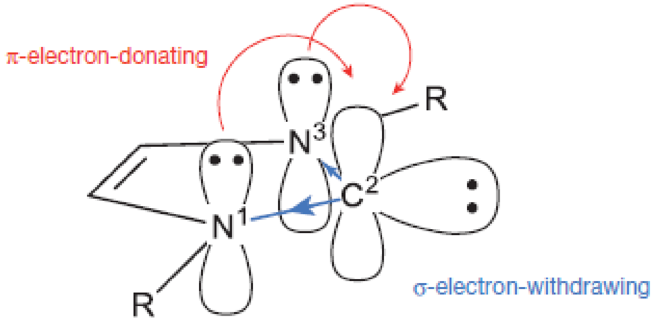
Scheme 2: first discovered Fischer-type (sx) and Schrock-type (dx) metal-carbene complexes.[2]

N-Heterocyclic Carbenes

N-heterocyclic carbenes (NHCs) are a peculiar class of carbenes described as heterocyclic species containing a carbene carbon and at least one adjacent nitrogen atom within the ring structure.[1]

This leads to the presence of a great variety of NHCs, with different ring sizes, substitution patterns and degrees of heteroatom stabilization.

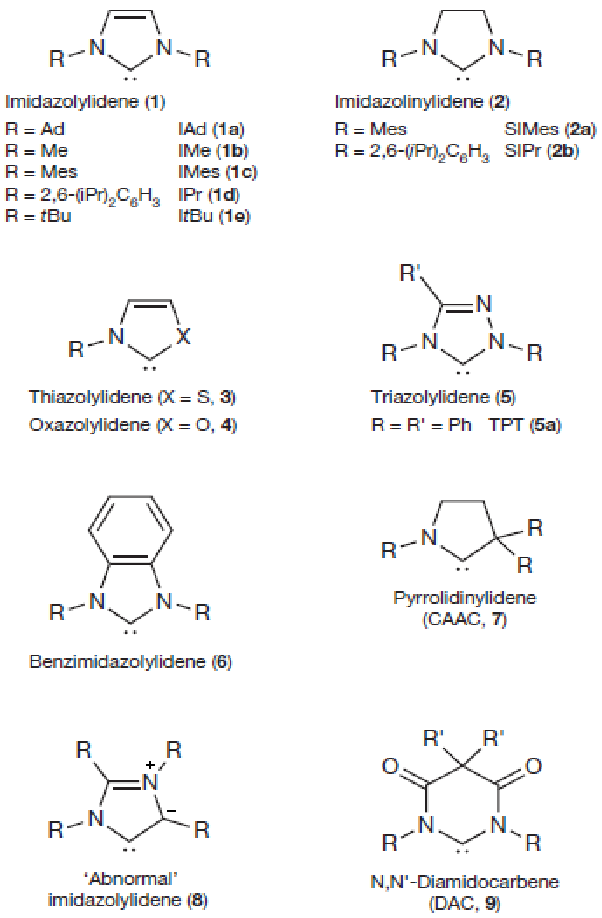
NHCs generally feature bulky substituent on the atoms next to the carbene carbon, that allow kinetic stabilization, sterically disfavouring dimerization. Furthermore, the presence of nitrogen atoms leads to electronic stabilization; NHCs show a singlet ground-state electronic configuration, with a sp^2 hybridized lone pair in the HOMO and an empty p orbital as LUMO (scheme 3). This is due to the fact that the nitrogen atom(s) possess σ-electron-withdrawing and π-electron-donating effects that stabilize the structure both inductively by lowering the energy of the HOMO and mesomerically by donating electron density to the LUMO. The cyclic nature of these compounds also helps their stability, because it forces the carbene carbon into a bent, sp^2-like arrangement.[1]



Scheme 3:effects of the presence of the nitrogen atom(s) on the ground state of an imidazolylidene NHC. [1]

NHCs are a very rich class of compounds; the ones deriving from heteroaromatic heterocycles have a positive contribution towards their stability for their partial aromatic character, and this allows less demand for steric bulk near the carbene carbon, that in turn leads to the possibility of obtaining free carbenes bearing, for example, methyl substituents. Aromaticity is not a key requirement, however, and neither is the presence of two nitrogen atoms adjacent to the divalent carbon. This leads to the possibility of obtaining NHCs with other heteroatoms such as S or O or even without a second heteroatom (called cyclic(alkyl)(amino)carbenes, CAAC). Remote NHCs, where the divalent carbon is not adjacent to a nitrogen atom have also been reported.

The size of the heterocyclic ring has also a significant effect on the characteristics of the carbene and confers variability in this class of compounds. Five-membered rings are the most common, but NHCs with smaller or larger ring sizes have been successfully synthesized; larger rings in particular lead to an increased steric bulk, as the cyclic nature of the compound forces the substituents on the atoms adjacent to the divalent carbon closer to it, and the geometric constraints also play a role in heteroatom stabilization (scheme 4).[1]



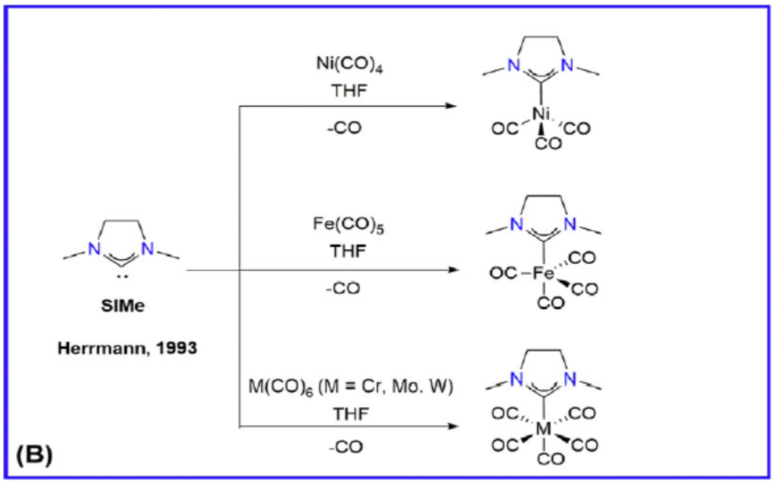
Scheme 4: different types of NHCs.[1]

NHCs form Fischer type metal carbene complexes with transition metals [2]. As already stated, the first report of a metal-NHC complex dates back to 1968, but the real interest for this type of ligand arose in 1991, when the isolation of the first free NHC-type carbene was performed[12]. The great number of studies on these compounds, encouraged by their remarkable stability and simple synthesis, shows that NHCs equal or exceed the ability of phosphines to bind to a great variety of metal centers. A very interesting and useful characteristic of NHCs, demonstrated by these studies, is their ability to bind to both hard and soft metal centers, making them very versatile as ligands.They possess many useful features, including a strong bonding ability arising from both strong σ-donating and tunable π-accepting interactions, high structural tailorability, and sensitivity of electronic and steric properties towards structural modifications. NHCs are able to coordinate to main group elements and can be active as organocatalysts, but the majority of the studies regarding these compounds involve their complexation to transition metals to form organometallic compounds, that have found applications in many fields such as catalysis, even in some of the most important transformations in the chemical industry, and biochemistry. [1][13][14]

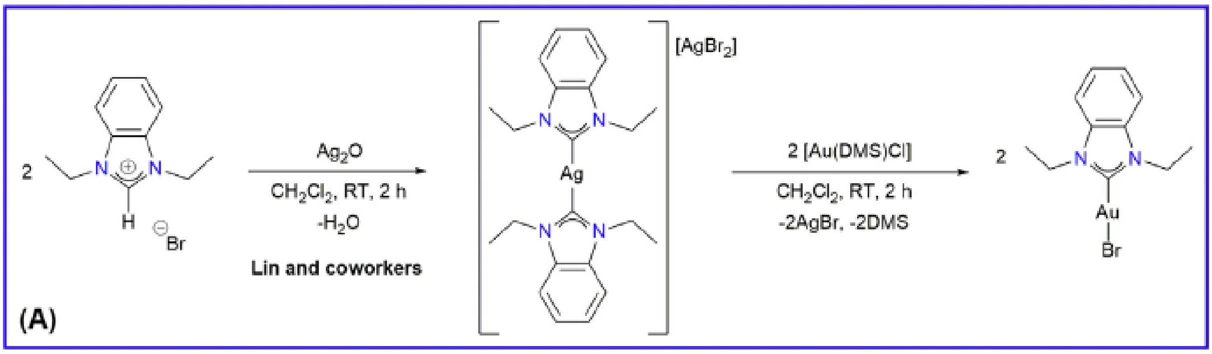
They can in fact be used in the formation of amide bonds from carboxylic acids, aldehydes, alcohols and nitriles in an atom-economical, not expensive and environmentally friendly way. [15] They can convert alcohols to carboxylic acids, hydrogenate alkenes, perform C-H bonds activation and they are active in the Suzuki-Miyaura coupling. They are also active in the Sonogashira-Hagihara coupling reaction, alkylation of amines (even with alcohols), oxidation of alcohols, A^3 coupling. [15]

The high success of these ligands is mainly due to the fact that they can form complexes that are very stable towards oxygen, moisture and heat, and this stability is one of the reasons that led to their growing use for medicinal purpose, especially for the development of new anticancer and antibacterial drugs,[16] together with the fact that they are less toxic than phosphane ligands and have comparable donor properties. In particular, metallodrugs developed with NHC ligands show a lower tendency to exhange ligands, a positive characteristic in physiological environment where substances such as glutathione can be present.[17]

There are different routes for the preparation of metal-NHC complexes; two classic routes are the use of free carbenes (scheme 5), generated in situ or isolated, and transmetalation (scheme 6).



Scheme 5: example of the use of free carbenes for the synthesis of metal-NHC complexes, through ligand displacement.[16]



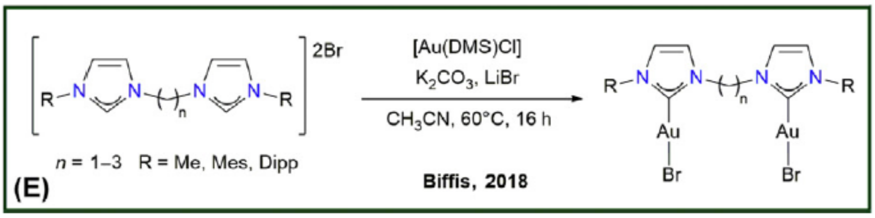
Scheme 6: example of a transmetalation procedure involving Ag for the synthesis of an Au-NHC complex.[16]

The first ligand displacement procedure dates back to the early 1990s, when M-NHC complexes were synthesized by Hermann starting from free carbenes and homoleptic metal-carbonyl complexes such as $Ni(CO)_4$. A more atom economical procedure involves the use of bridged dimeric precursors and two equivalents of free carbene. In these cases the carbene is obtained by the corresponding azolium salt via deprotonation with a strong base in aprotic solvents and inert conditions. Unstable carbenes could be obtained using this procedure, therefore the deprotonation is often performed *in-situ* in presence of the metal precursor of interest. The presence of an external base can be avoided using a metal precursor with basic character and this leads to a cleaner synthesis.

The transmetalation route involves the transfer of the carbene fragment from a suitable metal center (generally Cu(I) or Ag(I), that possess weaker M-NHC bonds and generate insoluble salts as a byproduct) to a precursor of the metal of interest. A great disadvantage of this type of synthesis is its poor atom-economy, that allows the use in large scale only if the byproduct can be recycled.

Less used synthetic routes involve direct oxidative addition of the C_2-H bond of the azolium salt, that requires an electron rich late-transition metal, or the use of electron rich olefins generated by the dimerization of free carbenes with a wide array of metal precursors.[16]

A more recent synthetic strategy to obtain these complexes involves the use of a weak base, such as K_2CO_3, triethylamine or NaOAc, in a reaction with an azolium salt and the metallic precursor (scheme 7). This method in theory allows to operate in air, with mild conditions and green solvents, and allows to obtain several complexes with different transition metals with high yield and purity. No free carbenes form during this reaction, and according to theoretical calculations a concerted mechanism in which the base aids in the formation of the transition state is the explanation. [16]



Scheme 7: example of weak base route for the synthesis of di-NHC Au dinuclear complexes. This procedure has been used during the thesis project to obtain [Au_2(di-NHC)X_2] complexes (X=halide).

In recent years NHCs have begun attracting interest in the field of nanoscience, for the preparation and stabilization of nanoparticles (NPs) and atomically precise nanoclusters (NCs).
The first example of NHC-stabilized NP dates back to 2005, while the first crystallographically characterized NC ligated by NHCs was reported in 2012. [13]

Ligand protected metal nanoclusters

Ligand-protected metal nanoclusters (NCs) are "atomically precise ultrasmall nanoparticles in which surface metal atoms are protected by organic ligands".[18] "Atomically precise" means that these systems are unambigously characterized by a precise number of atoms, arranged in a well-defined structure, equal for all the units. The most common are gold ones, with a number of atoms between 10 and 300. They represent intermediate systems between isolated metal atoms and nanoparticles (figure 1), and they are distinguished from the latter thanks to atomic precision, presence of discrete energy levels and the possibility to be described by an exact molecular formula. The ligands are a fundamental part, as stated in the definition, and allow structural stabilization as well as prevention of agglomeration. Common ligands for these species, known for decades, are thiolates, selenolates, alkynyl and phosphines, while, as stated before, NHCs represent a novel type of ligands that has recently demonstrated its ability to interact with clusters' metal core, together with halides.[18]

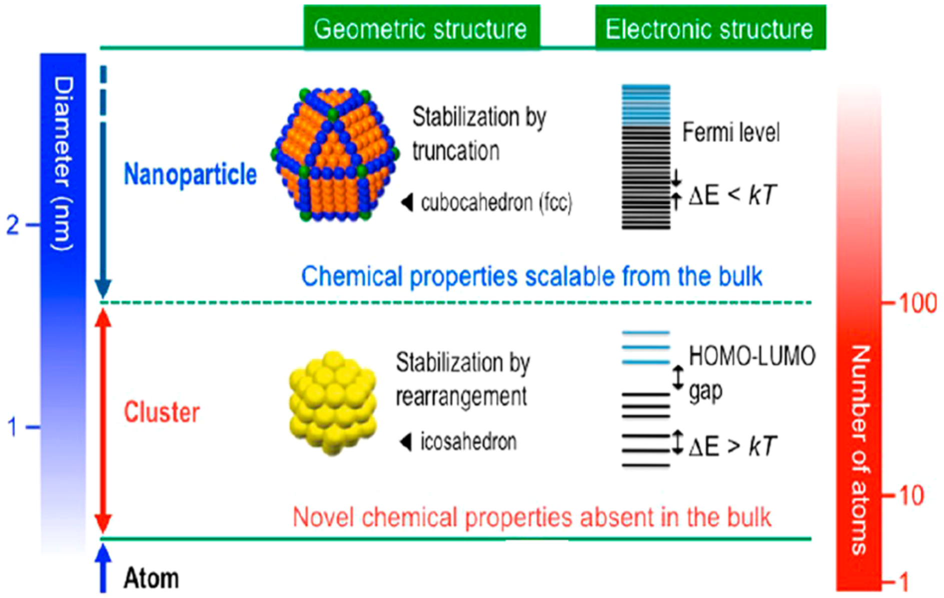


Figure 1: schematic representation of the difference between nanoparticles and nanoclusters, in terms of size, stabilization, properties and energy levels.[18]

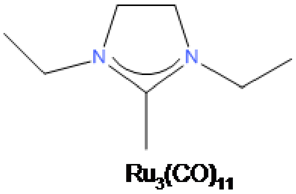
The properties of NCs, including AuNCs, are affected by metal configuration, ligand type and disposition and metal-ligand interface. NHCs allow to obtain NCs with a relatively high stability. Furthermore the ease of preparation of structurally diverse analogues, thanks to the wide variety of substituents that can be placed on the nitrogen atoms, allows a fine tuning of the stereochemical and electronic properties of the resulting NC. [19]

History of (noble) metal nanoclusters

The history of the research in the field of metal nanoclusters starts in the 1960s[20], in physics research gropus. Metal nanoclusters were obtained in gas phase under vacuum or inert atmosphere using methods such as laser ablation and gas condensation, and this allowed the determination of magic numbers, that will be discussed later, and also of the origin of these clusters and of the relation between the number of constituent atoms and the electronic/geometrical structures.[21]

The high interest in this research field, that exploded after the discovery of C_{60}, was due to the fact that these gas phase clusters represent species with a very high fraction of surface atoms, which is a characteristic that is extremely important in determining the properties of a material. The related problem is the fact that the consequent high reactivity of these "naked" clusters doesn't allow their storage, and they must be obtained in situ in experimental apparatuses that allow the study of their properties. The research on this topic has proceeded up to our days, and now is focused on depositing such species on supports to enhance their stability and allow for catalytic applications. [20]

The use of supporting ligands allows the synthesis of noble metal clusters using solution techniques. In the late 1960s and in the 1970s and 1980s, the studies proceeded, with the discovery of several atomically-precise noble metal clusters protected by ligands such as CO and phosphines. Gold represents the most studied metal in this field, and given the high amount of reported noble metal NCs, is impossible to treat exhaustively; nevertheless, given the pertinence with the aim of this thesis project, the focus will be on it. The first report of a ligand protected AuNC dates back to 1969, when $Au_{11}(SCN)_3(PPh_3)_7$ was discovered[22], followed by the determination of the structure of $Au_{11}I_3[(PC_6H_4\text{-}p\text{-}Cl)_3]_7$ in 1970[23]. Several other gold clusters were subsequently discovered, among which Au_{10} and Au_9 species, including the family of italian discovery $[Au_9(PAr_3)_8](X)_3$, where X is a non-coordinating anion.[24] Outside of the gold family it's worth to cite that in 1977 the first NHC-bearing noble metal nanocluster was obtained. In a study on the reactivity of tetraamino-alkenes with group 8 metal-carbonyls a trinuclear Ru cluster, $[Ru_3(Et_2H_2Im)(CO)_{11}]$ (scheme 8) was synthesized[25].

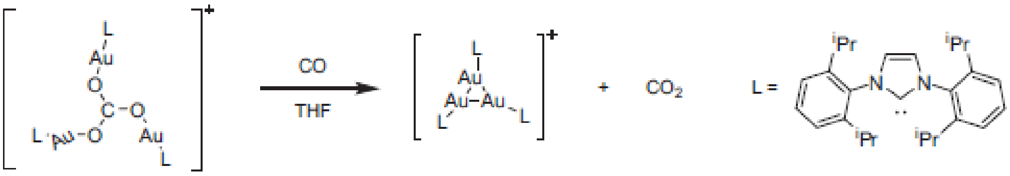


Scheme 8: first NHC protected cluster discovered in 1977; the structure of the NHC ligand is drawn for clarity.

In 1981 the crystal structure of Au_{13} clusters was resolved for the first time, after the prediction of its existence by many theoretical studies and calculations.[26] Around this time Au_{20} and Au_{39} clusters were synthesized thanks to phosphine protection, and also several Au/Ag alloy clusters have been discovered. In 1981 also an Au_{55} cluster, $Au_{55}(PPh_3)_{12}Cl_6$ was discovered[27], and it's worth citing because of its high tendency of forming mono, di and tri-dimensional organized structures. Au_{13} and Au_{55} clusters are significant and interesting to this day for the fact that they are full-shell clusters, meaning that each atom except the ones on the surface has the maximum coordination number, resulting in perfect geometries and in related high stabilities. [20]

In recent years there has been a rapid development of atomically precise metal nanoclusters of metals such as Cu, Ag, Au, Pt, stabilized mainly by phosphine and thiolate ligands.[28] Thiolates are very interesting, because clusters stabilized by the other already listed ligands are very sensitive to air, and can be difficult to synthesize properly, or they can undergo decomposition in solution. The first report of thiolate-stabilized NCs dates back to 1994, and the great advantages of them are the great stability in air and the ease of preparation (direct mixing of reagents in solution exposed to air), due to the strong Au-S bonds. These nanoclusters were considered for a long time as "small nanoparticles with almost uniform size", because they could only be synthesized and handled with a certain (narrow) distibution in the number of constituent atoms, unlike the others. In 2005, thanks to a decade of studies on high resolution separation techniques, the first systematic isolation of $Au_n(SR)_m$ species could be performed and their specific properties determined [28][29].

Very recently (2012), as already stated, the first crystallographically characterized AuNC ligated by NHCs, $[(NHC\text{-}Au)_3]^+$, was reported (scheme 9, figure 2), and it was determined by studies including a wide variety of stabilizing ligands that the Au-NHC bond was the strongest, and also that the bond was stronger in the case of Au in comparison to Cu and Ag. This led to a great interest in the research of NHC-protected Au clusters.[18][30]



Scheme 9: synthesis of the first Au_3^+ cluster protected by NHC ligands, as reported by Sadighi et al.[30]

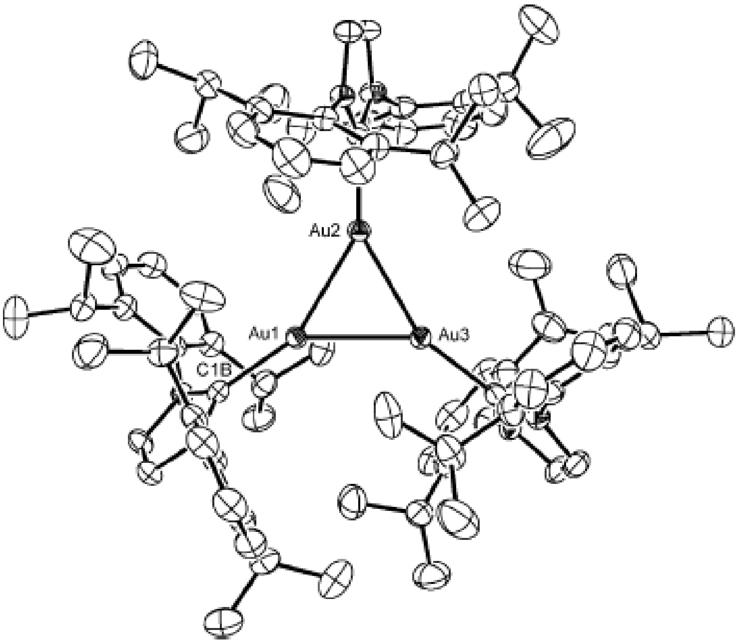
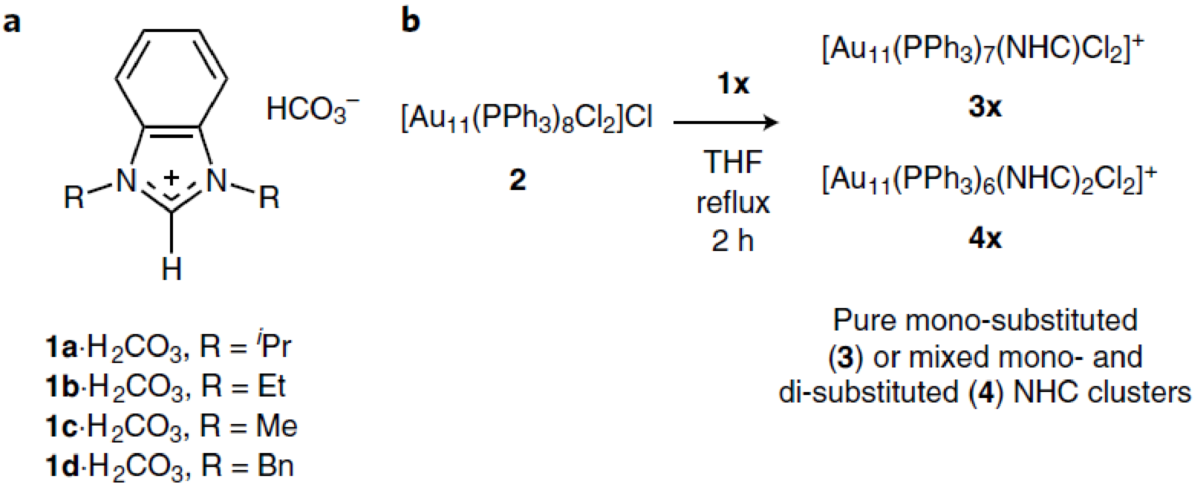


Figure 2: structure (thermal ellipsoid plot) of the first Au_3^+ cluster protected by NHC ligands, as reported by

Sadighi et al.[30]

In 2019 the first NHC-Au cluster with more than 3 Au atoms was discovered (scheme 10, figure 3): the introduction of several different NHCs was performed starting from $Au_{11}(PPh_3)_8Cl_2$. This allowed the discovery that even the introduction of a single NHC led to improvements in stability and electrocatalytic properties. [18][31]



Scheme 10: synthesis of the first Au_{11} clusters bearing NHC ligands as reported by Crudden et al.[31]

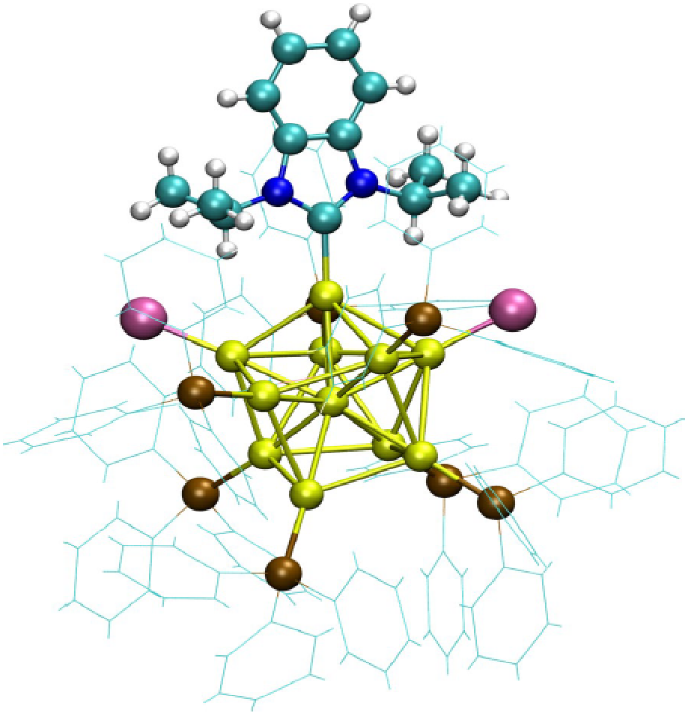
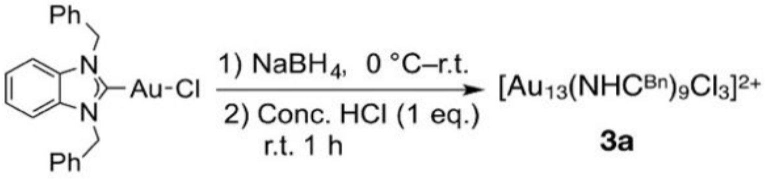


Figure 3: crystal structure of one of the Au_{11} clusters (3a in the previous scheme) bearing NHC ligands as reported by Crudden et al.[31]

Subsequently, Au_{13} clusters protected by NHCs and chlorides were obtained by the direct reduction of NHC-Au-Cl complexes with $NaBH_4$ (scheme 11, figure 4).[32]



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Scheme 11: synthesis of the first Au_{13} cluster bearing NHC ligands as reported by Crudden et al.[32]

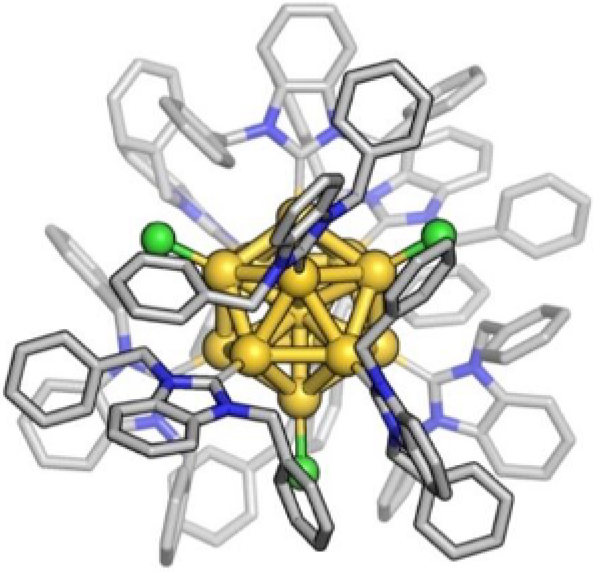


Figure 4: crystal structure of the first Au_{13} cluster bearing NHC ligands as reported by Crudden et al.

These clusters possess 8 valence electrons and a large HOMO-LUMO gap, and the CH-π and π-π interactions between coordinated ligands produce high luminescence quantum yields, conferring rigidity to the structure and discouraging non-radiative decay. By changing the structure of the NHC ligand many different properties can be conferred to the NC, in particular a rather open surface in the case of bulky ligands, that can enhance catalytic properties, a reversible visible absorption and solubility response to cycles of protonation and deprotonation in the case of pyridine-bearing wing-tip groups, and high luminescent quantum yields in the case of bidentate, benzyl rich ligands. [18][19]

Au_{13} clusters and derivatives (ex. Au_{25} ,made up of two Au_{13} units sharing a vertex) therefore show promising properties in the fields of catalysis, bioimaging and nanomedicine, but their synthesis is still a problem in terms of yield: the only approach that seems to grant an high yield is the direct reduction reported by Zheng et. al. for the synthesis of $[Au_{13}(\text{di-NHC})_5Br_2]^{3+}$ with a reported yield of 78% based on gold.[19] Usually reported yields are around 10%. Finding new synthetic routes that lead to better yields is an important open theme in this field.

Other examples of Au_{11} and Au_{13} clusters have been subsequently discovered, with different shapes and ligand patterns (figure 5).

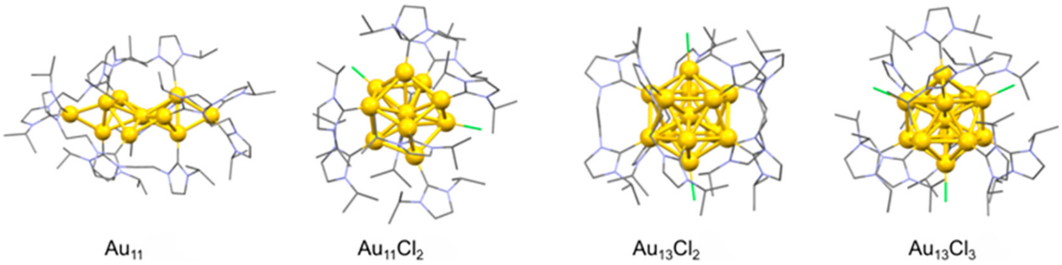
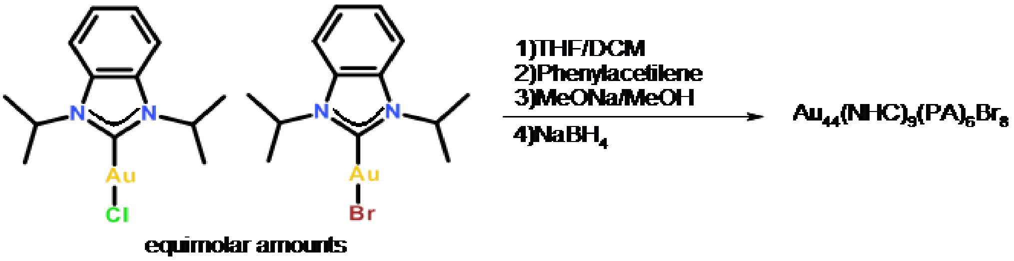


Figure 5: Geometries of Au_{11} and Au_{13} NCs protected by NHC ligands[13].

Synthesis of NHC-protected gold nanoclusters

Some of the synthetic strategies for the synthesis of NHC-protected clusters have already been discussed briefly. They will be repeated here for the sake of clarity and organization.[18][20][33]

1. Reduction with CO (scheme 9 in previous paragraph): carbon monoxide reduction of a trigold carbonate led to the synthesis of the first Au_3 cluster protected by NHCs. The same strategy can be employed using a CAAC ligated Au_3 oxo-bridged species, that can be obtained by reaction of (CAAC)AuCl complexes with Ag_2O or ligand exchange with $(Ph_3PAu)_3O^+$. One advantage of such procedure is the readily quenchable reaction, that can be an advantage to isolate intermediate species.
2. Ligand exchange (scheme 10 in previous paragraph): method used to obtain the first Au_{11} NHC-protected clusters. It involves the reaction of the phosphine-protected cluster with imidazolium-hydrogen carbonate salts or other carbene precursor, liberating the free carbene *in-situ*.
3. Reduction with $NaBH_4$ and acid condensation (scheme 11 in previous paragraph): Reacting NHC-Au-Cl complexes with $NaBH_4$ leads to the formation of miscellaneous clusters; however an acid condensation step (treatment of the reaction mixture with a solution of mineral acid) after the reduction allows the convergence of the products of the reaction towards Au_{13} moieties.
4. Co-reductions: The co-reduction of some NHC-Au-Br complexes together with $AuCl(SMe_2)$ allowed to obtain Au_{25} clusters.The one of NHC-Au-X (X=Cl, Br) in presence of phenylacetylene yields Au_{44} clusters with alkynyl ligands and NHCs (scheme 12, figure 6).[34]



Scheme 12: reaction used by Zheng et al. for the synthesis of an Au$_{44}$ cluster bearing NHCs and alkynyl ligands.

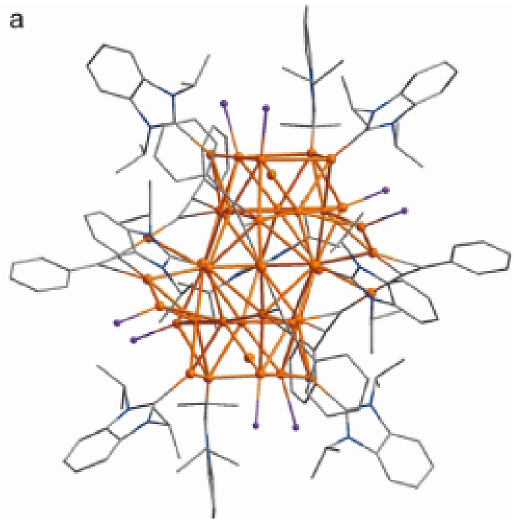


Figure 6: crystal structure of the Au$_{44}$ cluster bearing NHCs and alkynyl ligands, as reported from Zheng et al.

5. Stoichiometric synthesis (see chapter 4): new type of co-reduction under testing in our research group, in which a stoichiometric amount of Au complex with a labile ligand is introduced, given the ratio of NHC ligands to Au atoms in the expected product. This procedure allows to obtain higher yields in one step, avoiding the acid condensation, and allows the presence of anionic ligands different from halides in the resulting clusters.

Other synthetic methodologies, not utilized for NHC protected clusters, but still worth to mention, are the Brust-Schiffrin method and the Ligand Exchange Induced Structure Transformation (LEIST). The first method was invented in 1994, and revolves around the phase transfer of acqueous species into an organic solvent (ex: $HAuCl_4$ in toluene) using a phase transfer reagent, followed by the reduction in presence of a ligand, generally a thiolate. The second method starts from a preformed monodispersed AuNC, and with an excess of ligand and under heating directs the synthesis towards a specific product. [33]

Catalysis using NHC-protected nanoclusters

Nanocatalysis classically involves the use of nanoparticles deposited on the surface of metal oxides, for example by means of wet impregnation of a metal salt precursor, followed by drying and calcination. The inherent problem of such systems is that the product NPs are not uniform in size, morphology and structure.

Nanoclusters, owing to their atomic precision and precise molecular formula, are very interesting as well-defined catalysts that allow to obtain a molecular-level understanding of nanocatalysis. [35]

Catalytic studies using thiolate and phosphine protected nanoclusters have been performed extensively since their discovery. The ligands can be a problem for catalysis, but in some cases they can facilitate activation of reactants or provide means for activity and selectivity control. [35] As already stated, NHCs are species with higher ability to bind metal centers and that form stronger bonds with respect to phosphine ligands, and possess a very high tailorability of both steric and electronic parameters, so they are superior to thiolates in this regard. The discovery of their ability of stabilizing metal clusters therefore opens exciting perspectives in terms of nanocatalysis.

Catalytic studies have been performed on several different NHC-protected nanoclusters, but the continous progress in the development of this class of compounds leaves many routes still unexplored. Three examples are here reported to give some ideas of the possible applications of this class of ligand-protected clusters.

In 2019 Crudden et. al. reported the use of an NHC-protected Au_{11} cluster for the electrocatalytic reduction of CO_2 to CO, an important reaction since CO is a very useful and broadly employed building block in organic synthesis for the formation of C-C bonds. This reaction is perhaps even more interesting since it allows CO_2 valorization. The study was performed comparing the activity of several heteroleptic NHC-phosphine protected clusters with an analogous homoleptic phosphine protected cluster, and revealed that the electrocatalytic activity is higher for most of the heteroleptic protected clusters, and that one peculiar NHC led to the best activity. The performance of the catalyst was comparable to the one of the best other nanostructured catalysts; however it required higher overpotential since its loading had to be lower, because any attempt to increase it led to decreased efficiency, demonstrating agglomeration. This shows, however, that the cluster is more active than any other species such as nanoparticles that may form by means of its decomposition. Improvements in this aspect can be made using supports with higher surface areas than the one used in the study.[31]

Zheng et. al. between 2019 and 2020 performed catalytic studies on the hydrochlorination of phenylacetylene using a Au_{13} cluster protected by NHCs that possesses isopropyl groups as wing-tip substituent on the nitrogen atoms of an imidazolic ring. The study demonstrates that a concentration of 0,005 mol% of catalyst (based on gold), supported on activated carbon (XC-72) is extremely active in this reaction, achieving a conversion close to 100% after 4 hours at room temperature. The stability of the catalyst has also been demonstrated using TEM and UV-Vis spectroscopic fingerprints before use and after multiple runs of the reaction: no changes were observed in the spectroscopic features and particle size, and this allowed to confirm that the catalyst remained intact during the reaction.[19]
The same group worked with an Au_{25} cluster on the cycloisomerization of alkynyl amines to form indoles, important compounds in material science and for biological applications. The reaction was performed using 0,0015 mol% of catalyst, studying the effects of temperature and solvent. The best combination was demonstrated being 50°C in 1,2-dichloroethane, and the yield was higher than 99%, with full conversion after 10 h. The catalyst was demonstrated being stable under the reaction condition, using UV-Vis analysis as a tool, and much more active than the starting complex and also than the other two types of Au_{25} clusters known at that time, protected by thiolate and phosphine ligands.[36]

NHC-protected gold nanoclusters for bioimaging and nanomedicine

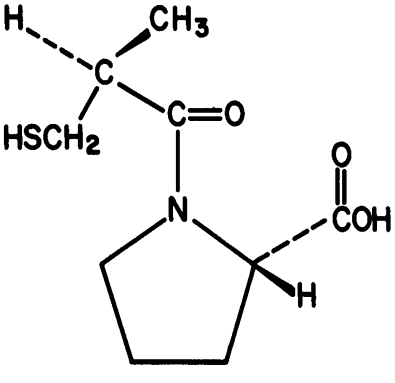
In recent years, there has been a significant effort devoted to the development of bioimaging probes from quantum dots, that possess large excitation windows and narrow, tunable, strong and stable emission. The presence of heavy metals limits their application in several in-vivo procedures, however, and this has led to the research of similar fluorescent nanomaterials with less inherent toxicity problems, and among these Au nanoclusters. [37]
Au NCs possess cluster nuclearity-dependent fluorescence, ranging from near-infrared to UV, arising from transitions between discrete energy levels. A great advantage is the fact that this emission is tunable according to cluster size and composition. [37]

Several AuNCs protected by NHCs show relatively high quantum yields, for example one reported by Zheng et. al. shows an emission at 650 nm with a quantum yield of 15%[9], and others reported by Crudden et. al. that reach 16% and 23% respectively[38][32]. One important aspect is the fact that the solubility of the clusters, and therefore their distribution inside cells, can be influenced by the presence of functional groups on the ligands and by their protonation/deprotonation.[19]

Almost none and non-definitive studies are available for the use of NHC protected AuNCs as pharmaceutical compounds, because of their recent discovery; however the promising features of both gold and the ligands give hope in this field of research.

Several studies have been performed on Au nanomaterials as therapeutic and theranostic agents, and an interesting example is the use of a thiolate (captopril, orally active angiotensin-converting enzyme inhibitor, scheme 13) protected Au_{25} cluster as a radioactive agent for cancer treatment. The radioactive cluster is reportedly produced by the direct irradiation of the non radioactive counterpart using a thermal neutron flux. The most abundant gamma-ray produced by the radioactive decay of the Au atoms is suitable for radionuclide therapy, and the clusters tend to accumulate in the cancer's site thanks to enhanced permeation and retention effects due to the properties of the ligand, giving an effective nanoradiopharmaceutical.[39][40]

Given the strength of the Au-NHC bond similar applications may be feasible using NHC-protected metal nanoclusters.



Scheme 13: structure of captopril, proline derivative commonly used for treatment of hypertension, used as ligand by Santos-Oliveira et al. in 2020 to produce an AuNC based radiopharmaceutical.[39][40]

Chirality of metal NCs

Nanomaterials can be chiral, and there are many applications that gain advantage of this property of matter; in particular the most interesting fields in which this property is investigated are biomedicine, catalysis and optical devices. Chiral nanomaterials can be used as ground for the investigation of the origin of chirality, since they represent intermediates between single molecules and macroscopic objects, and their properties can be tuned for the specific experiment.

Chirality at nanoscale can be caused by the presence of a twisted or elicoidal structure, chiral configuration of single achiral components, transfer of chirality from a chiral ligand towards an achiral metal core or chiral patterns formed by achiral ligands.[41]

One of the biggest problems in obtaining chiral NCs is the stability of their chirality; obtaining clusters with optimized properties and resistent to racemization is not trivial. Chirality has been extensively studied on thiolate-protected and phosphine protected clusters, separated by means of chiral HPLC[41]. An interesting species is $Au_{38}(SCH_2CH_2Ph)_{24}$, which shows high stability against racemization at room temperature, while at 80 °C racemizes in 30 minutes. Phosphine protected clusters are resolvable only in the case of chirality granted by the ligand structure, while rapid racemization occurs in solution if the chirality is granted by the ligand arrangement. The most notable example is $[Au_{13}(dppe)_5Cl_3]^{3+}$ (dppe = 1,2-bis(diphenylphosphino)ethane).

When dealing with NHCs, studies on chiral clusters have begun very recently. Crudden et al. reported first the synthesis and separation of several Au_{13} clusters, analogues to $[Au_{13}(dppe)_5Cl_3]^{3+}$, using bis-NHC ligands. These clusters are very thermally stable and possess high photoluminescent quantum yields.[38] More recently the same group obtained a chiral Au_{10} cluster, $[Au_{10}(bis\text{-}NHC)_4Br_2](O_2CCF_3)_2$, in which chirality is due to chirality transfer from a chiral bisNHC ligand to the metal core. [42]

Gold and its properties

The properties of nanoclusters are intimately connected to the properties of the metal that makes up their core; gold is a very interesting metal, since it possesses various uncommon characteristics, and the chemistry of its compounds is in many ways surprisingly different from the one of the compounds of related metals.[43]

First of all, gold is a noble metal, and as such is resistent to processes such as oxidation in normal atmospheric conditions. It shares this definition with other metals, namely ruthenium, rhodium, osmium, iridium, palladium, platinum and silver. This stablity allowed many of the hystorical uses of gold, such as the creation of red colloids for glass coloring [20].

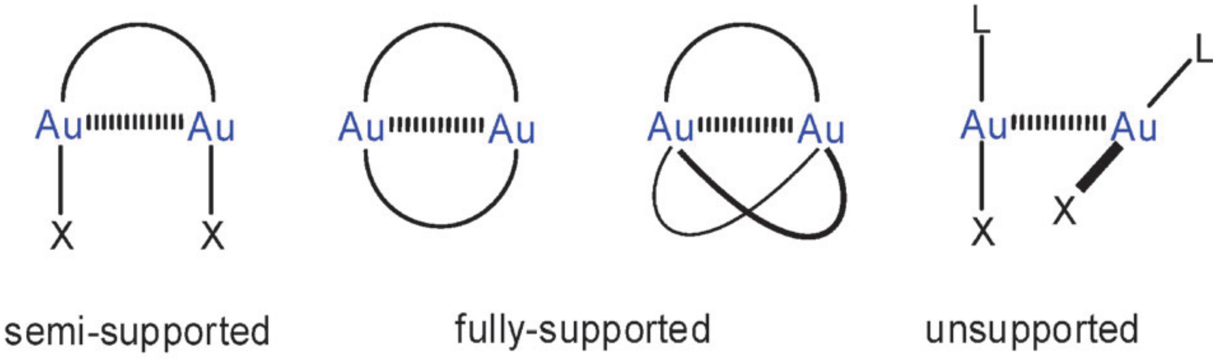
Gold forms short and strong bonds, suggesting small atomic and ionic radius, and has high electronegativity and electron affinity; it prefers low coordination numbers, 2 and 4, and has access to oxidation states I, II, III, V and also -I.

Gold is also compatible with biomolecules, and this allows many applications in the field of biomedicine, such as sensing, imaging and cancer therapy.

Another interesting property is the high tendency of gold (I) compounds, with low coordination numbers, to associate into dimers, oligomers, and uni- and multidimensional polymers via direct Au-Au contacts. This aggregation occurs through bonding between formally closed-shell metal centres ($5d^{10}$). The equilibrium distance is between 2.7 and 3.3 Å and includes the distance between gold atoms in gold metal and approaches or overlaps with the range of distances of Au-Au single bonds for two Au^{2+} cations ($5d^9$). Similar contacts have also been discovered within polynuclear molecules where the gold atoms reach a distance of about 3 Å. This phenomenon explains the multiple metallation and gathering of gold atoms on donor sites on substrates, difficult to achieve with other metals.[43] The presence of this behaviour makes gold very interesting for the preparation of NCs, that possess a significant fraction of Au atoms in the +1 oxidation state.

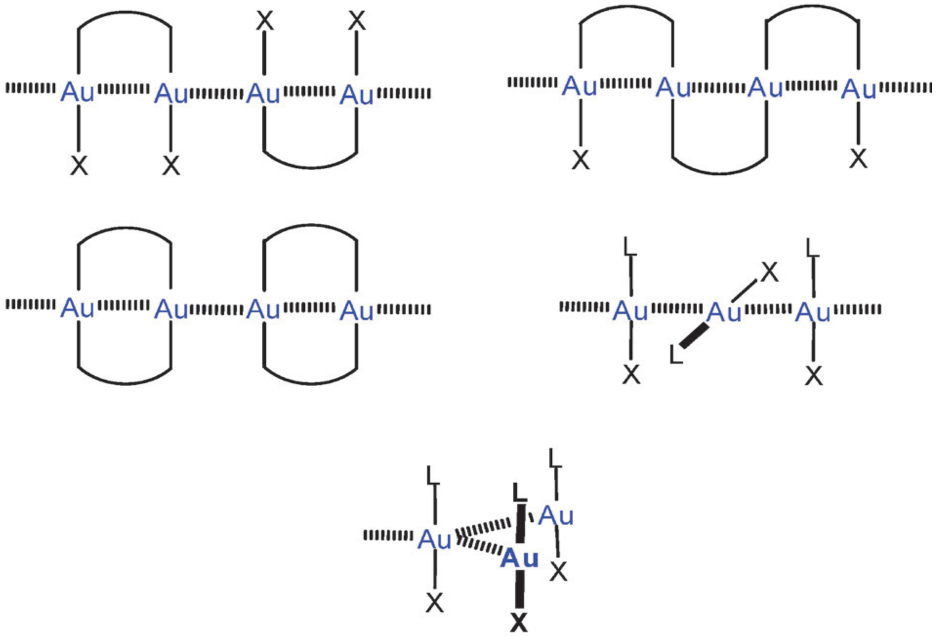
These closed-shell interactions have been described since 1987 with the terms "aurophilic interactions", and have an energy similar to the one of an hydrogen bond. In reality the phenomenon is general, it can be observed for heavy elements such as Ir, Pt, Hg, Tl and as already stated Au, and can be described by means of the general term "metallophilic interaction".[44] It is related to relativistic effects, and can be explained by means of them: electrons move at high speeds when close to an heavy nucleus, and the subsequent mass increase leads to energetic stabilization and radial contraction of s and p orbitals, while the d and f orbitals expand.[45] This enhances electron affinity and avoids the formation of ionic structure with bridging anions.[46] Au is the metal for which relativistic effects reach a maximum. [44]

Aurophilic bonding can be classified in several types according to its nature: there can be intramolecular interactions, divided into semi-supported and supported, or unsupported intermolecular interactions (scheme 14). The difference between supported and semi-supported interactions resides in the number of bridging ligands between the Au atoms: fully supported interactions involve two or more bridging ligands, while semi-supported only one.[44]



Scheme 14: different types of aurophilic interactions between two gold atoms. Arches refer to bidentate neutral ligands.[44]

Multiple Au-Au interactions between more than two gold atoms can give rise to the presence of chains or non-linear structures (scheme 15).



Scheme 15: structures generated by aurophilic interactions involving more than two metal centers. Arches refer to bidentate neutral ligands [44]

Another important point is that gold in the +1 oxidation state, commonly present in NCs, is a soft Lewis acid, according to Pearson's classification, and therefore it interacts better with soft Lewis bases as ligands.[47]

Theoretical models for electronic structure in AuNCs

Many theoretical studies have been performed to seek a general model that explains the stability of ligand-protected AuNCs. The first developed theory is the Polyhedral Skeletal Electron Pair theory, that successfully explains the electronic structures of many electron-deficient clusters from main groups elements to transition metals, developed comparing isostructural carboranes, higher boranes and borane anions and metal-carbonyl clusters. Cluster structures are described in terms of condensed polyhedra based on octahedral, tetrahedral, trigonal prismatic, and triangular fragments, that bind through a vertex, edge or face. This model, however, cannot be applied to gold clusters, for the almost inexistent overlap between d orbitals, due to inefficient screening effect increasing the atomic number (high electrostatic attraction between electrons in d orbitals and nucleus, inefficiently shielded by inner electrons), and also for the poor tangential (π) bonding ability of Au 6p orbitals and the high 6s-6p energy gap in gold, that explains the lack of s-p hybridization.[48][49][50]
The skeletal bonding in Au NCs is therefore dominated by the interactions between 6s orbitals, and this required the formulation of a more suitable bonding theory, the so-called Superatom Complex Model. In this theory the Au cluster is described as a superatom, and as an ordinary atom, it will reach its highest stability when it possesses a close (superatomic) electron shell. This gives rise to the existence of "magic numbers", number of electrons referring to electronic configurations that confer a peculiar stability to the cluster, analogous to the number of valence electrons of noble gases, for example 2 and 8.

The terms "superatomic orbitals" and "superatom" derive from the fact that the skeletal bonding orbitals have shapes recalling atomic orbitals. They are often called Jellium orbitals, because the model recalls the Jellium model originally developed for alkali metal clusters. This model works well for clusters with spherical shape, that have an approximately spherically simmetric superatomic nuclear potential.

For low simmetry clusters other models have been developed, such as the Super-Valence-Bond model, that introduces the ability of superatoms to form chemical bonds and therefore creates the concept of "superatomic molecule", or the SuperAtom-Network, in which a gold cluster is considered as a network of many two-electron superatoms instead of a single large superatom.

This last model has then been updated, giving rise into the Grand Unified Model (GUM), which describes the skeletal bonding of the cluster as a collection of triangular and/or tetrahedral elementary blocks, kept together by three- or four-centered bonds, with two electrons associated with each building block.[48]

This model is created in analogy to the quark model in particle physics, in which protons and neutrons are seen as composite particles, bound states of the elementary valence quarks and antiquarks.

In particular, it takes the Au atom as an elementary particle, and assigns one of three different "flavours" (types) to each atom in the cluster, 1e, 0,5e and 0e, called bottom, middle and top respectively. The role of the composite particle, as already stated, is assigned to triangular Au_3 and tetrahedral Au_4 blocks, that satisfy the duet rule. The stability of these two elementary blocks is somewhat confirmed by the existence of the clusters $[Au_3(IDipp)_3]$ (IDipp = 1,3-bis(2,6- diisopropylphenyl)imidazol-2-ylidene] and $[Au_4(PR_3)_4]$, and another proof is given by computational studies that show that the formation energies of the isoelectronic species, $Au_2(2e)$, $Au_3(2e)$, $Au_4(2e)$, $Au_5(2e)$ and $Au_6(2e)$ are strongly negative only in the cases of the triangular and tetrahedral species.[51]

A further layer of complexity: alloy clusters and clustering at common ligating atoms

Pure metal clusters are not the only type of ligand protected clusters that are present in the field of nanoscience. It has been demonstrated in several cases that alloying is possible even in nanoscale, giving rise to the so-called alloy clusters. Many have been synthesized, and have attracted the attention of scientists as a way to tune the properties of these nanomaterials. In particular the synthesis of several Au clusters doped with metals such as Pd, Cu and Ag, protected by thiolates, selenolates and phosphine ligands has been performed.[52][53]

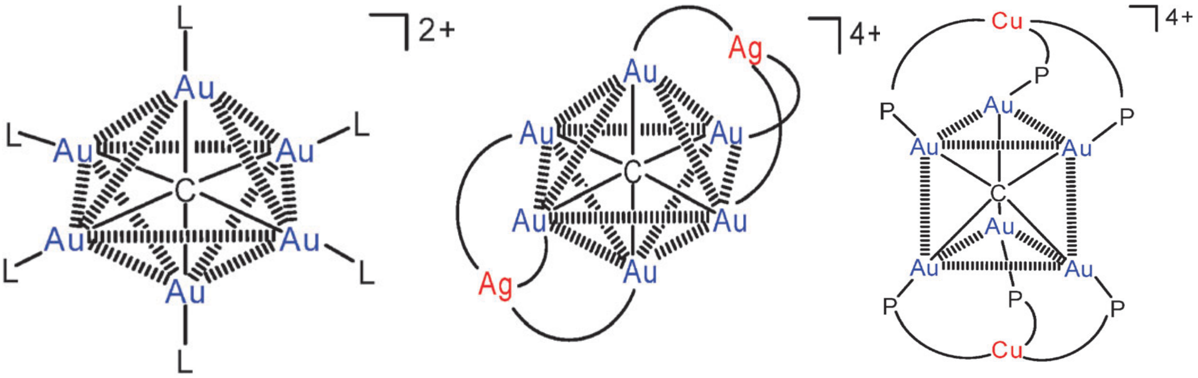
This type of clusters, however, is not the focus of our research project, so they will not be discussed further.

Au(I) metal centers, however, can form cluster species even with atoms of non-metallic elements. Methyl-gold interactions have been known for several decades, however no simple diauromethane complexes $H_2C(AuL)_2$ are known. The acidity of the protons of these species is supposed to allow the multiple auration of carbon, generating tri-, tetra-, penta- and hexa-aurated species (figure 7). This hypotesis is strongly supported by the possibility of obtaining disubstituted diauromethane species, with formula $X_2C(AuL)_2$. Penta- and hexa- aurated species show a peculiar stability despite exceeding the usual maximum coordination number for the central atom, granted by aurophilic interactions, and are formed starting from species with lower coordination numbers adding AuL^+ units, thanks to these effects. Hexa-aurated species, as outlined in figure 7, show an octahedral geometry in the disposition of Au(I) atoms.

Polyauration of silicon can generate anionic species, where silicon possesses formal coordination numbers 4 and 5, and geminal diauration of stanna-closo-dodecaborate anions generates neutral and anionic complexes with Sn-Au bonds and short Au-Au distances.

Alloy clusters with stoichiometry $[CAu_6M_2(L)_6]^{4+}$ have been produced from hexa-aurated methanium dications (figures 8 and 9), with M=Ag or Cu and are respectively present as an octahedron with two faces capped by Ag atoms or as a prism with the two triangular faces capped by Cu atoms.[44]

Clustering at nitrogen atoms can lead to the formation of tri-, tetra- and penta cationic aurated species.[44]



Figures 7, 8 and 9: examples of clustering of gold and gold alloys on a carbon atom.[44]

Chapter 2: Aim of the thesis project

As already stated, ligand protected, atomically-precise metal nanoclusters (NCs) are an important class of compounds that acts as a junction between molecular chemistry and material science. Among these, the most important and studied sub-class is the one of gold nanoclusters (AuNCs), as a consequence of the unique characteristics given by gold. Very recently, N-heterocyclic carbenes have been discovered as a new class of ligands that is able to stabilize atomically precise metal nanoclusters, and that can confer peculiar properties to these species thanks to their high degree of tailorability.

The first aim of this thesis project is therefore the discovery and optimization of the synthesis of NHC-protected metal nanoclusters, by means of direct reduction, stoichiometric synthesis and metathesis reactions, their purification, and their characterization to determine spectroscopic features such as UV-Vis absorption and eventually fluorescence, and possibly crystal structure and redox behaviour.

The second aim of the project is the research on the synthesis of an NHC ligand with enhanced π-accepting properties, and its possible use for complexes' and nanoclusters' synthesis.

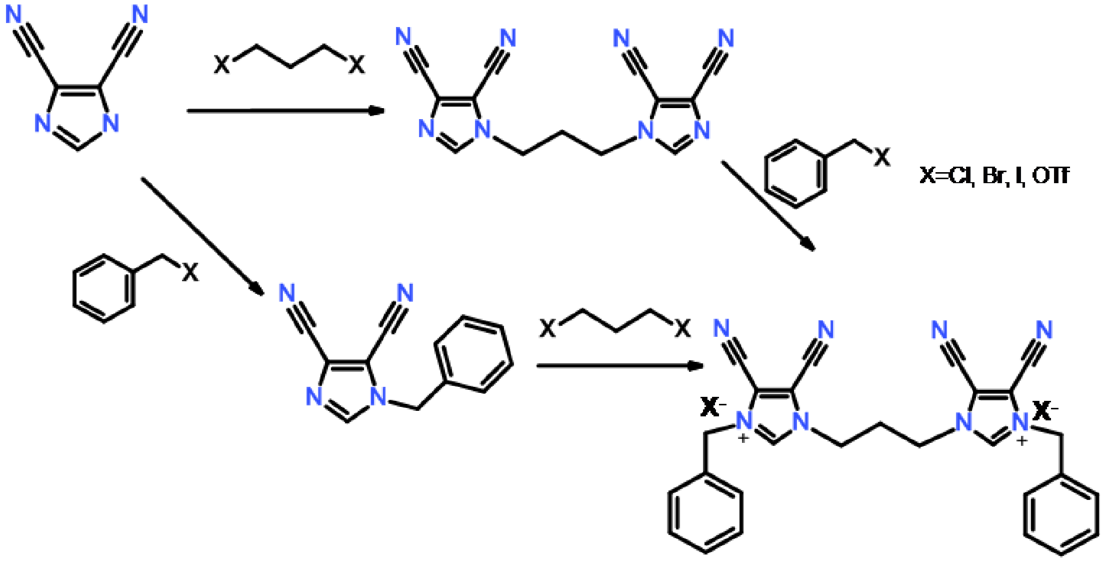
In particular, the use of bidentate carbene ligands (di-NHC) will be the focus, with the aim of obtaining useful features such as improved rigidity and consequent stability of the resulting products.

Chapter 3: Research of an NHC ligand with enhanced π-accepting properties

The design and synthesis of more π-accepting and less electron-donating NHC ligands has always been a challenge, especially for poly-NHCs. This can be achieved in three different ways: through the N-heterocyclic backbone, through the N-substituents and through functionalized heterocyclic carbons in remote position with respect to the carbene.

The first alternative allows an extensive variation of electronic properties, by means of the use of electron-withdrawing heterocyclic scaffolds such as benzimidazole or triazole. Aryl substituents with electron withdrawing groups are the most used alternative in the second strategy. The third strategy is the least used, possibly because of some synthetic difficulties, particularly high in the case of poly-NHCs[54]. An example is given by Peris et al. [55]that demonstrated that the synthesis of bis-imidazolium salts from dichloroimidazole was feasible only using a propylene bridge between the imidazole rings and not with shorter ones.[54]

The last strategy is the one that has been selected, and in particular the starting heterocyclic ring that has been chosen is 4,5-dicyanoimidazole. This compound is the most electron-poor starting imidazole for the synthesis of NHCs.[54] The synthesis of a bis-imidazolium salt with a three carbon bridge and benzyl groups as wingtip substituents has been attempted, using the conventional method that involves two subsequent nucleophilic substitutions (scheme 16).



Scheme 16: possible synthetic routes involving two subsequent nucleophilic substitutions for the synthesis of the desired bisimidazolium salt, starting from dicyanoimidazole.

An analogous of this ligand with methyl groups as wingtip substituents has already been synthesized in 2015 by our research group, but its preparation required the use of Meerwein's salt (Me_3OBF_4), which is a very strong electrophile, giving an idea of the strongly reduced nucleophilic character of the nitrogen atoms in the 4,5-dicyanoimidazole moiety.[54]

The hope was to obtain a bis-imidazolium salt and react in with AuCl(SMe_2) in presence of weak base to obtain the corrisponding Au_2(di-NHC)X_2 complex, and reduce this complex to obtain a gold nanocluster. The cluster, thanks to the enhanced π-accepting properties of the protecting ligand could in principle possess peculiar electronic properties, since it has been demonstrated that isostructural clusters with different ligands possess different HOMO-LUMO gaps.[56]

Ultimately, after formation of the 1,3-propylene bridge according to a literature procedure [54] (see figure 10 for ^{1}H NMR), many different benzyl substituted electrophiles have been tested, but everyone failed for low reactivity or concurrent processes leading to the formation of byproducts.

An alternative literature strategy involving the benzylation as first step, followed by the formation of the bridge using DMSO as catalyst has been attempted, but it gave no results, since even the first step of the reaction suffers from the low reactivity of the reagent. [57]

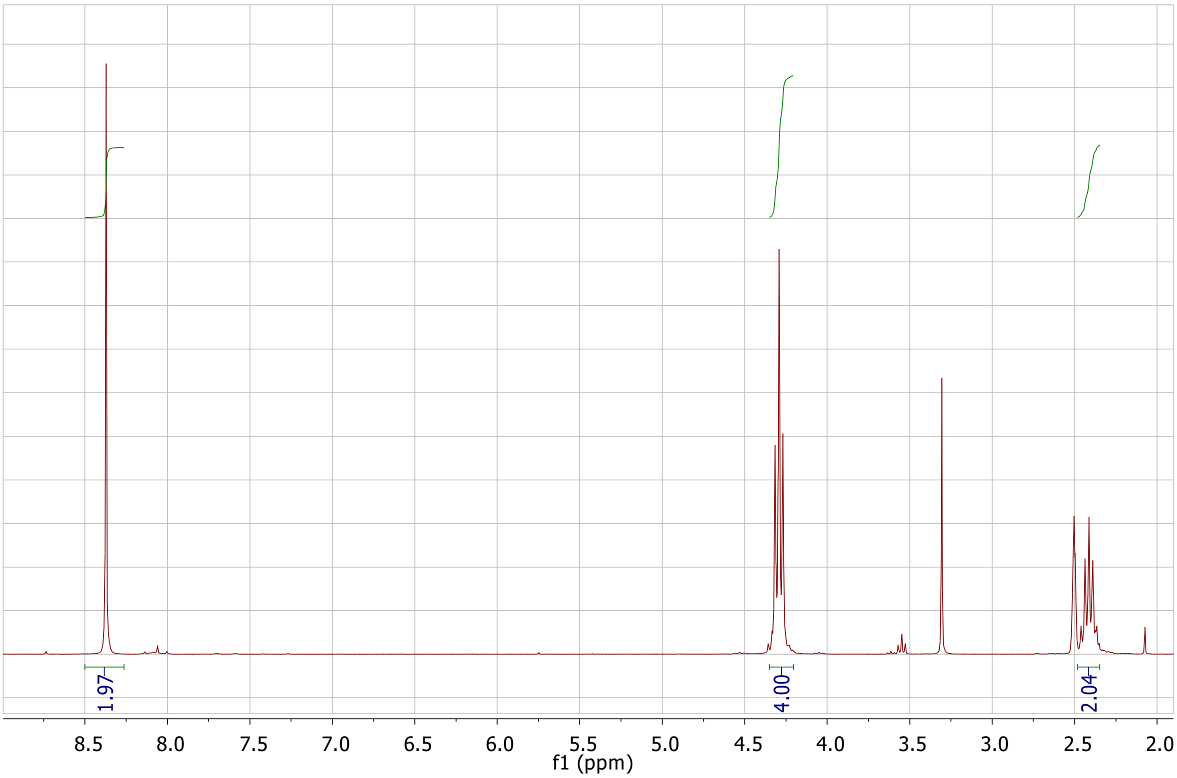
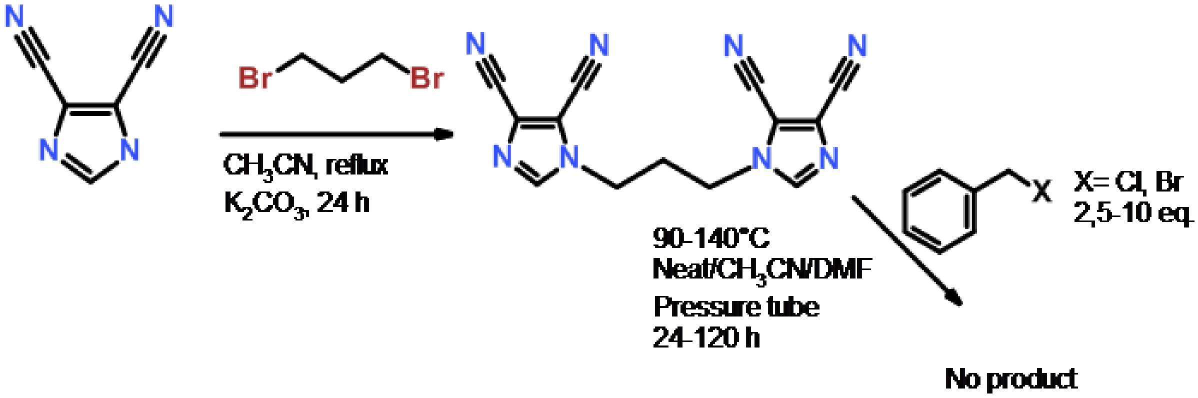


Figure 10: ^{1}H NMR spectrum, recorded in DMSO-d$_6$, of 1,3-bis(4,5-dicyanoimidazole)propane used for the attempted synthesis of the pre-ligand bisimidazolium salt. The signals at 2,50 ppm and 3,33 ppm are respectively attributed to the presence of non-deuterated DMSO and water; the signal at 5,75 ppm is attributed to DCM. From right to left the integrated signals refer to the propyl central CH$_2$, lateral CH$_2$ and imidazole protons.

Attempts with benzyl chloride and bromide

All the attempts performed using Benzyl chloride and bromide have completely failed, and are summarized in scheme 17:



Scheme 17: summary of the 1,3-bis(4,5-dicyanoimidazole)propane synthesis and of the benzylation reactions attempted using benzyl bromide and benzyl chloride.

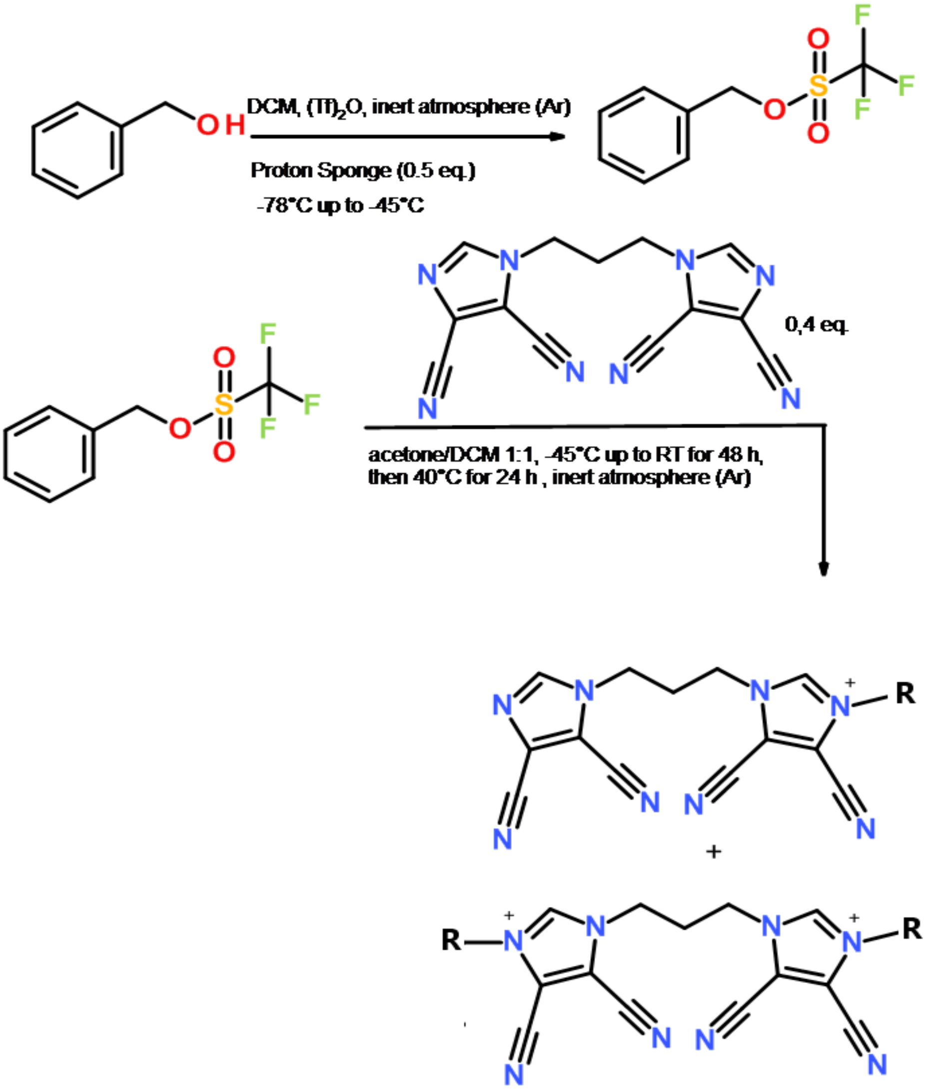
All the previous syntheses have been plagued by the very low solubility of 1,3-bis(4,5-dicyanoimidazole)propane in both benzyl halides and acetonitrile, and by the presence of nucleophilic impurities in DMF, which attack the benzyl halide.

First, second and third attempts using benzyl triflate

After these failures the synthesis has been attempted generating in-situ a strong electrophile, benzyl trifluoromethanesulfonate, using trifluoromethanesulfonic anhydride, benzyl alcohol and a non nucleophilic base, modifying a literature procedure[58]. The choice of the base fell on 1,8-bis(dimethylamino)naphthalene (commercial name: Proton Sponge), already available in the lab. The reaction procedure and the results have been summarized in scheme 18.
The NMR spectrum of the reaction product is reported in figure 11. It is possible to appreciate the almost total lack of aromatic signals, indicating that the benzylation of the dicyanoimidazole rings has failed. The highlighted peaks, however, show that some group is bound to the nitrogen, generating an imidazolium salt, mostly monosubstituted.
The reaction has been repeated a second time on larger scale, changing the amount of base from 0,5 equivalents to 1 equivalent, since there is an high difference between pK_{b1} and pK_{b2} for the Proton Sponge.

After this reaction an article was found describing the low, but existing nucleophilic properties of 1,8-bis(dimethylamino)naphthalene at one of its carbon atoms (labelled as 5). The use of this compound as nucleophile in an electrophilic aromatic substitution, possible only with very strong electrophiles, leads to the formation of a strongly coloured compound (dark red) that exhibits solvatochromism (see figure 12), same behaviour of at least one compound present in the reaction mixture in the previous procedure. (DMSO solution --> yellow, dichloromethane solution --> dark red). [59]

Based on these findings, in order to avoid decomposition of benzyl triflate, the reaction has been repeated using another base, in particular 2,6-di-tert-butyl pyridine, common non-nucleophilic base used when triflates are involved. Results, however, didn't change.



Scheme 18: summary of the first attempted benzyl trifluoromethanesulfonate synthesis and of the first benzylation reaction attempted using it. The second reaction has been performed using 1 eq. of proton sponge, the third using 1 eq. of 2,6-di-tert-butyl pyridine.

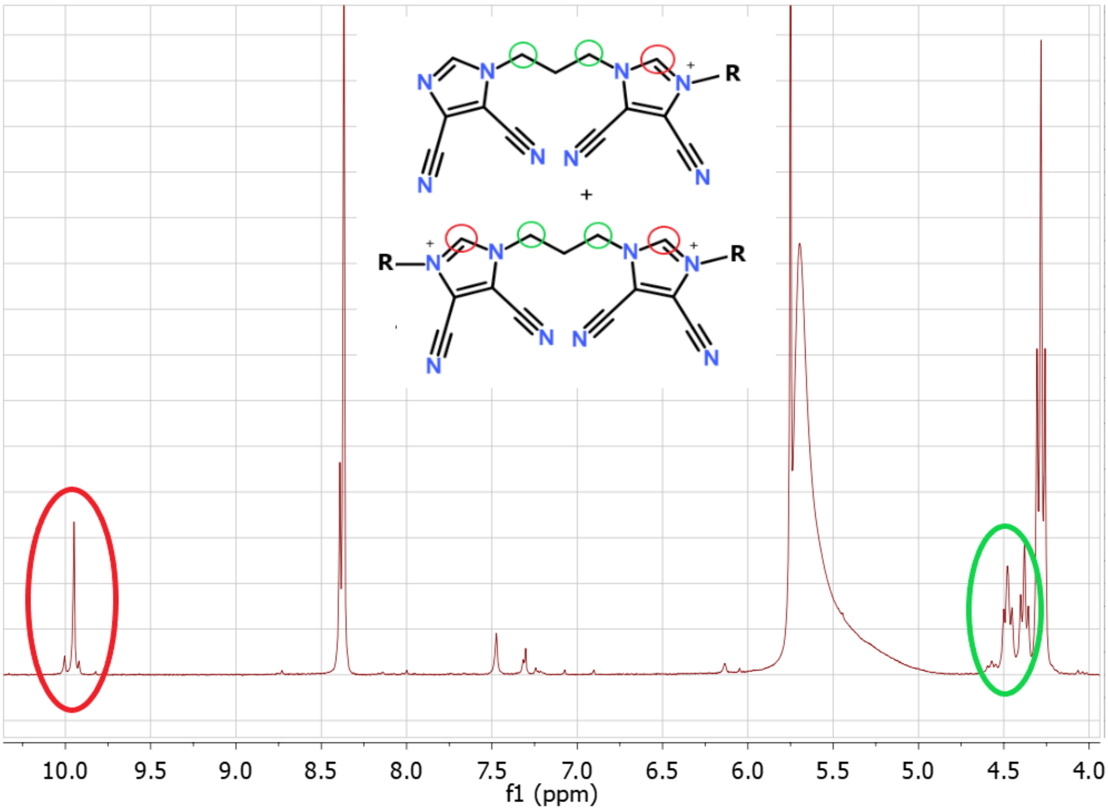
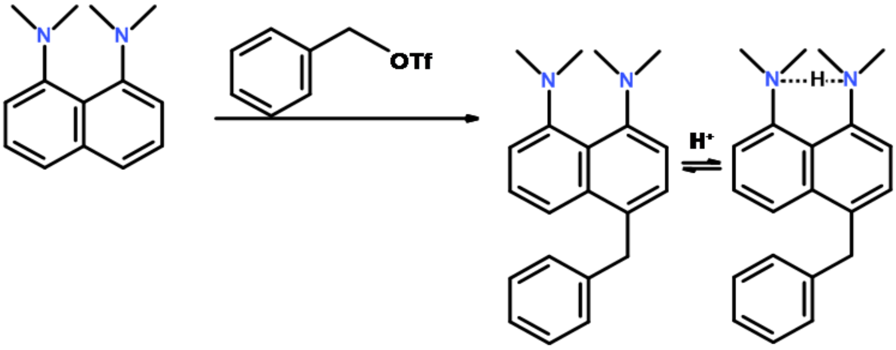


Figure 11: detail of the ^{1}H NMR spectrum of the product of the second attempted synthesis of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(trifluoromethanesulfonate).

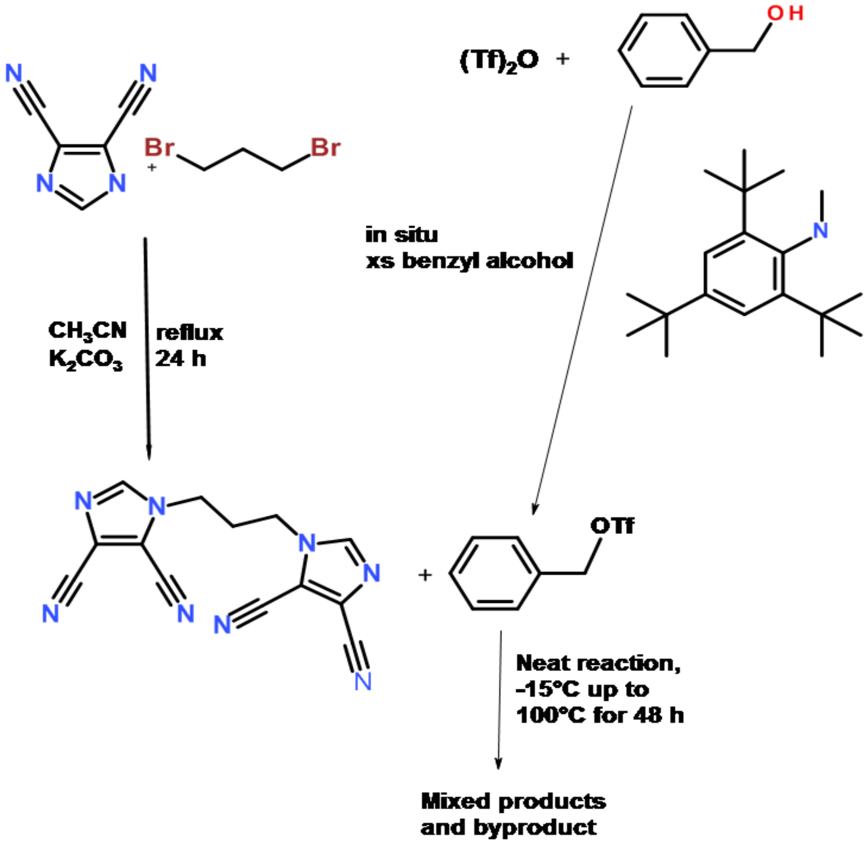
The highlighted signals confirm the presence of some substitution since monosubstitution gives loss of simmetry and doubling of the signals of the bridge (higher signals, green), and disubstitution generates a compound with a 2+ charge, resulting in a single triplet with higher chemical shift (smaller triplet, green); these outcomes are confirmed by the presence of the N-CH-N protons (red). As seen, these signals are two, the more intense is coherent with monosubstitution and the less intense with disubstitution, according to their integrals.



Scheme 19: in the case of Proton Sponge (1,8-bis(dimethylamino)napthalene), a nucleophilic substitution in position 5 leads to the formation of a strongly coloured compound, that changes colour according to the protonation degree, and exhibits solvatochromism.[59] In our case the supposed reaction concerns benzyl triflate as an electrophile.

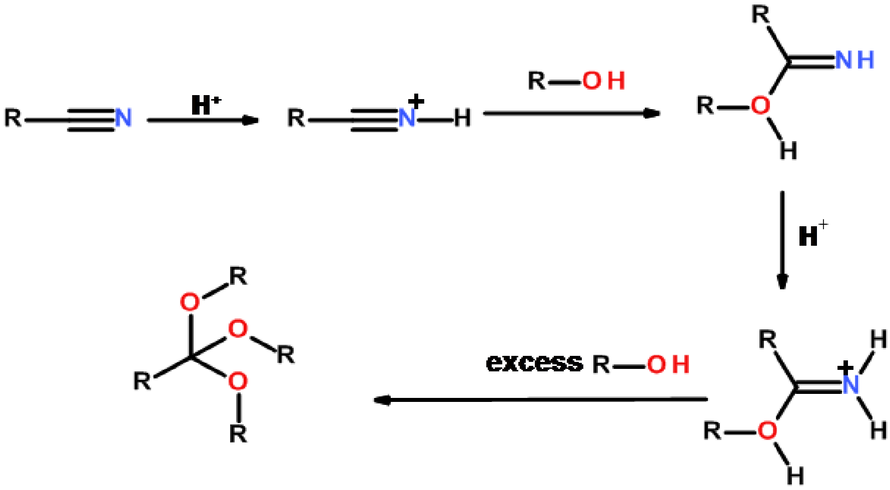
Fourth, fifth and sixth attempts using benzyl triflate

Benzyl triflate was selected again as an electrophile, and the reaction conditions changed in order to avoid its decomposition. In particular, in all the previous cases acetone has been used as a component of the solvent mixture, because 1,3-bis(4,5-dicyanoimidazole)propane is soluble only in it and in few other solvents such as DMSO or DMF, that possess disadvantages such as difficult removal or presence of nucleophilic impurities. In the literature however benzyl triflate is commonly used in dry dichloromethane (DCM), and acetone has therefore been identified as the probable cause of the failure of the reactions, since the results were similar with the two different non-nucleophilic bases.
After this reasoning another reaction was planned, as always generating benzyl triflate from benzyl alcohol and triflic anhydride in-situ, exploiting an excess of benzyl alcohol as solvent, and operating in a pressure tube under heating (scheme 20). 2,4,6-tri-tert-butyl-N-methyl aniline has been selected as a non-nucleophilic base.



Scheme 20: summary of the 1,3-bis(4,5-dicyanoimidazole)propane synthesis and of the synthesis from trifluoromethanesulfonic anhydride of benzyl trifluoromethanesulfonate and of the benzylation reaction attempted using it.

The reaction generates multiple products, as evidenced by the ^{1}H NMR spectrum containing broad bands where the peaks of the products were supposed to be. This is evidenced comparing the spectra of the reagent and the product obtained after a preliminary work-up, as shown in figure 12. The hypotesis is that the presence of excess benzyl alcohol caused a Pinner reaction between the benzyl alcohol itself and the nitrile functionalities of the reagent (scheme 21).[60]



Scheme 21: general mechanism of the Pinner reaction and evolution under excess alcohol conditions.

The reaction has been attempted two additional times, using a stoichiometric quantity of benzyl alcohol in the first attempt and 2,6-di-tert-butylpyridine as a base in the second attempt. The first attempt generated a solid, and no reaction happened. The second gave the same result discussed above. Several washings with different solvents and column chromatography have been attempted for the separation of the pyridinium salt, with no results.

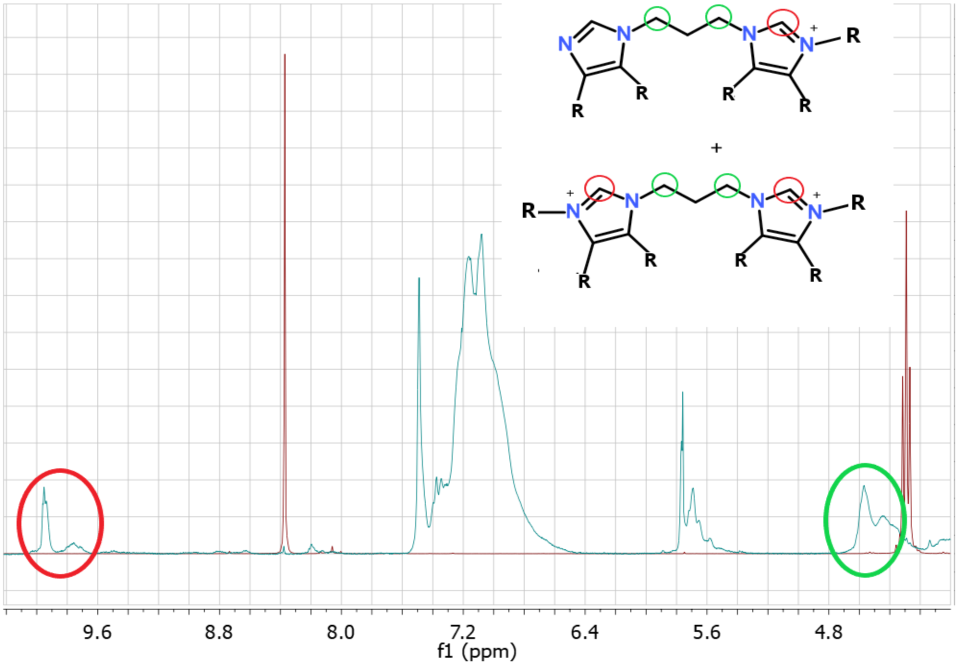


Figure 12:detail of the ^{1}H NMR spectrum of the product of the fourth attempted synthesis of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(trifluoromethanesulfonate) (light blue), compared with the one of the reagent (dark red).

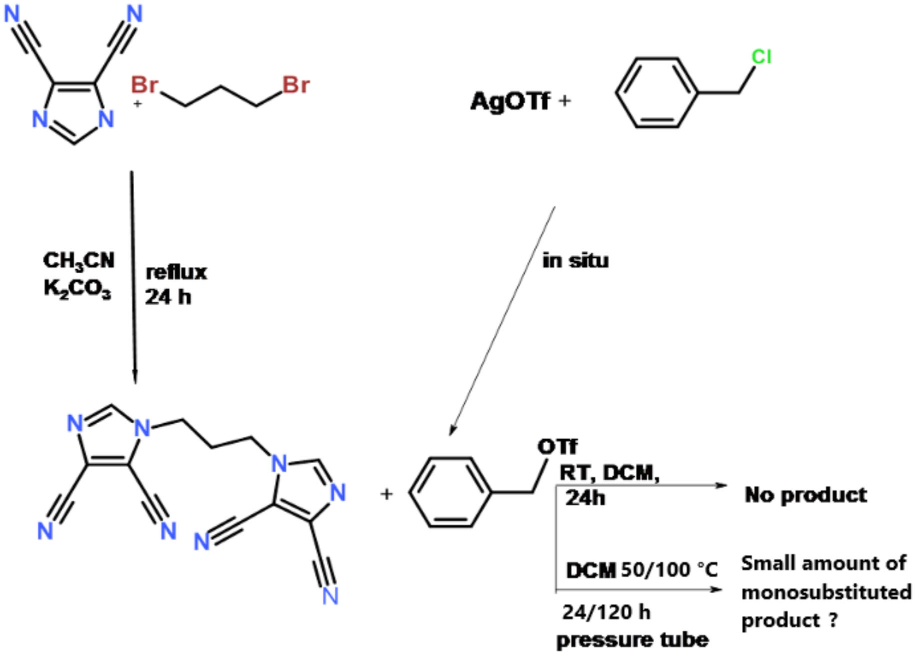
Seventh, eighth and nineth attempts using benzyl triflate

The last attempt at the synthesis of the pre-ligand has been performed using silver trifluoromethanesulfonate and benzyl chloride to generate benzyl triflate.[61] This method allows to completely remove the use of non-nuclephilic bases, since it doesn't generate trifluoromethanesulfonic acid, allowing for a cleaner synthesis. Two screening attempts have been performed using a classic inert atmosphere apparatus (round-bottom flasks) and a pressure tube, using DCM as solvent. The reactions are reported in scheme 22.

The pressure tube reaction gave a low degree of substitution, and mostly monosubstitution. Aromatic signals are clearly present around 7,10 ppm. The benzylic CH_2 signals could be covered by other signals, namely the one at 6,30 ppm, but without certainty of their presence conclusions on the success of the benzylation can't be drawn (figure 13).

DCM has been used to avoid the use of CCl_4, employed in the literature procedure for obtaining benzyl triflate in this way; an important problem is that the solubilty of silver triflate and 1,3-bis(4,5-dicyanoimidazole)propane in DCM is very low.

The pressure tube reaction has been therefore repeated doubling the amount of benzyl triflate and heating more. It has also been left stirring for 120 h, to counter the low solubility of the reagents. Despite the harsher reaction conditions the results were almost the same, with just a slightly higher conversion, appreciable from ^{1}H NMR analysis (figure 13).



Scheme 22: summary of the 1,3-bis(4,5-dicyanoimidazole)propane synthesis and of the synthesis from silver trifluoromethanesulfonate of benzyl trifluoromethanesulfonate, and of the benzylation reaction attempted using it.

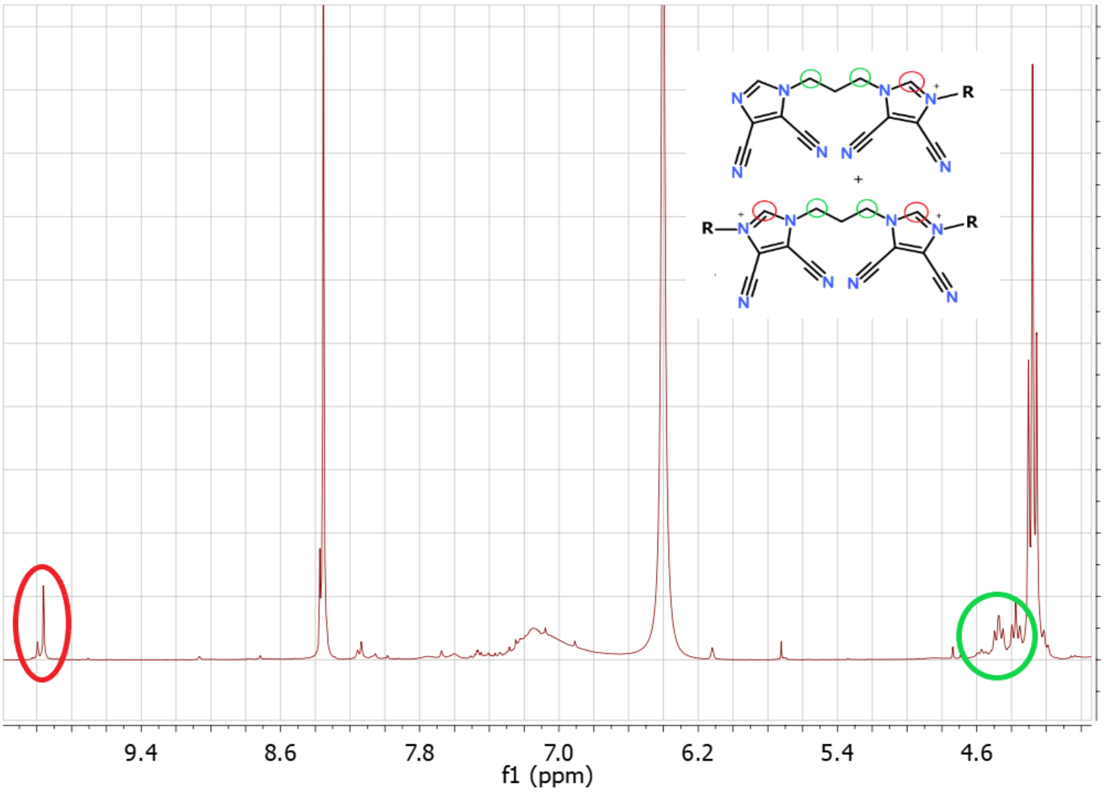
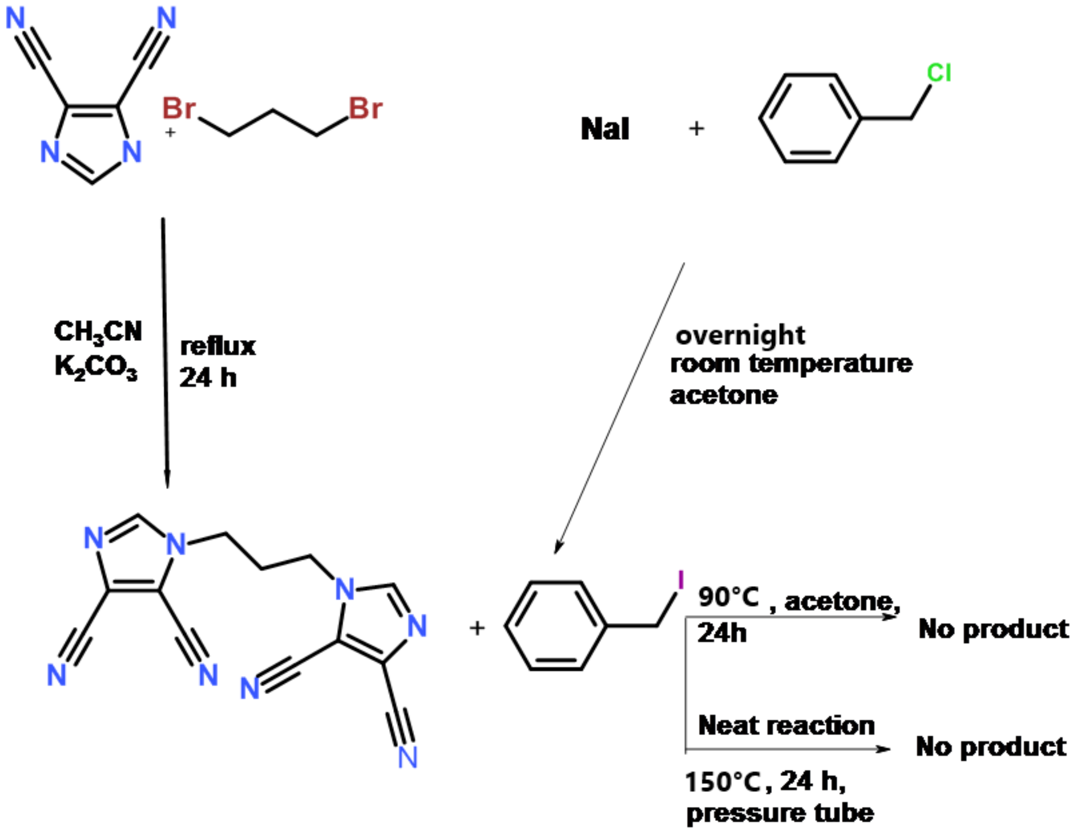


Figure 13: detail of the ^{1}H NMR spectrum of the product of the nineth attempted synthesis of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(trifluoromethanesulfonate). This time, aromatic signals are clearly present around 7,10 ppm. The benzylic CH_2 signals could be covered by other signals, namely the one at 6,30 ppm.

Attempts with benzyl iodide

Due to the stability issues of benzyl triflate, a change in procedure has been planned. Benzyl iodide has been prepared starting from NaI and benzyl chloride[62], and two attempts of reaction with 1,3-bis(4,5-dicyanoimidazole)propane first in acetone and then in absence of solvent have been performed. The reactions are summarized in scheme 23:

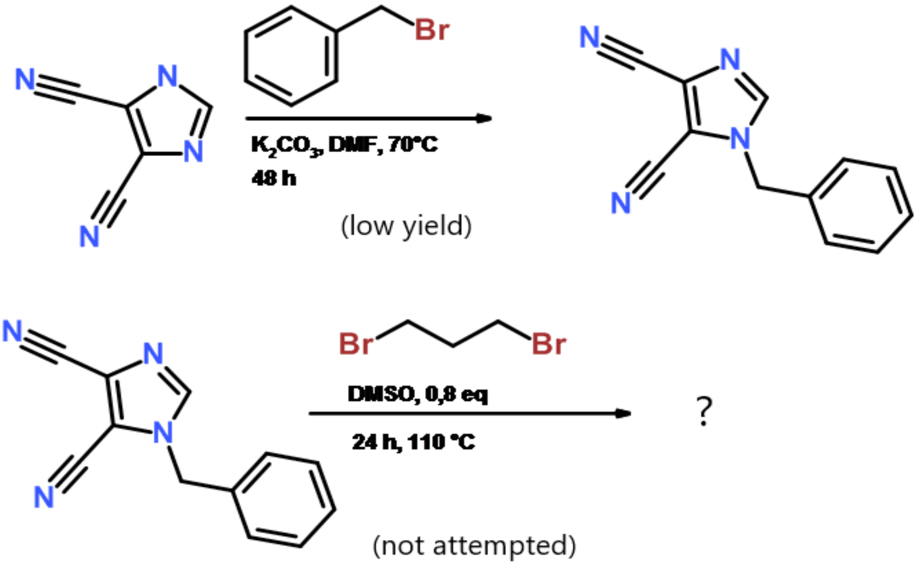


Scheme 23: summary of the 1,3-bis(4,5-dicyanoimidazole)propane synthesis and of the synthesis benzyl iodide, and of the benzylation reaction attempted using it.

Both the attempts failed, confirming that the reactivity of benzyl iodide is too low for this reaction.

Attempt with reverse order of substitution

The alternative route involving the benzylation of 4,5-dicyanoimidazole followed by the formation of the propylene bridge is reported in scheme 24; the first reaction had a much lower yield than the one reported in the literature, even extending the reaction time, as seen from ^{1}H NMR (figure 14), so with the use of these reagents it is not a viable option. The product of the first step as a result hasn't been isolated. Reaction conditions are listed for the second step even if the reaction hasn't been performed, for clarity.



Scheme 24 summary of the alternative route that was scheduled for the synthesis of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(bromide).

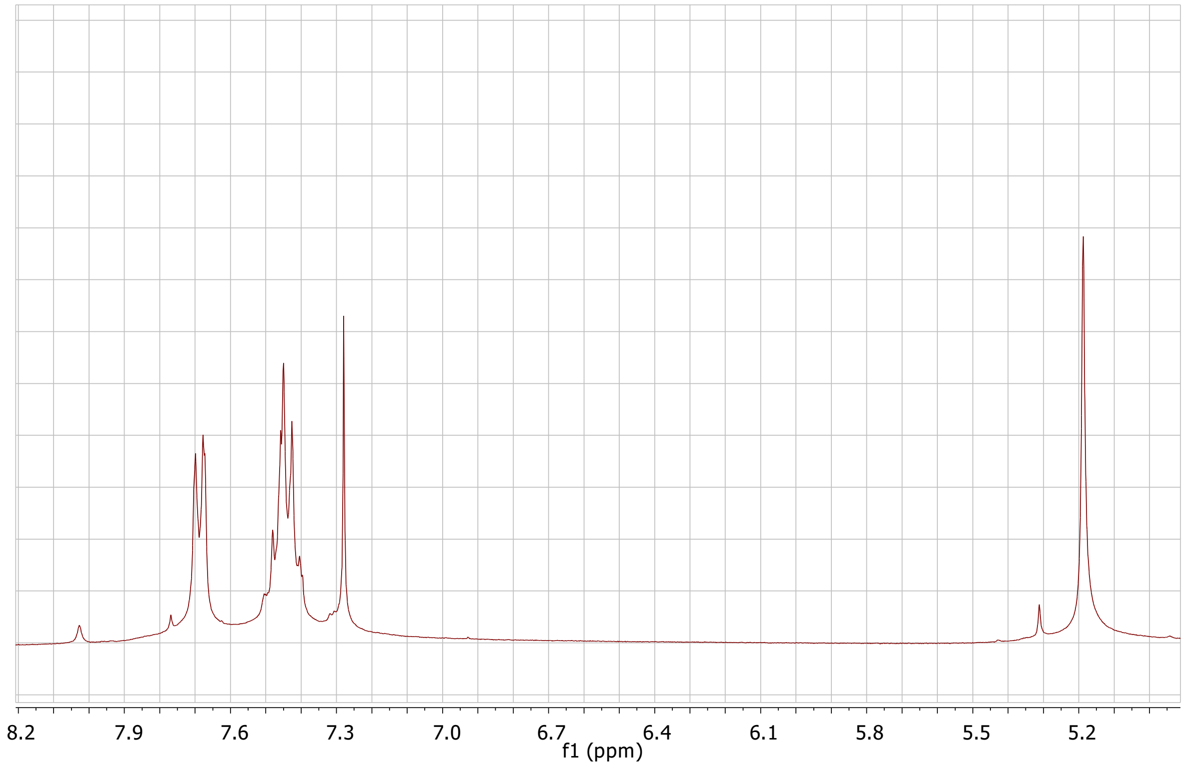


Figure 14: detail of the ^1H NMR spectrum of the products of the first reaction presented in scheme 9 recorded in $CDCl_3$. The signal at 7,26 ppm is attributed to chloroform; the signals of the product are very low (5,28 ppm) or covered by the others (7,27-7,47 ppm, 7,68 ppm).

All the performed attempts are reported in detail in the experimental section (Chapter 9).

Chapter 4: Optimization of the synthesis of Au NCs: $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$, $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$ and $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$

As already stated in the introduction, Au_{13} NCs are particularly stable species thanks to the presence of a 5+ charge associated to their metal core and therefore of 8 valence electrons. In the literature several examples are present, bearing different protecting ligands. [19][63][64][65]

The structure of this cluster's metal core has been first discovered in 1981, and the protecting ligand employed to stabilize it was a monodentate phosphine (PMe_2Ph) [26]. Examples with bidentate phosphines and alkynyls have been discovered more recently.[63][64][65]

The first examples of Au_{13} nanocluster stabilized by NHCs dates back to 2019 and 2020.[19][32] During their study Zheng et al. synthesized three different clusters with the same metal core and changing the ligand properties, to show how the tailorability of NHCs could be interesting to influence the properties of the final cluster (figure 15, schemes 25-27).[19] This study is also the first to report the synthesis of an AuNC bearing bidendate carbene ligands, that are found to confer superior rigidity and enhanced luminescence to the cluster, together with the presence of benzyl groups.

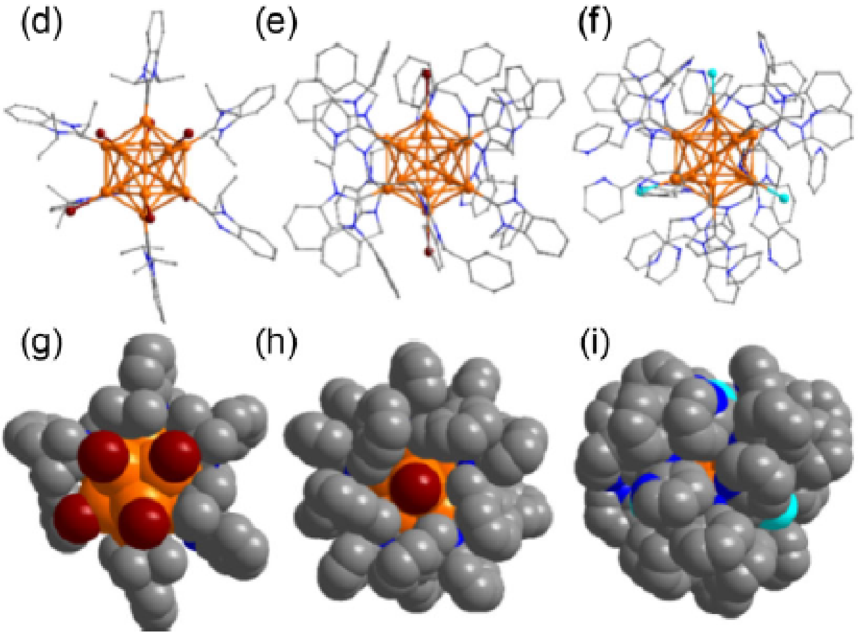
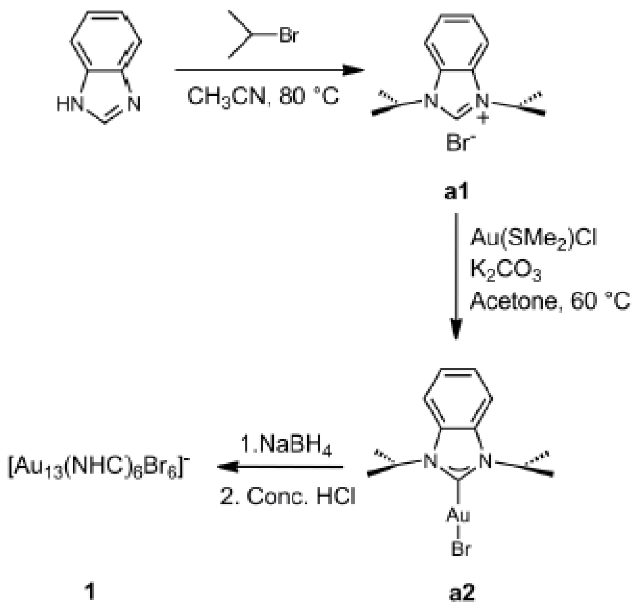
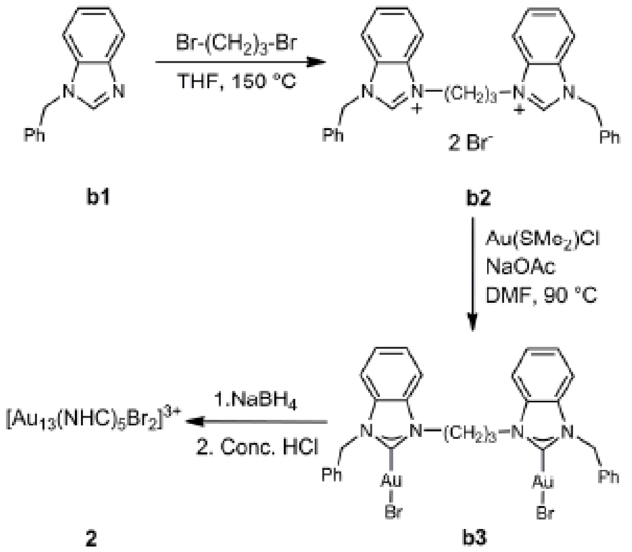


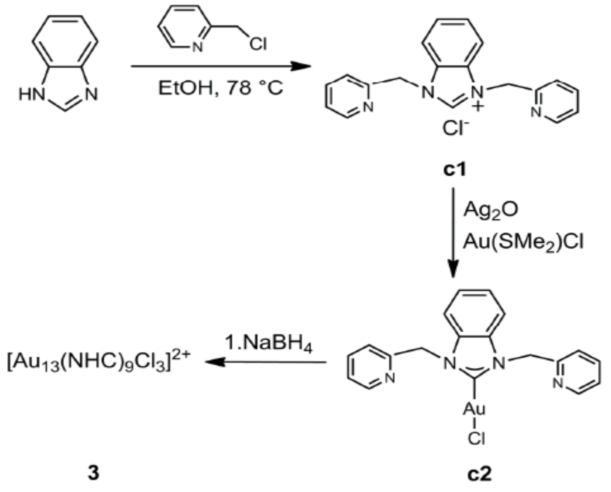
Figure 15: Au_{13} clusters synthesized by Zheng et al.[19]



Scheme 25: synthesis of the first Au_{13} cluster obtained by Zheng et al.[19]

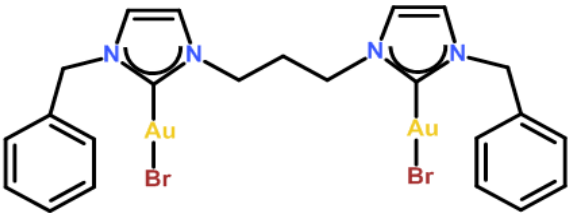


Scheme 26: synthesis of the second Au_{13} cluster obtained by Zheng et al. using a di-NHC ligand.[19]



Scheme 27: synthesis of the third Au_{13} cluster obtained by Zheng et al.[19]

Our research group, during the last year, has conducted a screening regarding the synthesis of several NCs starting from different Au-NHC complexes. Of particular interest, the synthesis of an Au_{13} cluster via reduction of a dinuclear gold complex different from the one reported in article [19] (complex H, scheme 28) was accomplished. The synthesis was modified with respect to the one reported in the literature, that involves a final acid condensation to bring several small clusters to Au_{13} species. In particular, a stoichiometric approach was employed, in which, for every 5 equivalents of dinuclear complex, 3 equivalents of $AuCl(SMe_2)$ were added. This synthetic procedure leads to a high increase in yield and to the possibility of obtaining NCs with anionic ligands different from halides, namely BH_4^- (two or one).



Scheme 28: structure of complex H, used for the synthesis of three novel Au_{13} NCs.

This last aspect is very important, since in literature $Au-BH_4$ bonds are almost absent. $Au(BH_4)_3$ is a species that can be synthesized only under very controlled conditions (-120 °C, diethyl ether) and decomposes thermally to gold, diborane and hydrogen gas.[66] $AuBH_4$ has been ruled out as a possible existing species because, thanks to theoretical calculations, it has been demonstrated that it is most stable as metal hydride $HAuBH_3$ and has a low barrier for rearrangement.[67] The obtained cluster species is a very interesting finding about the interaction of an Au(I) center and tetraborohydride anions.

Complex H has been synthesized according to a literature procedure. Purity has been checked via ^1H NMR (figure 16).[68]
It has then been subjected to stoichiometric co-reduction trials (scheme 29).

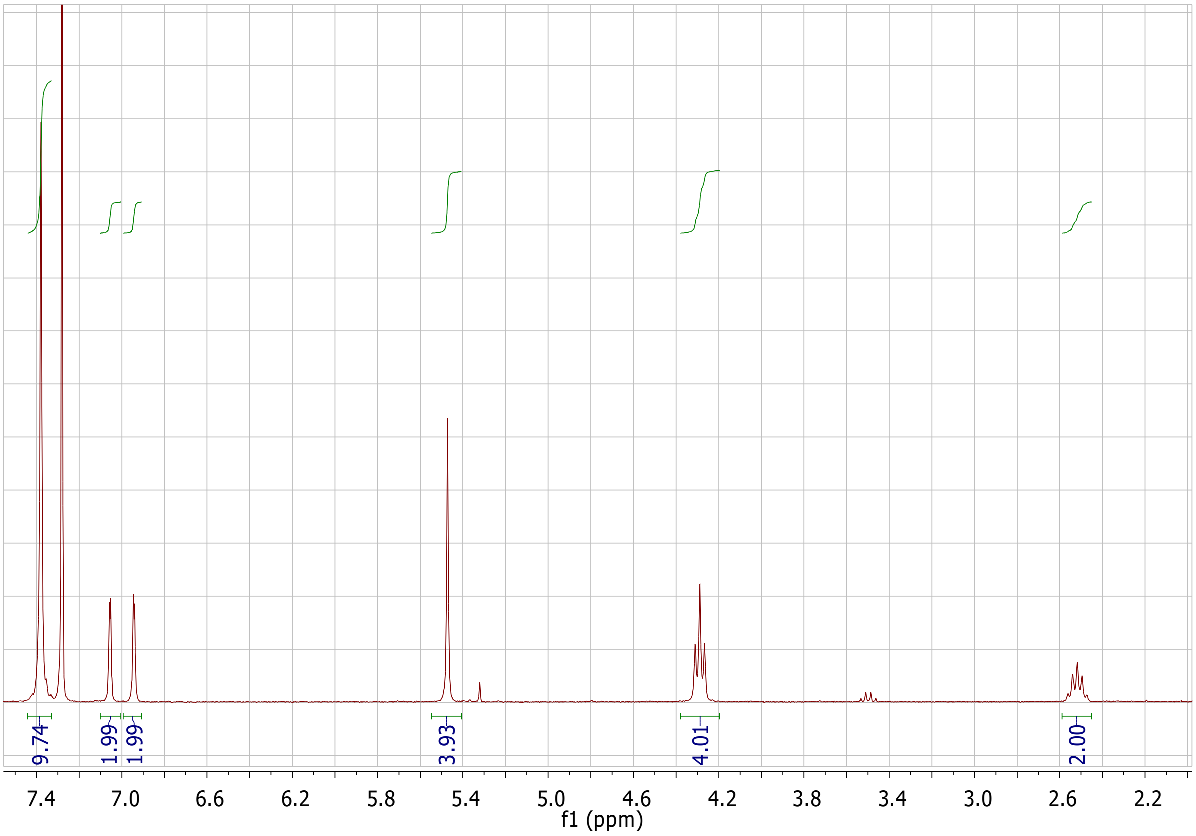
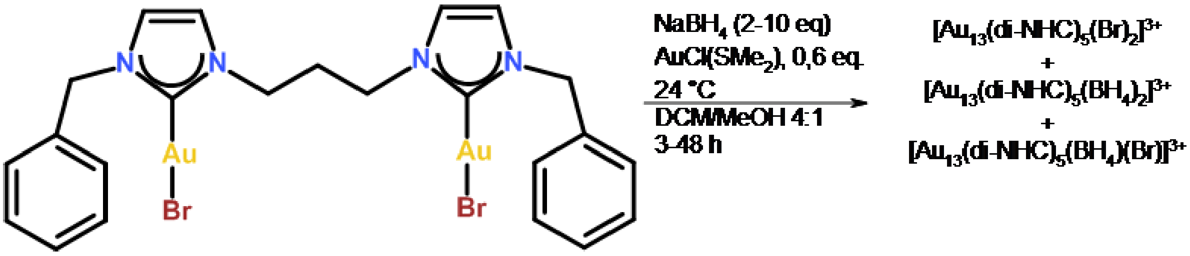


Figure 16: ^{1}H NMR spectrum of complex H, recorded in $CDCl_3$. The signal at 7,26 ppm is attributed to chloroform. The quartet at 3,48 ppm is attributed to diethyl ether. Identification of the integrated peaks is available in the experimental section.



Scheme 29: stoichiometric co-reduction reaction employed for the synthesis of the Au_{13} clusters, starting from complex H. The ratio of the products is highly dependent on the reaction conditions.

The presence of the cluster bearing two or one borohydride anions as anionic ligands, together with the one bearing two Br anions prompted our group to study the effect of the modification of the amount of reducing agent used, since it is the source of borohydride anions.

The synthesis has been performed with varying conditions, mantaining room temperature and the reducing agent ($NaBH_4$) and observing the effect of the change of n. of equivalents of reducing agent, reaction time, halide ligand on the starting complex and presence of traces of water in the reaction mixture on the resulting product.

The reaction consists, as outlined in the previous scheme, in the dissolution of 1 equivalent of complex H and 0,6 equivalents of AuCl(SMe$_2$) in a 4:1 DCM/MeOH mixture (DCM = dichloromethane), followed by the dropwise addition of an ethanol solution of NaBH$_4$. To study the effect of the amount of reducing agent three separate syntheses have been carried out, using respectively 1, 2 and 10 equivalents of it.

Withdrawals have been carried out at 3, 24, 48 and 72 hours. They have been dried and subjected to a work-up to eliminate water soluble salts and as many impurities as possible, and then they have been redissolved in DCM and subjected to ESI-MS analysis.
MS analysis allowed to determine that, as predicted, 2 equivalents of reducing agents are appropriate conditions to obtain the cluster bearing 2 Br anions as ligands, while 10 equivalents allow to obtain the one with mixed anions in largest percentage. In particular the best results have been obtained for:

- 2 Br anions: 3 h, 2 equivalents of NaBH$_4$ (figures 17-19)
- Mixed anions: 48 h, 10 equivalents of NaBH$_4$ (figures 20-22)

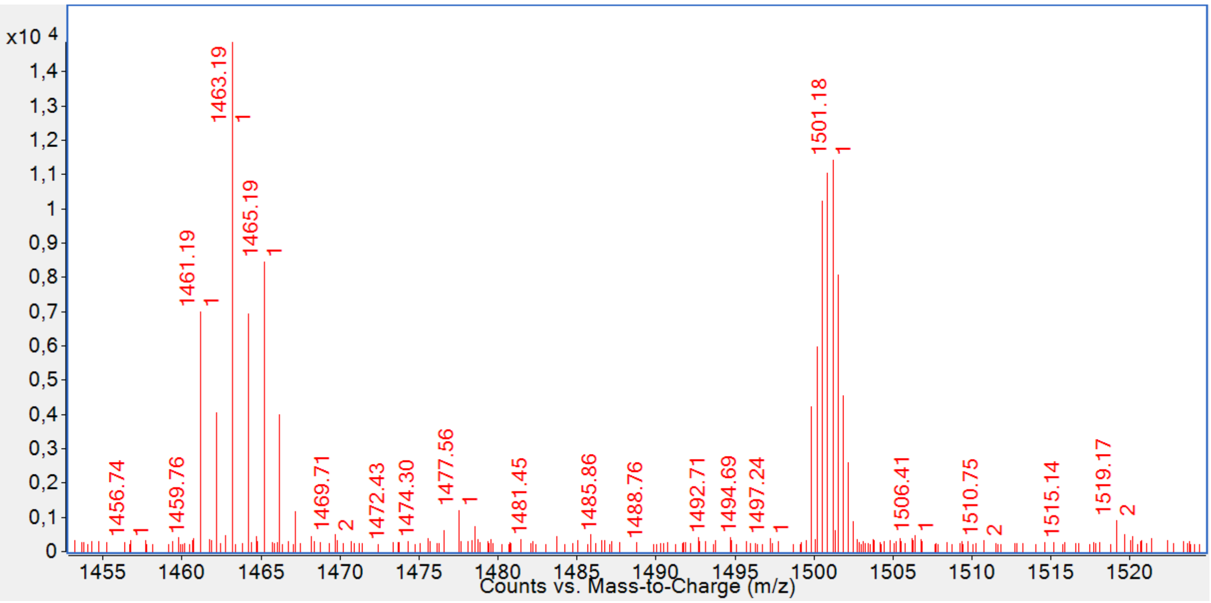


Figure 17: results obtained from ESI-MS analysis of the reduction performed using 2 eq. of NaBH$_4$ *at 3 hours. The peak at 1501,18 is relative to the cluster bearing two Br anions. The other clusters are absent. The charge is erroneously assigned as 1+, but zooming in is clear that it is 3+ since the distance between peaks of the isotopic pattern is 0,33 m/z units.*

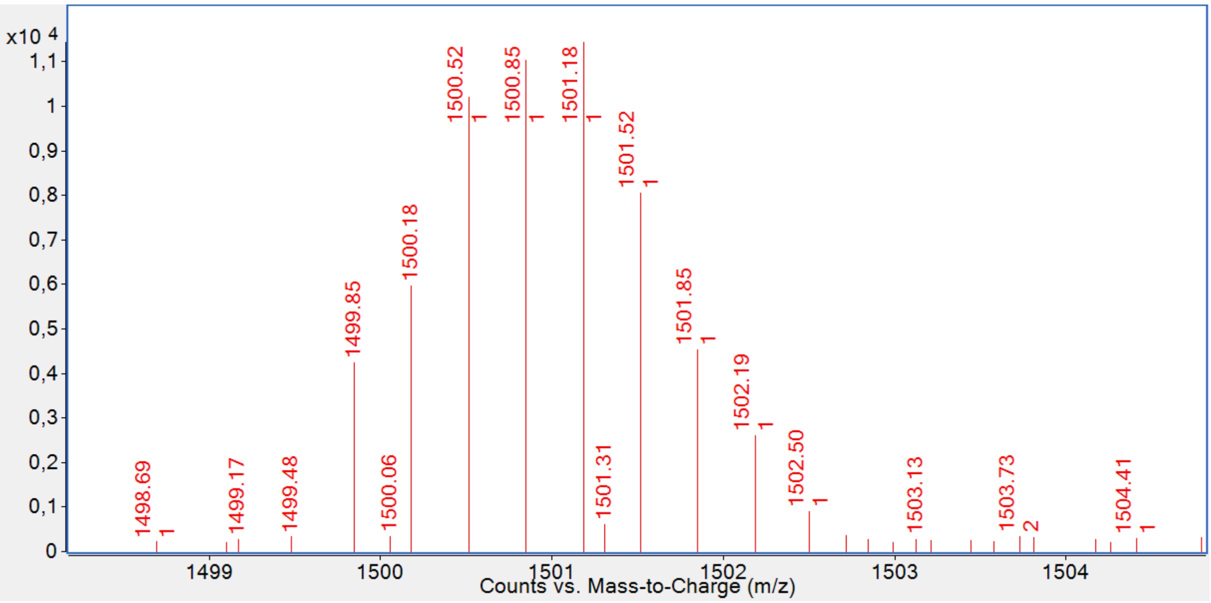


Figure 18: zoom on the isotopic pattern of the previous figure.

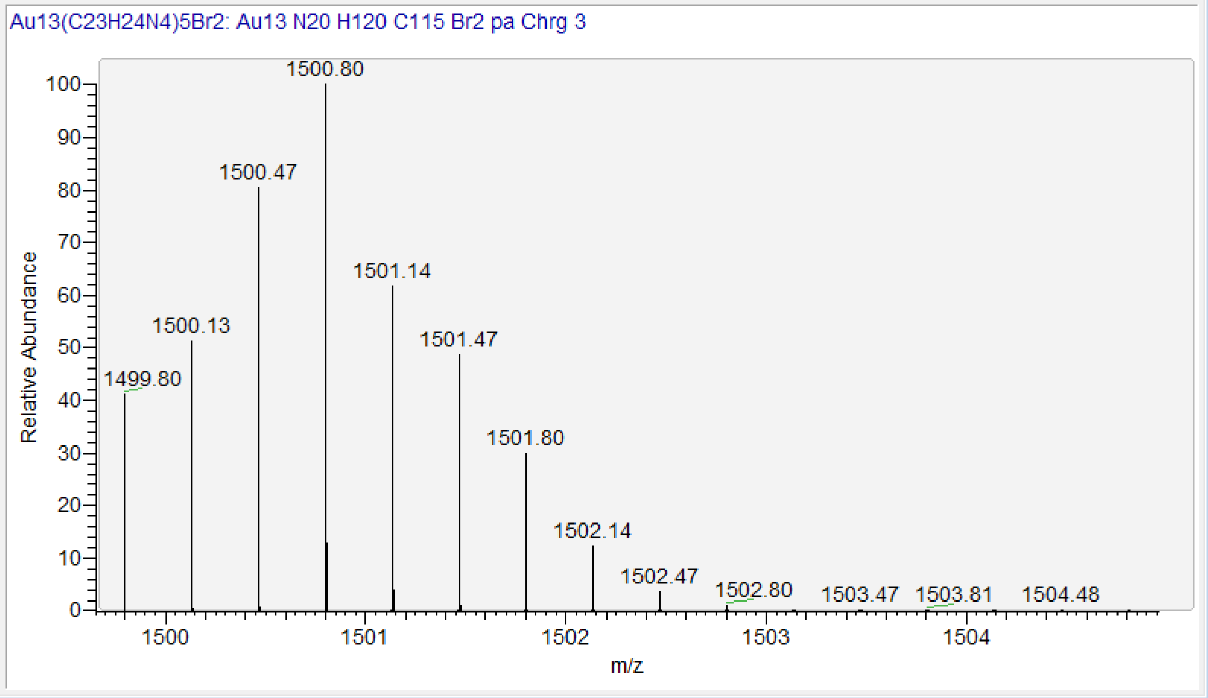


Figure 19: simulated isotopic pattern for the cluster bearing two Br anions.

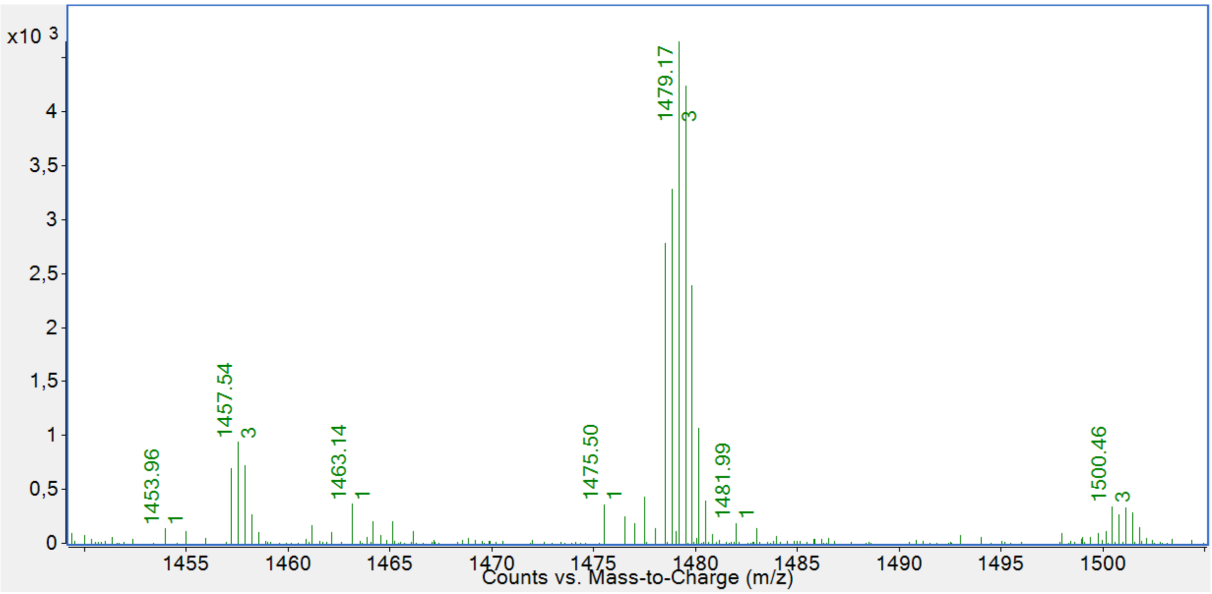


Figure 20: results obtained from ESI-MS analysis of the reduction performed using 10 eq. Of NaBH$_4$ at 48 hours. The peak at 1479,17 is relative to the cluster bearing one bromide and one tetraborohydride anions. The peaks at 1500,46 and 1457,54, minoritary, to the clusters bearing respectively 2 Br anions and 2 BH$_4$ anions.

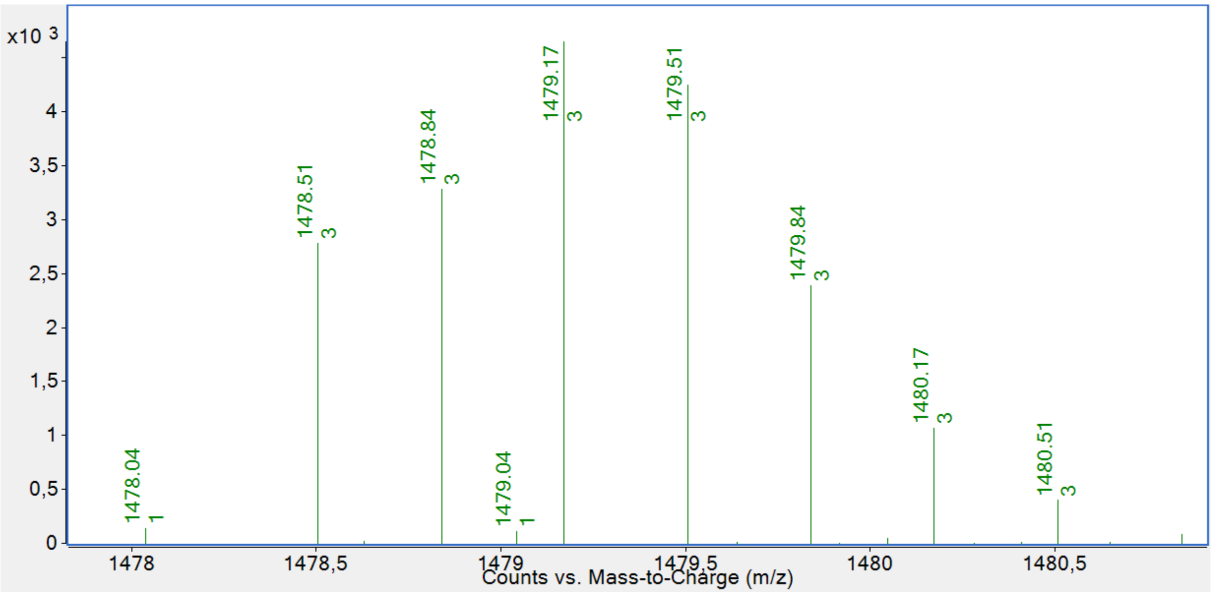


Figure 21: zoom on the isotopic pattern of the previous figure.

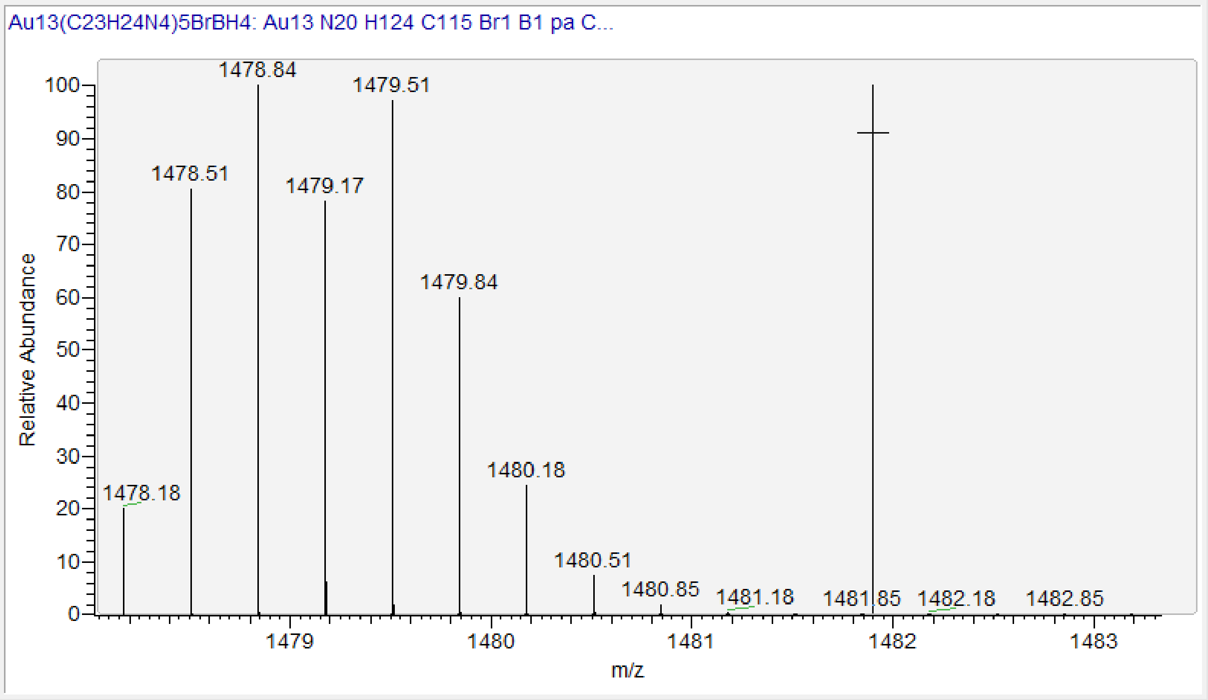


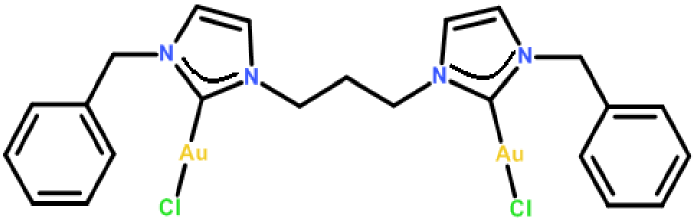
Figure 22: simulated isotopic pattern for the cluster bearing two BH_4 anions.

The isotopic patterns are slightly different from the simulated ones, and there is a slight shift in the m/z values. Also, in the experimental isotopic pattern for the cluster with mixed anions the first peak of the pattern is missing. This is probably due to the low concentration of the sample, together with some instrumental or software error due to limited processing ability. Indeed, trying to extract the ms spectrum from the chromatogram multiple times leads to different outcomes in all the cases. The missing peak reappears and the relative intensities change, even significantly.

The cluster with two borohydride anions could not be obtained in significant yield in these trials.
The yield is 15% (2 Br) and 23% (mixed anions) respectively.

Further trials have been performed using 3,3 and 4,3 equivalents of $NaBH_4$. The aim was to check if the cluster bearing mixed anions could be obtained in higher purity with these conditions. In the second case both $NaBH_4$ exposed to air and anhydrous $NaBH_4$ have been used, in order to check the effect of traces of water. The reactions have been followed with the same withdrawal and analysis protocol seen for the previous ones. MS analysis highlighted no effect of water, and that both synthethic procedures gave worse results in terms of prevalent product with respect to the ones already tested, giving a mixture of the two already obtained clusters.

The synthesis of a complex analogous to H, but with chloride anions as ligands (H_Cl_2, scheme 30), has been performed and analogous reduction tests have been carried out to check the effect of the halide ligand in the starting complex. The complex has been prepared starting from the corresponding bisimidazolium salt, prepared starting from 1-benzylimidazole and benzyl chloride. ^{1}H NMR spectra for the salt and the complex are reported in figures 23 and 24, respectively.



Scheme 30: structure of complex H_Cl_2, used to check the effect of the halide ligand in the starting complex.

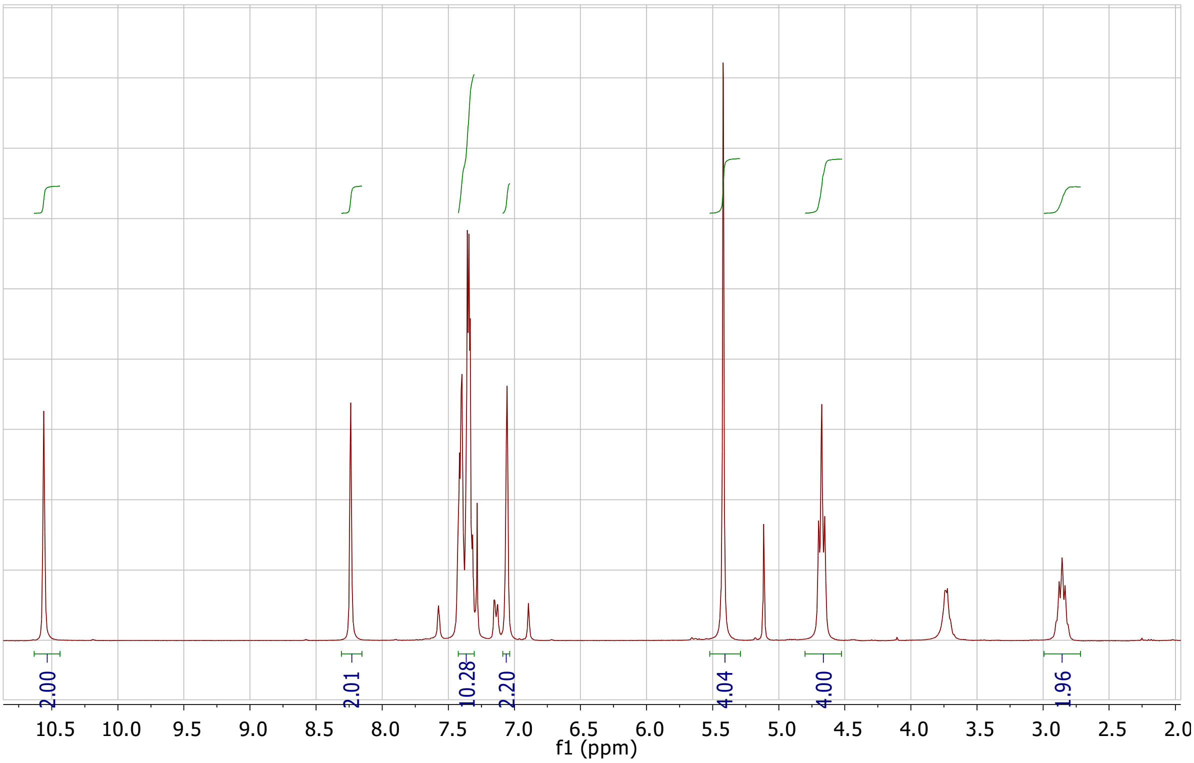


Figure 23: ^{1}H NMR spectrum of the bisimidazolium salt used as precursor for the synthesis of complex H_Cl_2. The spectrum shows the presence of some residual reagents, removed subsequently with the work up. The identification of the integrated signals is reported in the experimental section.

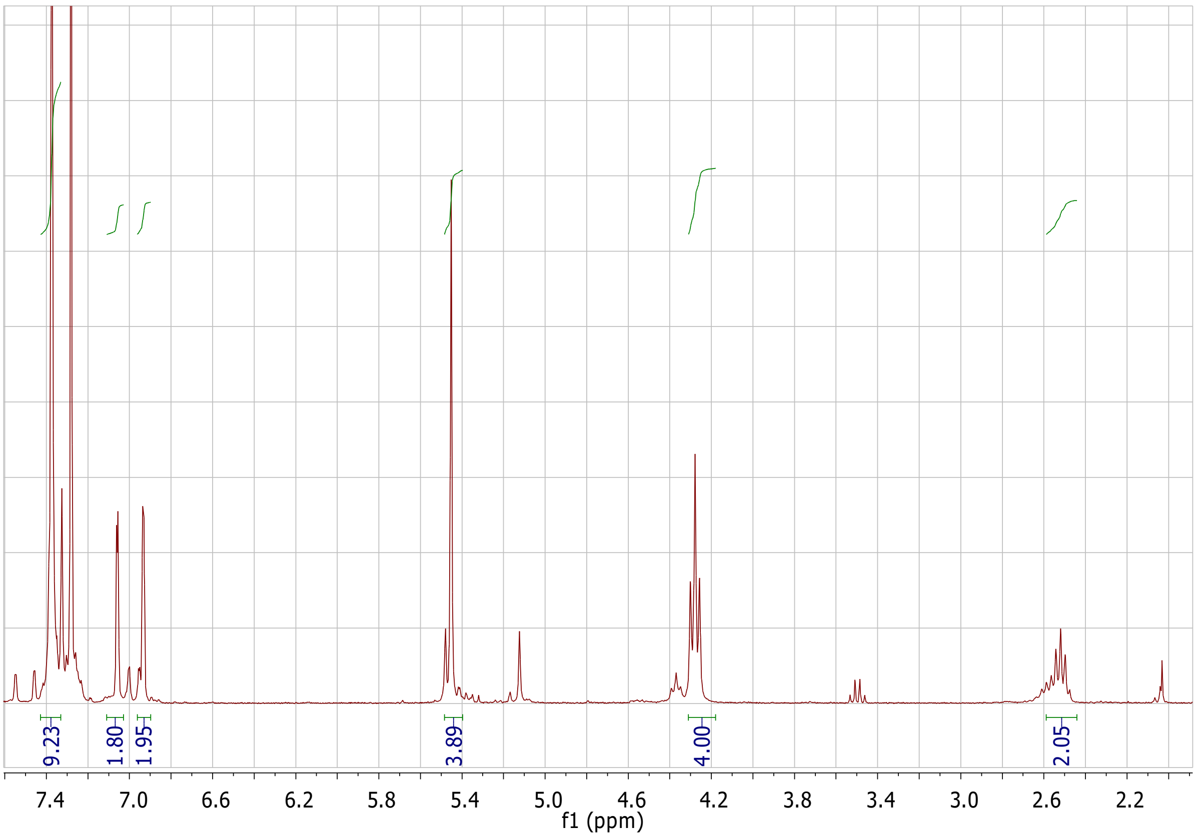


Figure 24: ^{1}H NMR spectrum of complex H_Cl$_2$. The spectrum shows the presence of some minoritary impurities. The peak at 7,26 ppm is attributed to chloroform, while the quartet at 3,48 ppm to diethyl ether. The identification of the integrated signals is reported in the experimental section.

Two reductions have been attempted with the same reaction conditions that have been employed for the synthesis of clusters$[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$and $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$. The first synthesis (2 eq. $NaBH_4$, 3 h) created a very evident metallic gold mirror, and a very low amount of NCs has been obtained. The second one (10 eq. $NaBH_4$, 48 h) gave a high amount of clusters, and with a very dark colour.

ESI-MS analysis has been performed on the products of the second reaction, and the results show the presence of the species $[Au_{13}(di\text{-}NHC)_5(Cl)(BH_4)]^{3+}$and $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$, as evidenced in figure 25.

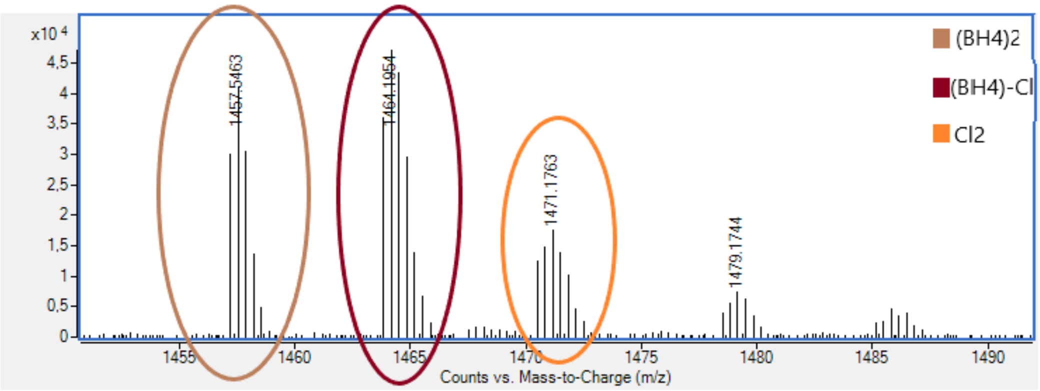


Figure 25: detail of the ESI-MS spectrum at 48 h for the preliminary synthesis involving complex H_Cl$_2$. *The peaks at 1457,5463 (brown) and 1464,1954 (dark red) are respectively assigned to clusters* $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ *and* $Au_{13}(di\text{-}NHC)_5(Cl)(BH_4)]^{3+}$, *while the one at 1471, 1763 (orange) to the cluster* $[Au_{13}(di\text{-}NHC)_5(Cl_2)]^{3+}$. *The peaks on the right are assigned to* $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$ *and* $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$, *and their presence is ascribed to impurities in the ESI-MS apparatus, belonging to the precedent analysis.*

The second reaction has therefore been repeated and followed by means of withdrawals. The withdrawals have been dried and subjected to a work-up to eliminate water soluble salts and as many impurities as possible, as in the previous case, and then they have been redissolved in DCM and subjected to ESI-MS analysis.The analysis show the presence of a great abundance of cluster bearing mixed anions at 3 to 72 hours, and an almost equivalent amount of this cluster and the one with 2 Cl anions after 96 hours (figure 26).

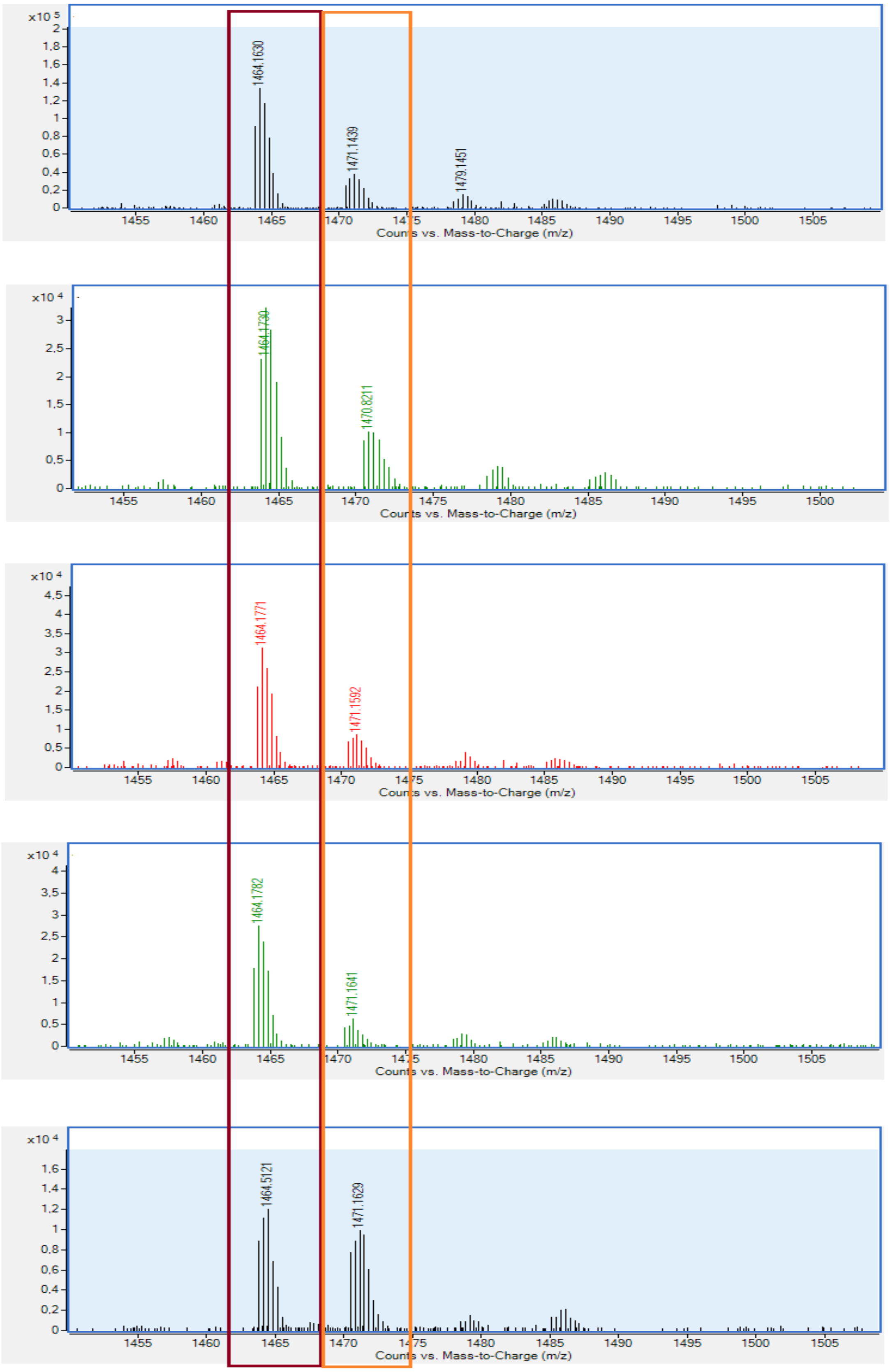


Figure 26: Detail of the ESI- MS spectra of the withdrawals (3, 24, 48, 72, 96 h) carried out on the second synthesis attempted using complex H_Cl$_2$*. Orange =* $[Au_{13}(di\text{-}NHC)_5(Cl_2)]^{3+}$*; Dark Red =* $[Au_{13}(di\text{-}NHC)_5(Cl)(BH_4)]^{3+}$*. The cluster* $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ *is absent.*

In summary, the reaction conditions for the synthesis of the three clusters, after preliminary trials, have been determined to be:

- 2 Br anions: complex H (1 eq.), $AuCl(SMe_2)$ (0,6 eq.), $NaBH_4$ (2 eq.), DCM/MeOH 4:1, 3 h.
- Mixed anions: complex H (1 eq.), $AuCl(SMe_2)$ (0,6 eq.), $NaBH_4$ (10 eq.), DCM/MeOH 4:1, 48 h.
- 2 BH_4 anions: not reproducible synthesis

Subsequent trials determined poor reproducibility issues even for the synthesis of the cluster bearing mixed anions. In particular, it can be obtained as the major product with the cited conditions, but variable and non-negligible amounts of the other two cluster species are present.

As of today, reaction conditions for the reproducible synthesis of cluster $[Au_{13}(\text{di-NHC})_5(BH_4)_2]^{3+}$ have been obtained by one of the PhD students of our research group, allowing for its study and the determination of the nature of the interactions between Au(I) and tetraborohydride anions.

Characterizations

The products with two Br anions and mixed anions obtained from the reactions have been subjected to recrystallization from DCM/diethyl ether vapours and dried; their purity has been checked by means of ESI-MS analysis and then they have been subjected to characterizations. ESI-MS spectra are reported in figures 27 and 28. The full spectrum is reported, to give an idea of the degree of purity that the cleaning procedure has yielded. The product obtained from the first reaction using complex H_Cl_2 was a mixture with no clear prevalent product, and the reaction was not reproducible, so the recrystallization and characterization haven't been performed.

In both the recorded spectra the molecular peak of the target cluster is the second highest peak, second only to the peak of the dicationic complex $[Au_2(\text{di-NHC})_2]^{2+}$. This species is common as a byproduct in clusters' synthesis, but is also formed due to fragmentation in ESI conditions. The spectrum of the cluster with mixed anions shows the presence of an higher relative concentration of dicationic complex, indicating that the cleaning procedure has been less effective or that the fragmentation is more extensive with respect to the cluster with two bromide anions.

Single crystals have not been obtained yet in order to perform SC-XRD structural analysis for any of the clusters.

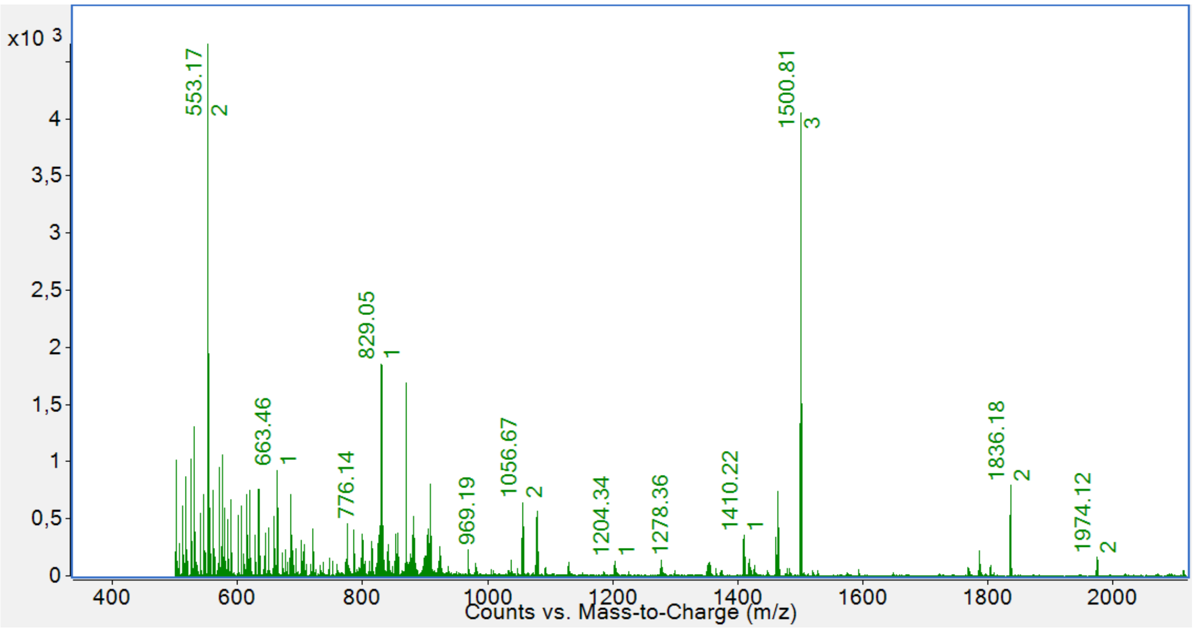


Figure 27: ESI-MS spectrum of $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$post-crystallization. m/z = 1500,81: $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$. m/z 553,17 = $[Au_2(di\text{-}NHC)_2]^{2+}$ (impurity+fragmentation).

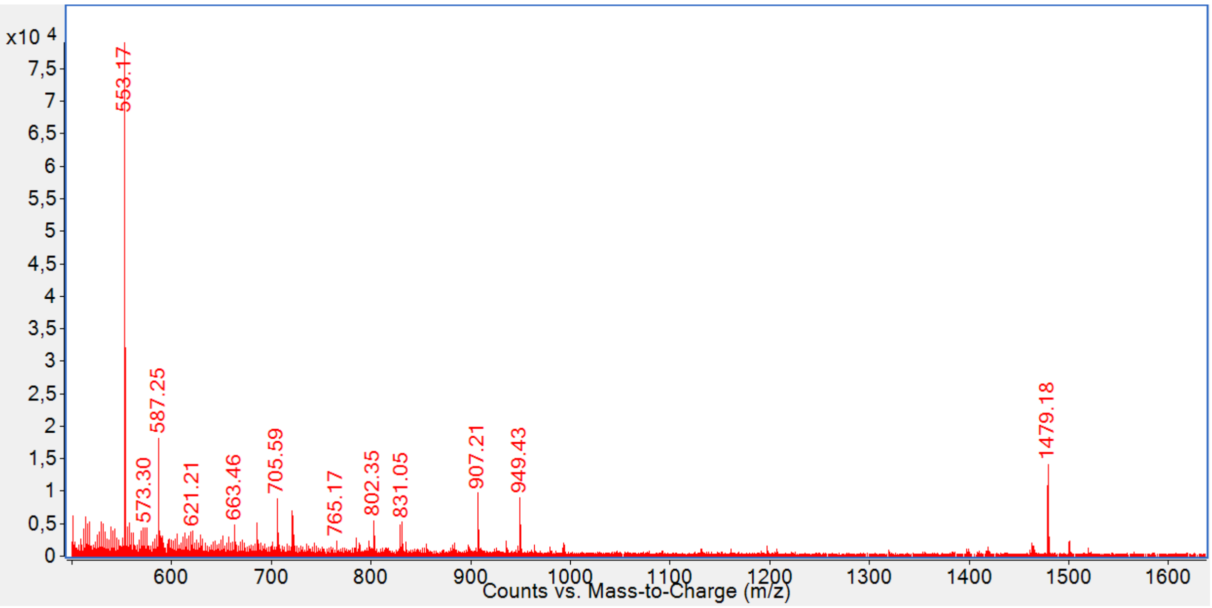


Figure 28: ESI-MS spectrum of $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$post-crystallization. m/z = 1479,18: $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$. m/z 553,17 = $[Au_2(di\text{-}NHC)_2]^{2+}$ (impurity+fragmentation).

^{1}H NMR has been performed as a mean to characterize the products of the reactions, but the technique is flawed by the complexity of the products themselves; it's difficult to obtain structural information due to the splitting and broadening of the signals that arises from the interaction of the ligands with a complex structure, such as the one of the metal core, and from the interactions between ligands that are due to their proximity (ex: π-π stacking between aromatic rings). The technique is useful to control the purity of the compounds since it allows to clearly distinguish signals arising from impurities, much less broad, such as the dicationic complex $[Au_2(di\text{-}NHC)_2]^{2+}$. The recorded NMR spectra are here reported in figures 29 and 30:

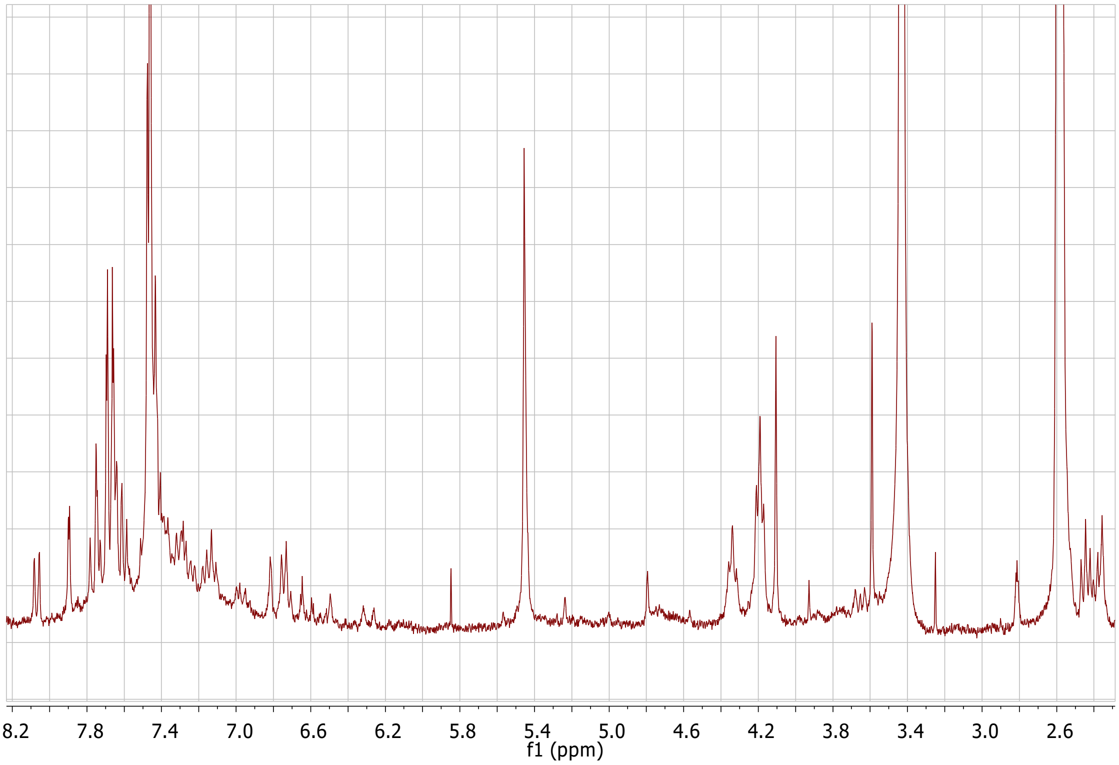


Figure 29: detail of the NMR spectrum of $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$*(*$CD_3CN$*). The signals at 4,20 ppm (t), 5,45 ppm (s) have been assigned to the dicationic complex* $[Au_2(di\text{-}NHC)_2]^{2+}$ *thanks to ESI-MS.*

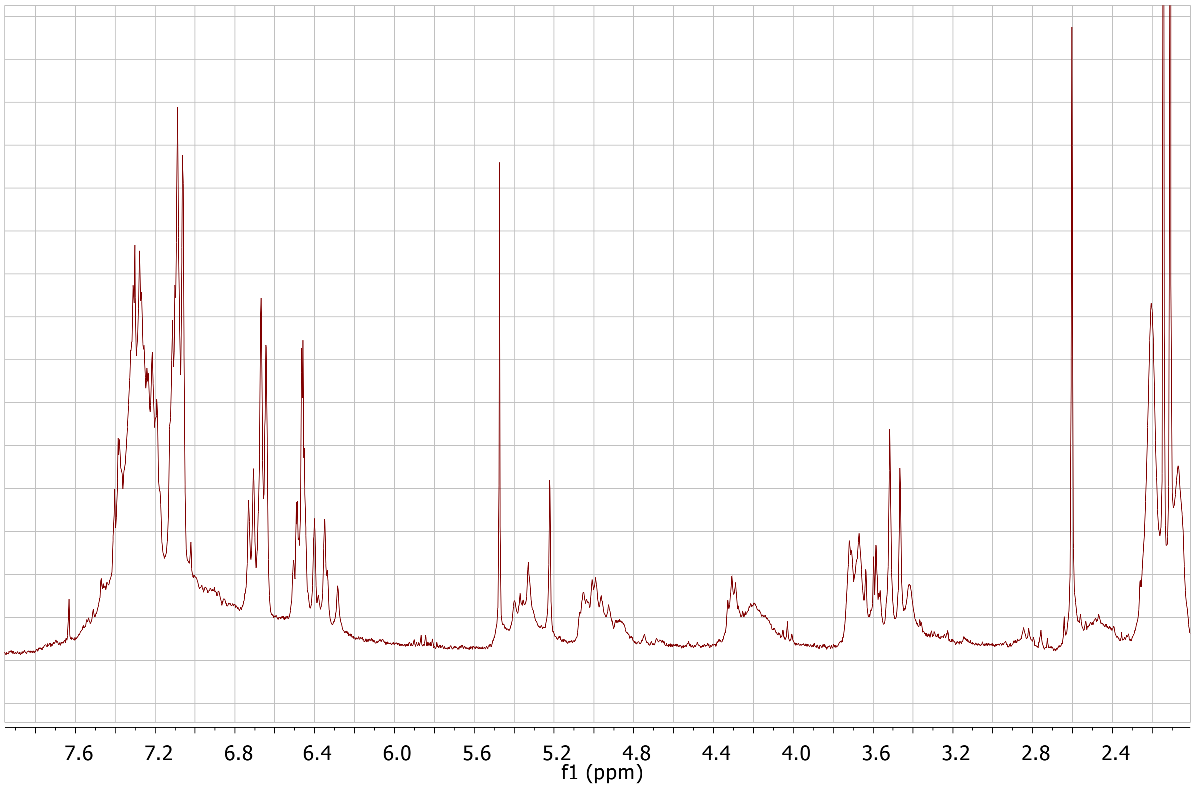


Figure 30: detail of the NMR spectrum of cluster $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$ *(*CD_3CN*). The peak at 2,16 ppm is due to the presence of water in the deuterated solvent.The signals at 2,55 ppm (q), 4,20 ppm (t), 5,45 ppm (s) have been assigned to the dicationic complex* $[Au_2(di\text{-}NHC)_2]^{2+}$ *thanks to ESI-MS.*

Comparing the NMR spectra is clear that in the one of the cluster bearing mixed anions the dicationic complex impurity is present in lower amount. This goes in contrast with what is evidenced by ESI-MS, and the explanation could be the lower stability in ESI conditions of the cluster bearing BH_4 anions. This hypothesis is substained by the fact that the dicationic complex is an usual fragmentation product in ESI-MS analysis of AuNCs. Another interesting fact is that the peaks of the dicationic complex are broadened in the spectrum of the cluster with mixed anions, where it is present in lower concentration. This seems to suggest some interactions between the complex and the cluster, leading to this effect. The presence of these interactions, at least in ESI conditions, has been revealed in several occasions (see chapter 5, figure 42 and relative discussion). This spectrum seems to suggest that it's not an event relative only to ESI, but happens also in solution under normal circumstances.

UV-Vis spectroscopy measurements have been performed on both NCs in DCM. From figures 31 and 32 it is possible to appreciate a significant difference between the two, that implies the existence of a certain effect of the anionic ligands on the separation in energy between superatomic orbitals. In particular, in the case of the cluster with mixed anions, more peaks are present and a certain shift of one of the common signals arises; also, there is a broad band that extends from 400 to 700 nm in the spectrum of the cluster with two Br anions, while in the cluster with mixed anions the band is relatively higher in intensity.

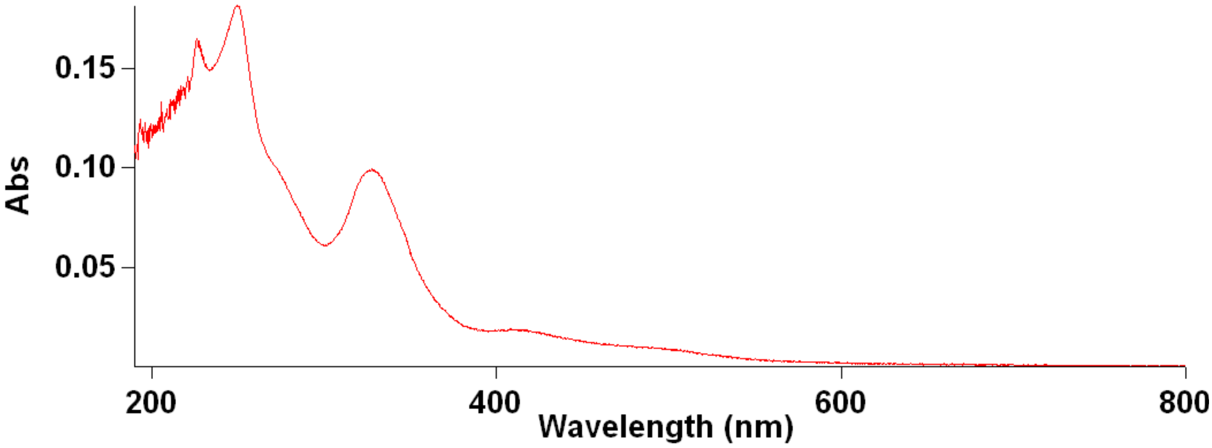


Figure 31: UV-Vis spectrum of cluster$[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$ *(DCM).*

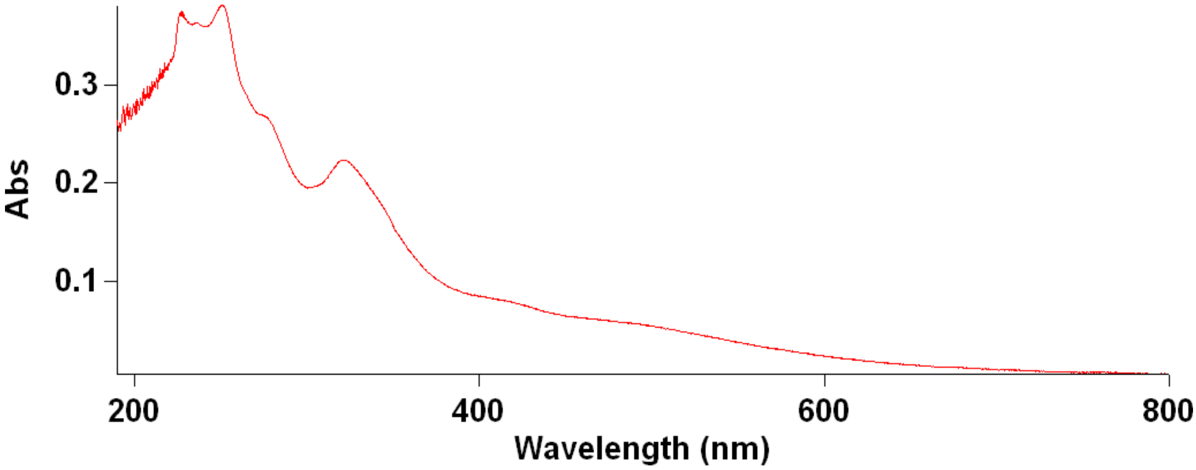


Figure 32: UV-Vis spectrum of cluster$[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$ *(DCM).*

$[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$

226 nm, 249 nm, 328 nm, 412 nm.

$[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$

226 nm, 232 nm, 249 nm, 293 nm (hump on the side of the previous main peak), 326 nm. There is a hump in the broad band that extends up to 700 nm at about 410 nm consistent with a peak similar to the last maximum in the previous spectrum.

All this information shows that there are some signals in common between the two species, namely 226 nm and 249 nm (and probably 412 nm as well). These signals are unaffected by the presence of different anionic ligands. The simmetry break granted by the presence of two different anionic ligands, however, seems to generate new signals at 232 nm and 293 nm, and also grants a slight shift to the signal at 328 nm, that goes towards lower wavelenght values (326 nm). The superimposed normalized spectra are reported in figure 33.

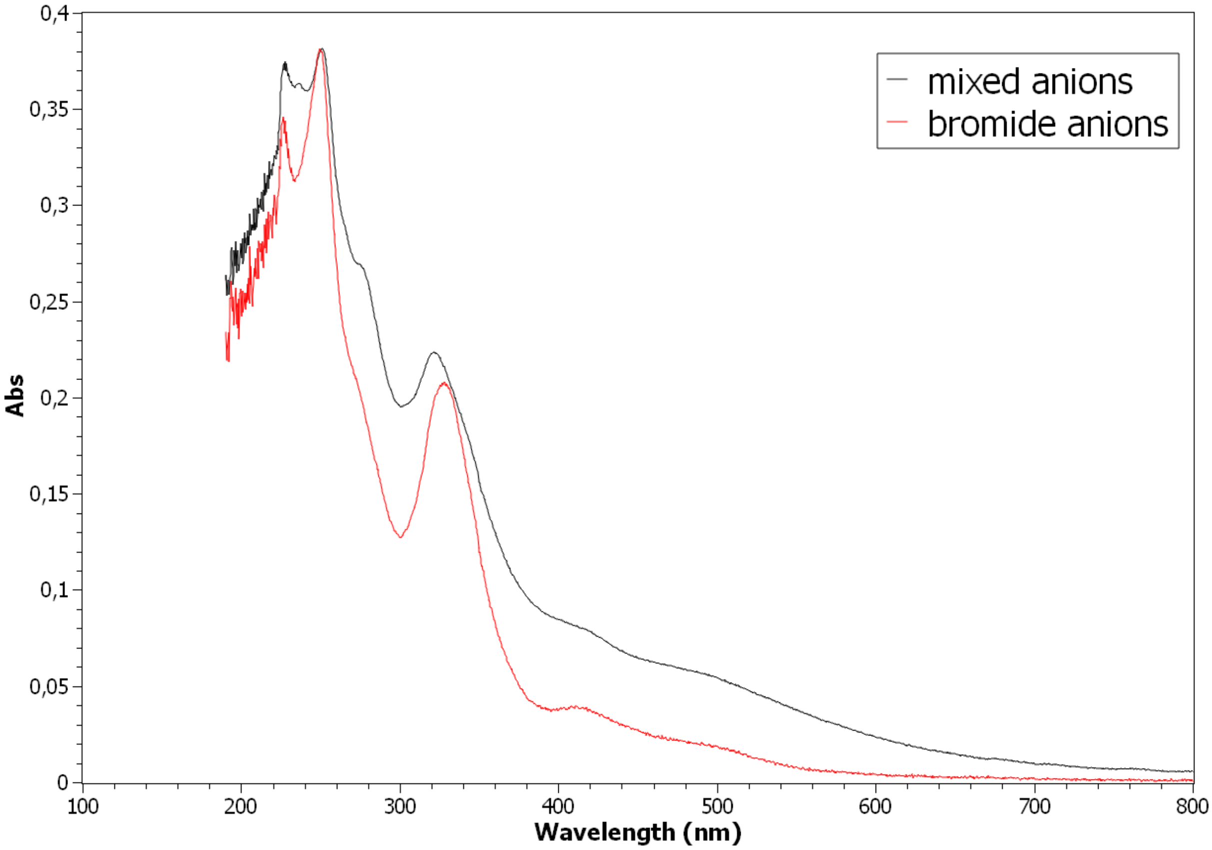


Figure 33: superimposed UV-Vis spectra of the cluster with mixed anions and two bromide anions, normalized at the absorbance of the peak at 249 nm.

Chapter 5: Testing of new reducing agents - hydrazine

Gold nanoclusters are mainly prepared by the direct reduction method, a one pot synthesis consisting in the addition of a solution of a reducing agent to a solution of a gold salt or complex. This method dates back to 1857, when Faraday prepared the first gold colloid from the reduction of gold(III) chloride by phosphorous, and was rediscovered and developed further in the last 30 years. This type of methodology allows to control the synthesis of Au NCs, and the main controlling parameters are temperature, solvent, ligand and reducing agent.

Ligands influence thermodynamics and kinetics of the process, and allow the formation of NCs of different sizes according to their steric hindrance, electronic structure, bonding style and other characteristics. Ligands with a larger steric bulk lead to the formation of smaller clusters according to experimental observation, and affect the atomic packing mode and its distortion. An important effect on distortion is also given by the polarity of the ligands.

Depending on the type of ligand temperature can have different effects, regarding always the kinetic and thermodynamics of the process: increases in temperature can lead to a faster formation of the desired product or to the transformation of the product in several byproducts, depending on the specific conditions.

Solvents have a great effect on the aggregation of Au complexes and on the dispersion of intermediate Au NCs, and can influence the architecture of the resulting clusters. Moreover they have thermodynamic effects, since they influence the stability of the reacting species.

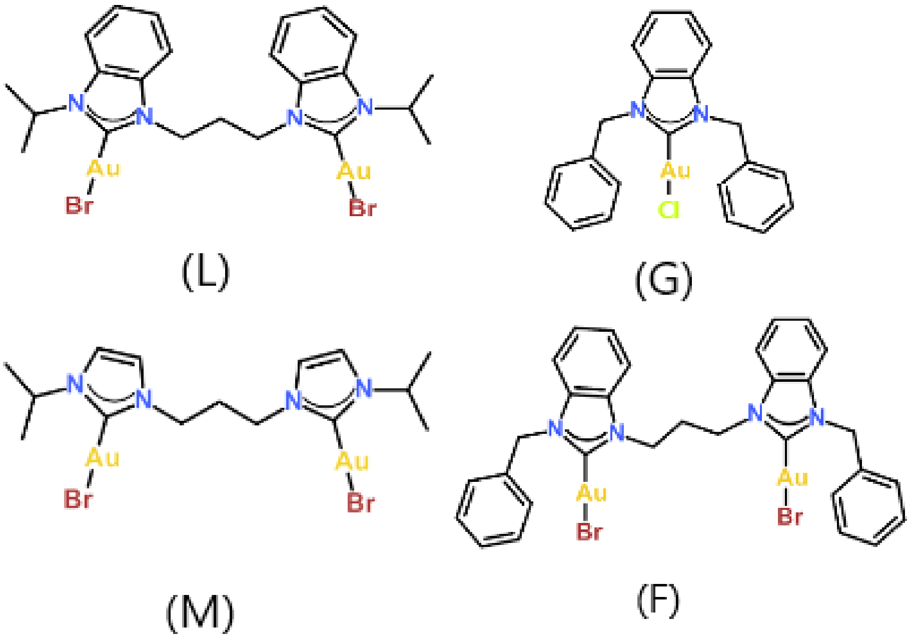
The reducing agent is an important piece of the puzzle since it controls the kinetic of the reduction process, allowing to obtain different clusters and size distributions. In the already available literature sodium borohydride is the reducing agent of choice in the preparation of NHC-protected gold nanoclusters, and offers fast kinetics, that in turn lead to a broader size distribution of intermediate clusters. Weaker reducing agents can slow down the kinetics of the process and therefore lead to different clusters. Borane-tert-butylamine complexes, CO and sodium cyanoborohydride were used for such reactions.

The amount of reducing agents also plays a huge role, as outlined in the previous chapter. For example the use of a stoichiometric quantity can lead to the formation and identification of many intermediate clusters, giving mechanistic informations on the reduction process and also enriching the library of existing NCs.

Last but not least, a special case concerns the use of assisting reagents: the presence of acids, bases and foreign metal ions in the reaction mixture has been proven to have some kind of influence on the reaction kinetic and thermodynamics. [69]

Hydrazine is a reducing agent that can be used in two sets of conditions, in solution with or without an assisting base such as KOH, NaOH or NaO^tBu, or exploiting finely divided metals that act as an hydrogenation catalyst, receiving hydride anions from hydrazine itself and transferring them to the substrate. It's a strong poison that can deactivate some enzymatic pathways, and should be handled with care[70]. It's mostly supplied as hydrazine hydrate, with a concentration of 64%, since the only significant use of anhydrous hydrazine has been as rocket fuel or propellant for spacecraft and satellites.[71]

Although hydrazine has been used extensively as a reducing agent for metal ions, no reports on the use of hydrazine hydrate as a reducing agent in the synthesis of Au NCs are available in literature, therefore our research group decided to perform a trial regarding its use in the reduction of some mononuclear and dinuclear gold complexes, here reported (scheme 31):



Scheme 31: complexes used for the preliminary trial with hydrazine as a reducing agent.

The four complexes have been synthesized (except complex L, already available) according to the same literature procedure used to obtain complex H, starting from the corresponding imidazolium or bisimidazolium salt; the ligand precursor for complex G has also been synthesized.[68] ^{1}H NMR spectra are reported in figures 34-37.

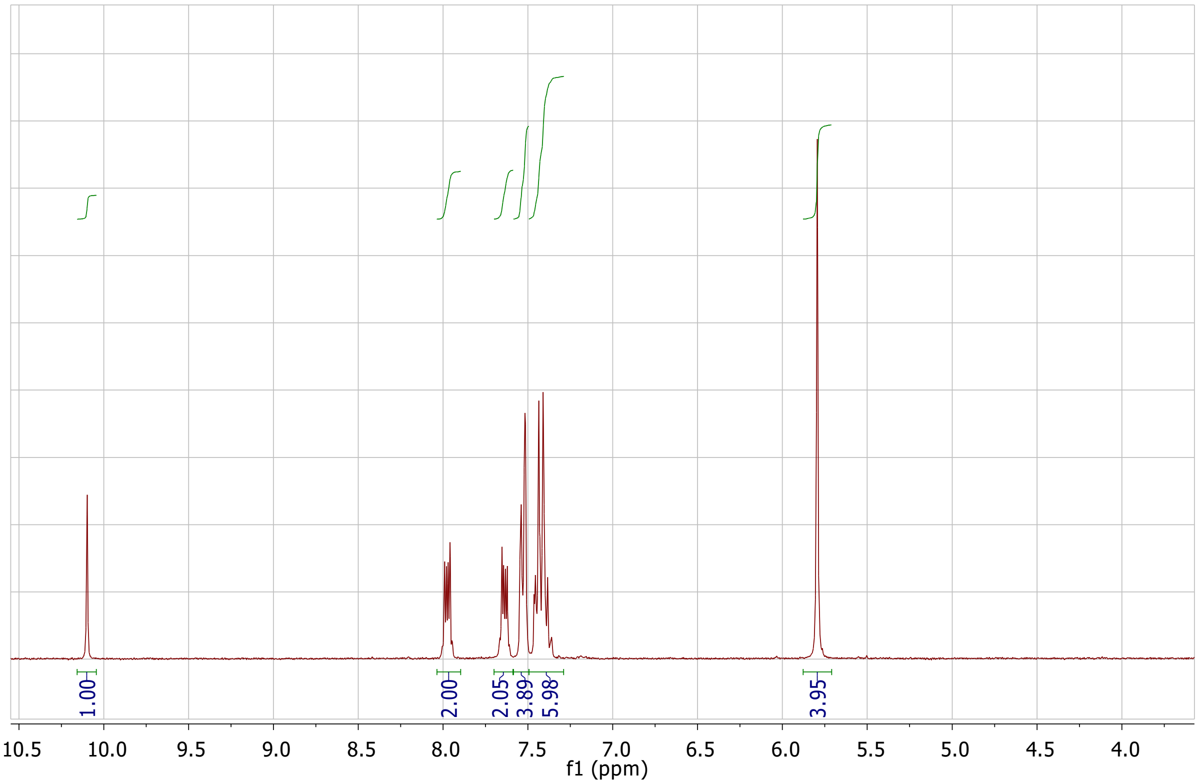


Figure 34: ^{1}H NMR spectrum of the imidazolium salt, ligand precursor for complex G, in DMSO-d_6.

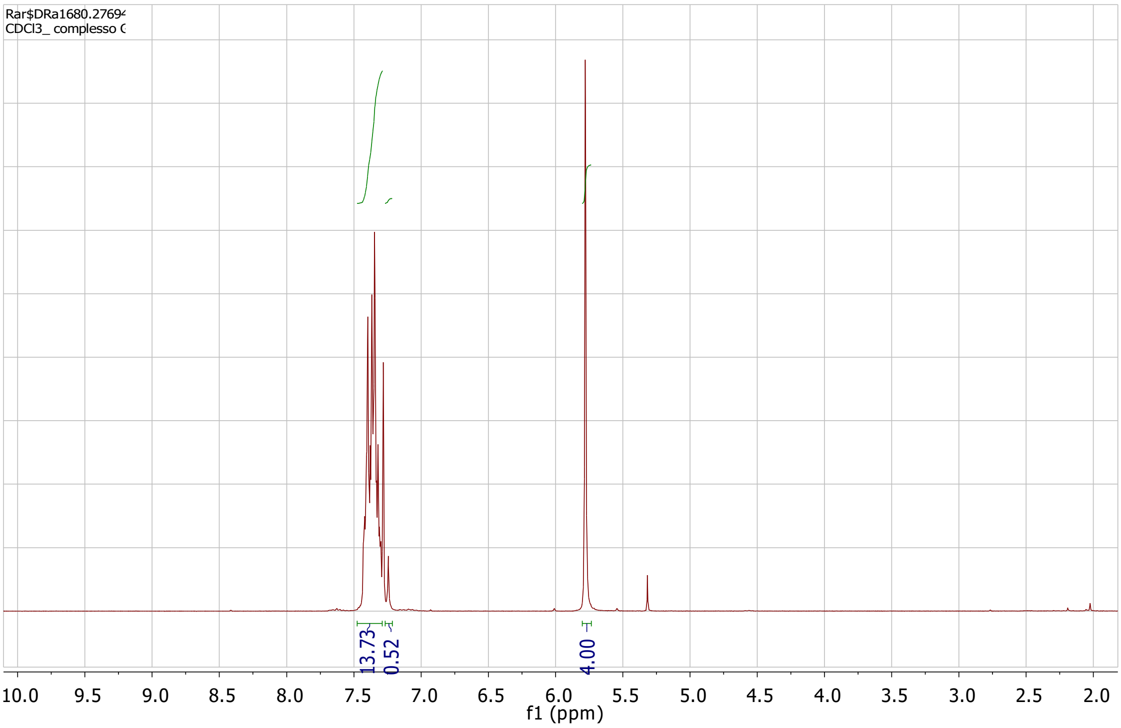


Figure 35: ^{1}H NMR spectrum of complex G in $CDCl_3$. The signal at 7,26 ppm is attributed to chloroform.

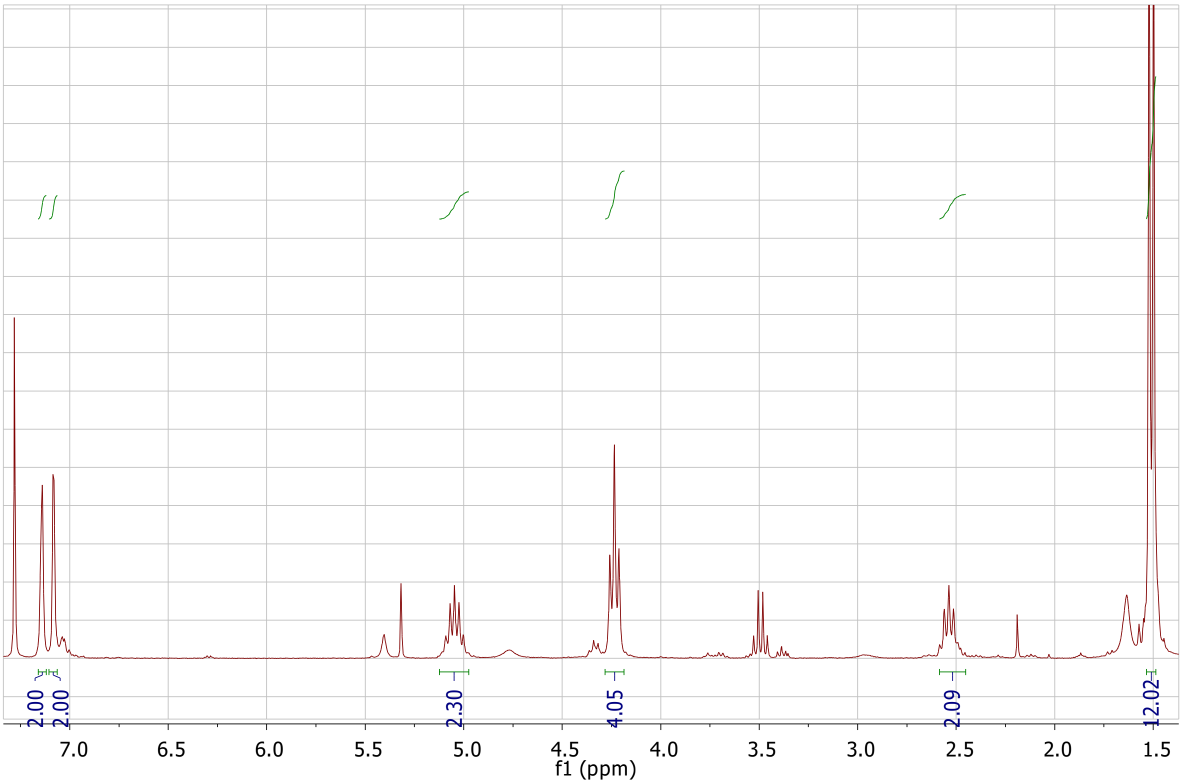


Figure 36: ^{1}H NMR spectrum of complex M in CDCl$_3$; the singlet at 7,26 ppm is due to chloroform, the one at 5,30 ppm to DCM, the quartet at 3,48 ppm is due to residual diethyl ether, the singlet at 1,56 ppm is due to water and the one at 2,17 ppm to acetone.

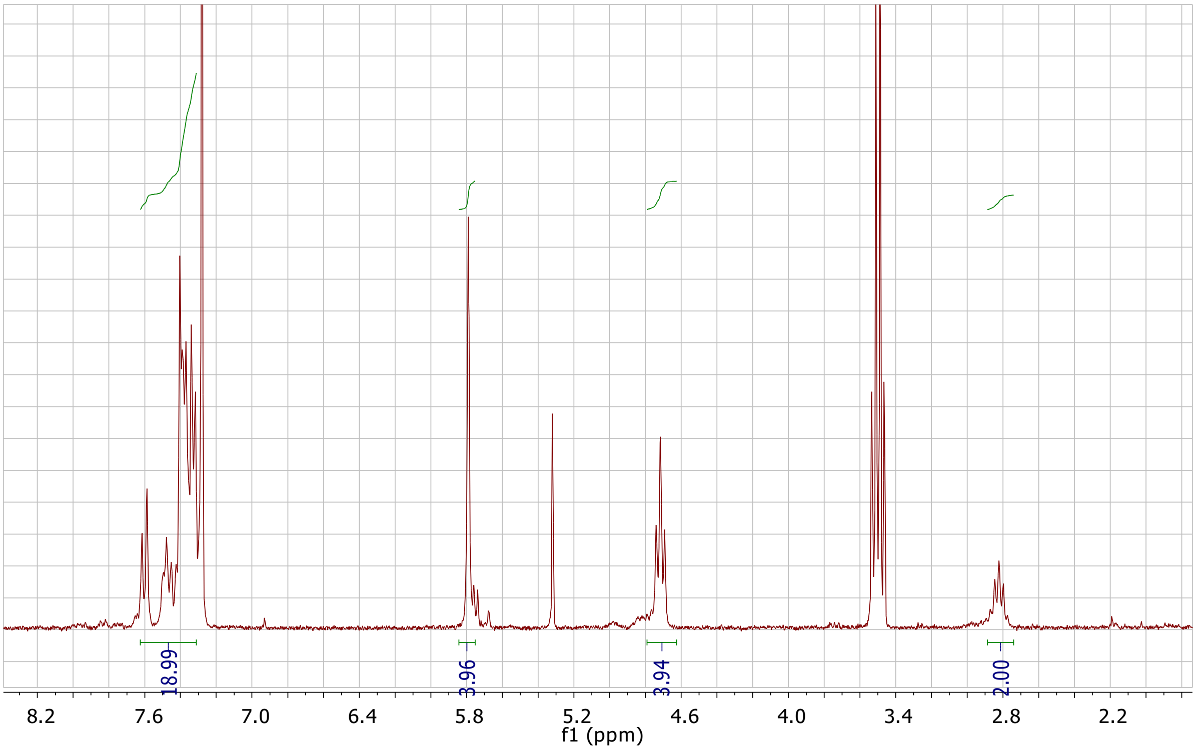


Figure 37: ^{1}H NMR spectrum of complex F in CDCl$_3$. The quartet at 3,48 ppm is due to the presence of diethyl ether, the singlet at 5,30 ppm to DCM and the singlet at 7,26 ppm to chloroform.

The four complexes were reduced using the same reaction conditions:

1) Room temperature.
2) 10 equivalents of hydrazine monohydrate as reducing agent.
3) DCM/MeOH 4:1 mixture as solvent.
4) 100 equivalents of KOH as reagent for hydrazine activation.

The reactions have been followed by means of withdrawals at 3 h, 24 h, 48 h, and 72 h. These withdrawals have been analyzed by ESI-MS, after removal of KOH.
Thanks to mass analysis the convergence of the reactions towards a major product has been determined in the cases of complexes G and L (figures 38-41). For complexes F and M the reaction yields a mixture of cluster species. In particular the clusters obtained from the first two reactions have a molecular formula $[CAu_6(\text{di-NHC})_3]^{2+}$ or $[CAu_6(NHC)_6]^{2+}$ according to the nature of the starting complex (mononuclear/dinuclear).

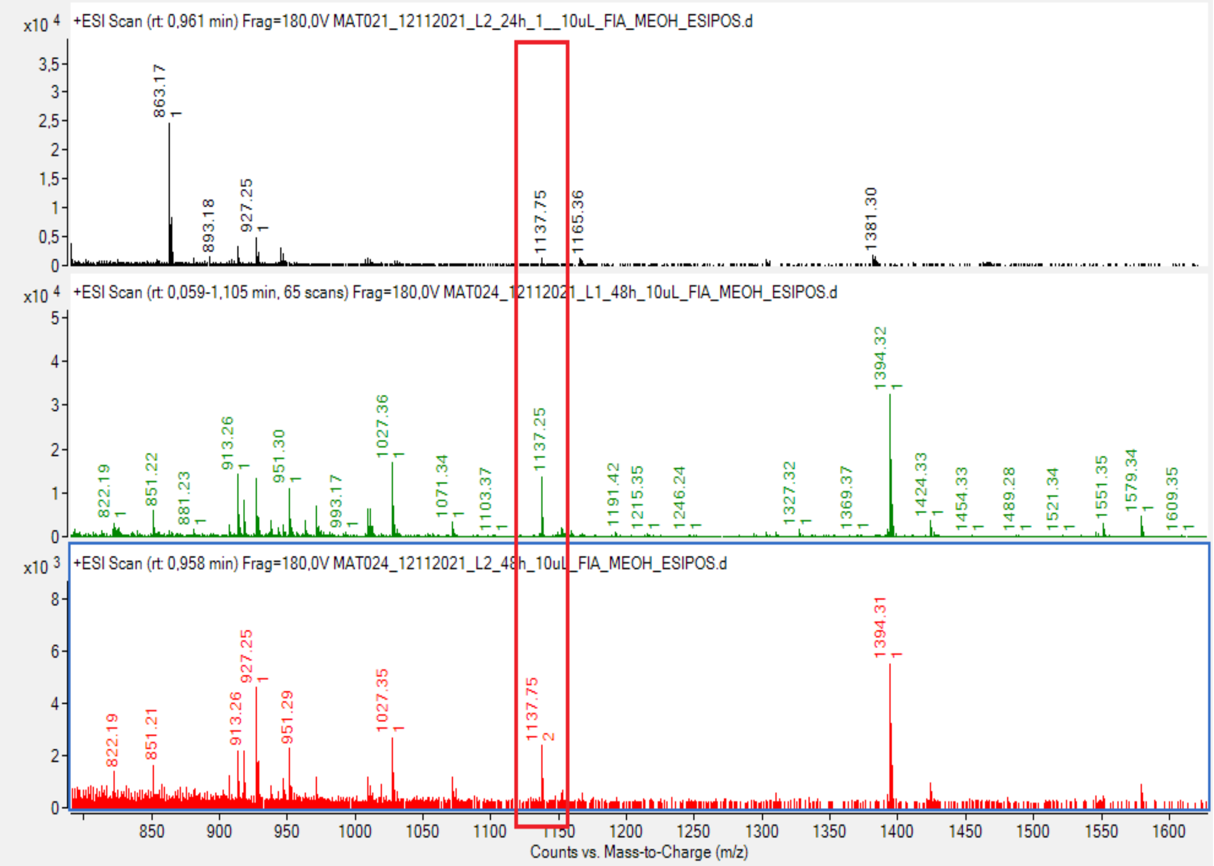


Figure 38: ESI-MS mass spectra of the withdrawals carried out at 24, 48 and 72 h on the preliminary reduction of complex L. The peaks highlighted by the red rectangle refer to the $[CAu_6(\text{di-NHC})_3]^{2+}$ *species, and are compatible with the simulated pattern. The peak at 1394.31 m/z units is consistent with a species of stoichiometry* $[Au_3(\text{di-NHC})_2(Cl)_2(CH)]^{+}$.

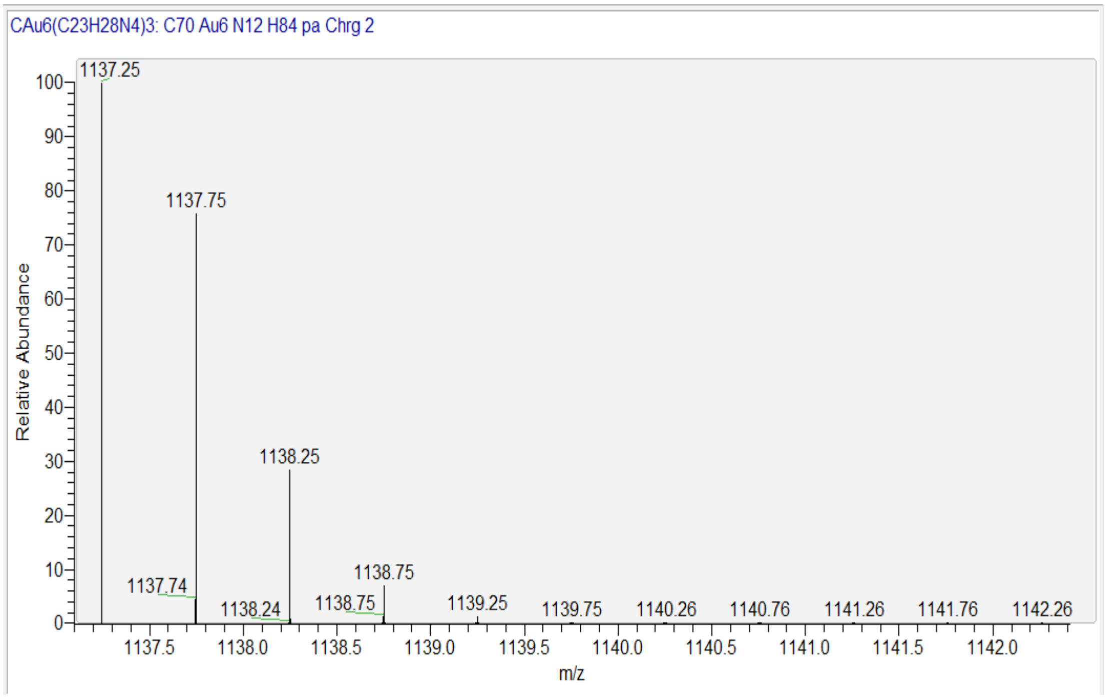


Figure 39: simulated pattern for the $[CAu_6(di\text{-}NHC)_3]^{2+}$ species derived from the reduction of complex L.

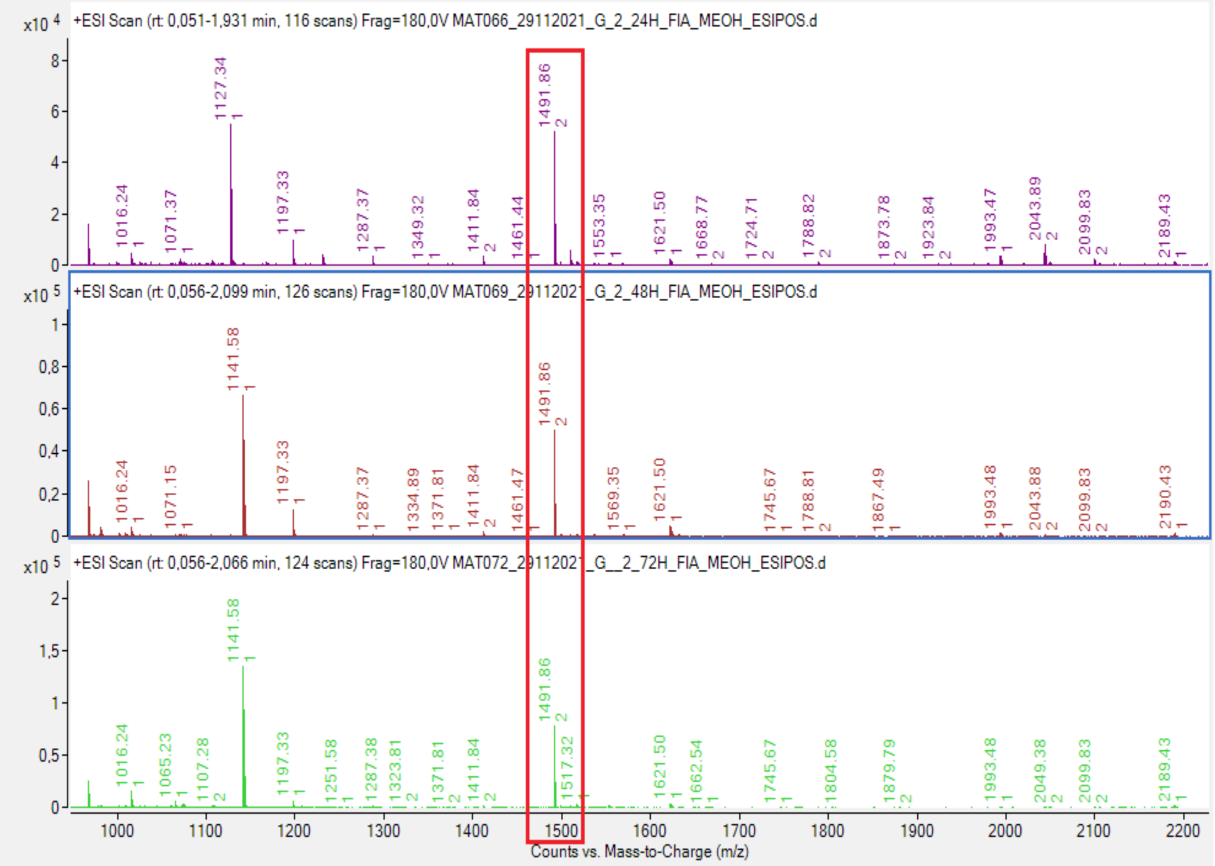


Figure 40: ESI-MS mass spectra of the withdrawals carried out at 24, 48 and 72 h on the preliminary reduction of complex G. The peaks highlighted by the red rectangle refer to the $[CAu_6(NHC)_6]^{2+}$ species, and are compatible with the simulated pattern.

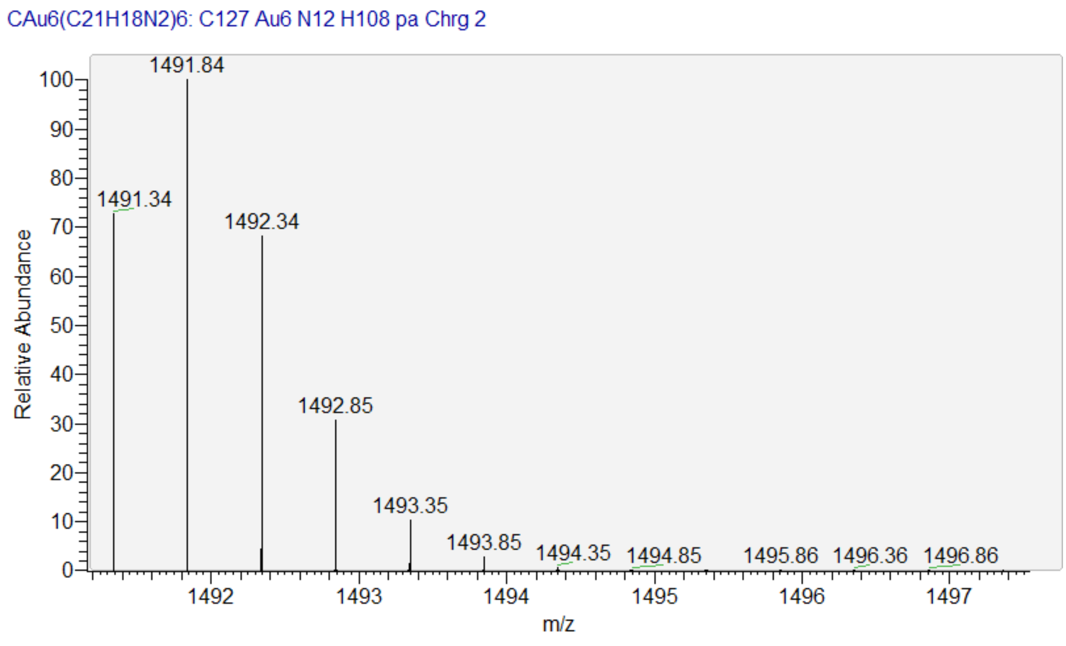


Figure 41: simulated pattern for the $[CAu_6(NHC)_6]^{2+}$ species derived from the reduction of complex G.

Examples of such clusters, hexa-aurated methanium dications, are present in the literature since 1992, and mainly show the presence of phosphane ligands as stabilizing moieties[72]. More recently, Shionoya et al. reported the synthesis of a new cluster of such structure with the aid of NHCs as stabilizing ligands (figure 42).[73]

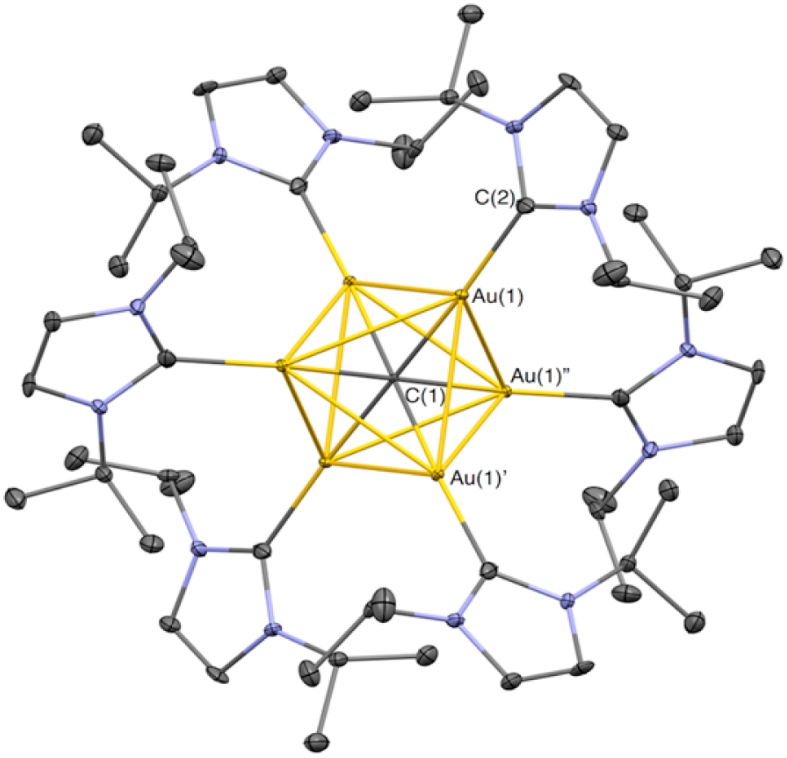


Figure 42: structure of $[CAu_6(NHC)_6]^{2+}$ as reported from Shionoya et. al in 2018. [73]

The interesting point resides in the fact that the cluster reported in this study has been prepared by means of a complicated two step synthesis, involving the preparation of an oxygen-centered trinuclear complex and then its reaction with (trimethylsilyl)diazomethane as a carbon source, with a total yield of 16%[73].

The synthetic strategy involving the use of hydrazine monohydrate is much simpler, and the use of benzyl groups and bis-carbenes confers novelty even in what concerns the product.

Another important point is the fact that Shionoya's synthetic strategy is not a viable option if working with bis-carbenes, for the nature of the intermediate complex, that has three carbenes bound to three Au atoms. With bis-carbenes an odd number of carbene units interacting with metal centers is in theory not achievable.

As an interesting side note, the presence of a species of supposed formula $[Au_3(di\text{-}NHC)_2(Cl)_2(CH)]^+$ at 1394.31 m/z units is reported in the MS spectra. The theoretical m/z value is 1394.31, and the simulated and experimental isotopic patterns are very similar.

The products from the trial regarding complex F have been subjected to recrystallization. This procedure has been attempted because of the fact that in this case the reaction generated a lot more byproducts, and the $[CAu_6(di\text{-}NHC)_3]^{2+}$ species were minoritary. The procedure failed to deliver a cleaner product, and has been followed by an acid etching procedure using HBr, reported by Konishi et al. [74] and in several other articles, which is a common practice to aid the convergence of the reaction products towards a single species. ESI-MS analysis performed on the obtained red solid shows the convergence of the products towards Au_{13} species (figure 43). The major obtained cluster is the same reported by Zheng et al. in 2019, with Br ligands instead of Cl.[19] This indicates that the clusters originally formed upon reduction with hydrazine are unable to sustain acidic conditions and decompose to Au_{13} products.

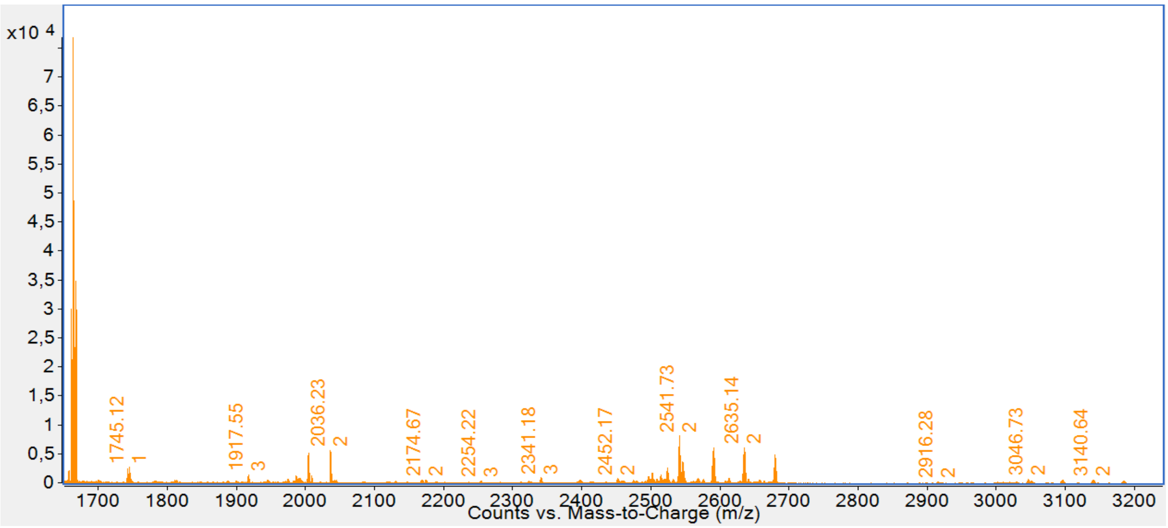


Figure 43: detail of the ESI-MS spectrum of the products obtained from the acid etching following the reduction with hydrazine of complex F.

Identified Peaks:

1667,52 (theor: 1667,52): $[Au_{13}(\text{di-NHC})_5Br_2]^{3+}$

2541,73 (theor: 2541,74): $[Au_{13}(\text{di-NHC})_5Br_2]^{3+}Br^{-}$

2680,17 (theor: 2680,18): $[Au_{13}(\text{di-NHC})_5Br_2]^{3+}(AuBr_2)^{-}$

2004,52 (theor: 2004,52): $[Au_{13}(\text{di-NHC})_5Br_2]^{3+}\cdot[Au_2(\text{di-NHC})Br_2]$

1986,54 (theor 1986,54) : $[Au_{13}(\text{di-NHC})_5Br_2]^{3+}\cdot[Au_2(\text{di-NHC})(Br)(CN)]$.

The reaction of complex L has been repeated two additional times, giving worse results than the first (more byproducts, less hexa aurated species), and the reason has been identified as a probable difference the amount of hydrazine used. Since the quantities are very small, even a single additional drop can represent multiple equivalents and have a great impact on the synthesis.

After these preliminary trials, therefore, the reaction of complex L was optimized for what concerns the amount of reducing agent. Four parallel reactions have been set up, using the same amount of solvent mixture (2,25 ml) with the same composition (DCM/MeOH 4:1), the same temperature (24°C), the same amount of complex (10,0 mg) and KOH (76,4 mg) and varying the amount of reducing agent. The reactions have been followed by means of withdrawals at 3, 24, 48, 72 and 96 hours and ESI-MS analysis. The spectra are not reported for sake of brevity.

1) 1 eq. of hydrazine monohydrate --> minimal formation of the desired product, several other peaks relative to byproducts of lower molecular weight.
2) 2 eq. of hydrazine monohydrate --> same outcome as 1 eq.
3) 5 eq. of hydrazine monohydrate --> same outcome as the previous cases, the spectrum shows the presence of other byproducts' peaks.
4) 20 eq. of hydrazine monohydrate --> formation of the desired product, its peak increases in height if compared to the others, and the reaction converges towards it at the 96 hours mark.

In all the mass spectra relative to these trials the peak at 1394,31 m/z units is absent, and a peak at 1381,30 m/z units is present ($[Au_3(di\text{-}NHC)_2(Cl)_2]^+$ or $[Au_2(di\text{-}NHC)_2]^{2+}(AuCl_2)^-$), together with one at 1303,27 m/z units (unidentified).

While this four synthesis were ongoing, the product of the preliminary synthesis has been subjected to column chromatography. TLC testing of various eluents allowed to determine that a DCM/Acetone 8:1 mixture was able to separate some impurities, while a DCM/MeOH 8:1 mixture was able to separate the different cluster species present in the product.
Column chromatography has been performed using first the DCM/Acetone mixture, then the DCM/MeOH one and in the end washing the column with pure methanol, resulting in four fractions.
ESI-MS analysis of the fractions allowed to determine that the third fraction contained the desired product with relatively high purity (figure 44).

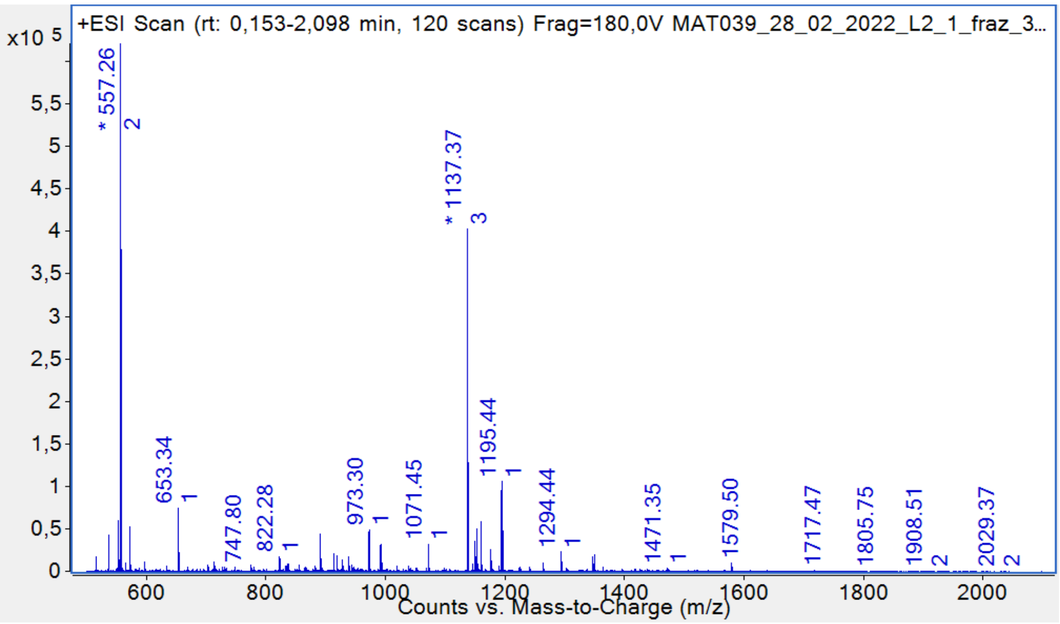


Figure 44: ESI-MS of the third fraction extracted from the column performed on the product of the preliminary reduction of complex L with hydrazine. 1137,37 = [CAu$_6$(di-NHC)$_3$]$^{2+}$; 557,26 = [Au$_2$(diNHC)$_2$]$^{2+}$(fragmentation); 1195,44 [Au$_2$(diNHC)$_2$]$^{2+}$(Br)$^-$(fragmentations + impurities deriving from previous analysis).

A slight shift (instrumental or software error) is present and the resulting m/z ratio is 1137.37 instead of the predicted 1137.25. The charge is also erroneously assigned as 3+, but zooming in its clear that the real charge is 2+, since the space between two adjacent peaks of the isotopic pattern is 0,5 m/z units (figure 45).

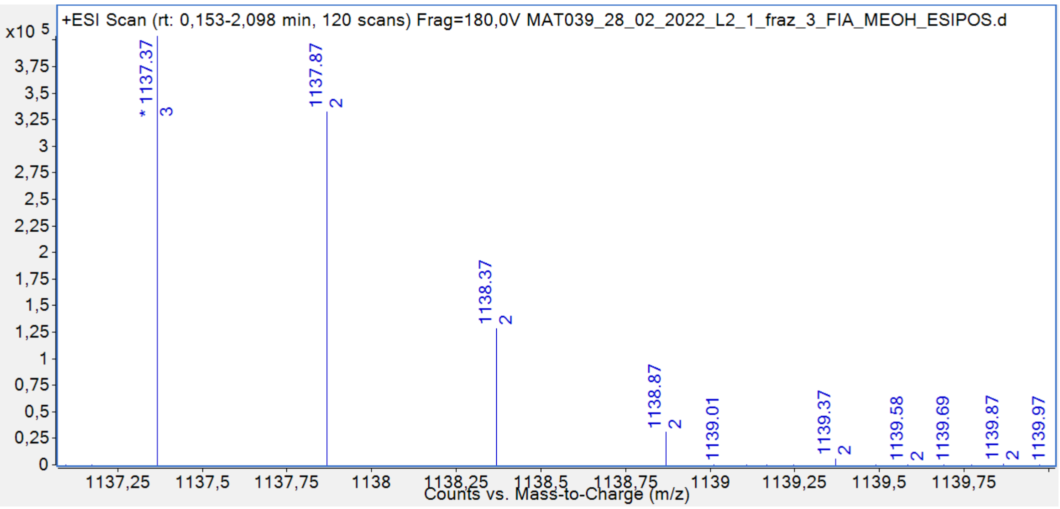


Figure 45: detail of the isotopic pattern of [CAu$_6$(di-NHC)$_3$]$^{2+}$.

Work on complex G reduction has been halted due to the fact that a similar cluster has been discovered and published by Shionoya's group while our work was ongoing. The synthetic strategy which is employed is the same as the one seen in the previous work of the same group.[75]

Characterizations

Due to the small quantity of clean product that has been obtained starting from complex L and performing column chromatography, only ^{1}H NMR characterization could be performed. The spectrum clearly shows the peaks relative to the alkyl regions of the ligands, that appear broadened by the interaction with the metal core, and the well-defined aromatic region (figure 46).

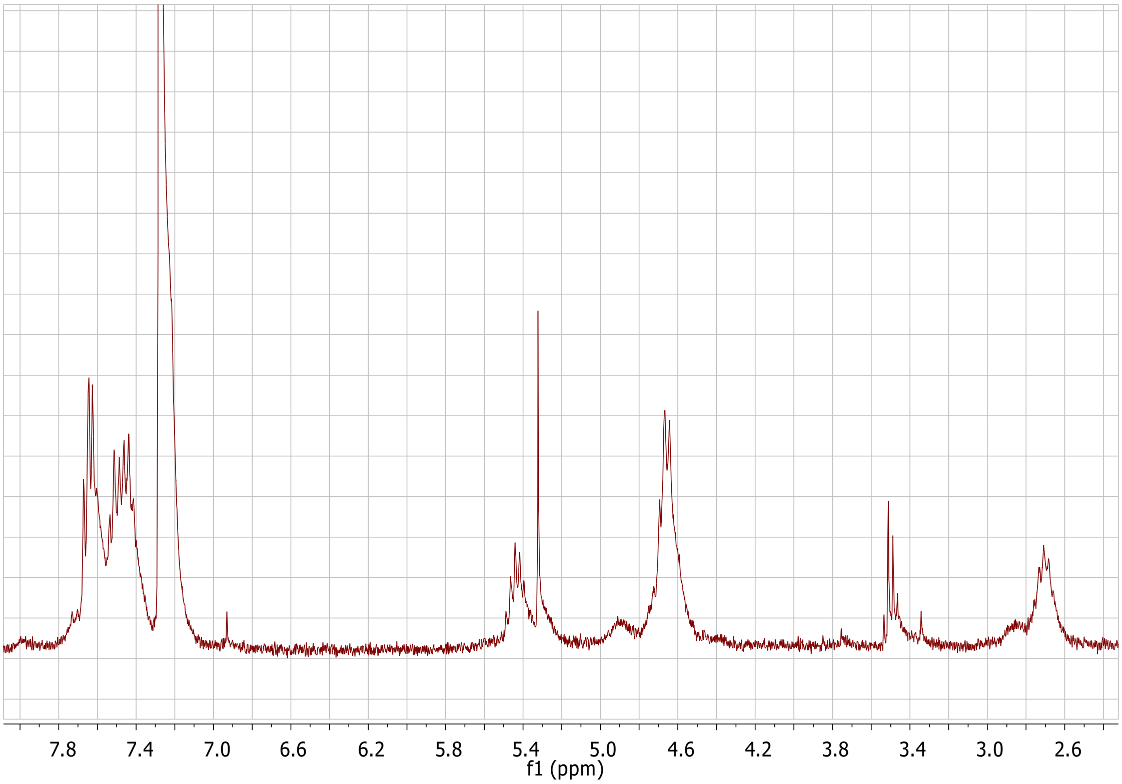


Figure 46: ^{1}H NMR spectrum of the cluster $[CAu_6(di\text{-}NHC)_3]^{2+}$ obtained from complex L, recorded in $CDCl_3$. The signal at 2,17 ppm is due to acetone, the quartet at 3,48 ppm to residual diethyl ether and the singlet at 5,30 ppm to residual DCM. The signal at 7,26 ppm is due to non-deuterated chloroform. The doublet at 1,75 ppm, relative to the isopropyl CH_3, is deformed for the presence of the wide water peak (not shown) at 1,56 ppm.

The identified signals are:

1,75 ppm (36 H, doublet, CH_3CHCH_3);

2,71 ppm (6H, quintet (broad), $CH_2CH_2CH_2$);

4,67 ppm (12H, triplet (broad), $CH_2CH_2CH_2$);

5,44 ppm (6H, heptet (broad), CH_3CHCH_3);

7,34-7,68 ppm (24H, multiplet, bimi-H).

^{13}C NMR has not been performed, since, according to the literature, the central carbon atom is not visible[75], and the dilution was too high to obtain a spectrum without multiple days of acquisition.

Chapter 6: Trials on a peculiar cluster: $[Au_9(PPh_3)_8](NO_3)_3$

As already stated in the introduction of this thesis, several different models have been developed to explain the peculiar stability of the many existing atomically precise, ligand protected metal nanoclusters. These models however are basically electron counting rules, and for this reason they possess some limitations [21]. In particular the superatom complex model predicts a particular stability for approximately spherical clusters with a full superatomic valence shell. This explains the existence of $[Au_3]^+$ triangular species, as well as $[Au_{11}]^{3+}$ and $[Au_{13}]^{5+}$ species, that possess respectively 2 and 8 electrons on the superatomic valence shell. Other models have been developed to explain the stability of non-spherical and low-simmetry clusters (Super-Valence-Bond model, SuperAtom-Network, Grand Unified Model), and are relatively successful in doing so. [21]

However there are some examples of clusters that do not follow these models strictly. In particular, a family of phosphine-protected gold clusters, $[Au_9(L)_8](X)_3$, displays a particular stability and ease of preparation despite being an almost spherical entity in what concerns the metal core and not having a complete superatomic valence shell (9 gold atoms, 3+ charge, 6 total valence electrons).

This family of clusters has been discovered in 1971 by Sansoni et. al. in Milan.

Important prerequisite for obtaining them is the presence of non-coordinating anions, together with phenyl or monosubstituted aryl functionalized phosphines.

The group was able to succesfully determine the structure of one of these compounds, and the result is an arrangement described as a centered icosahedron in which one of the equatorial rectangles of atoms has been removed. [16] A 2008 study confirmed this for all the compounds of the family (figure 47). [76]

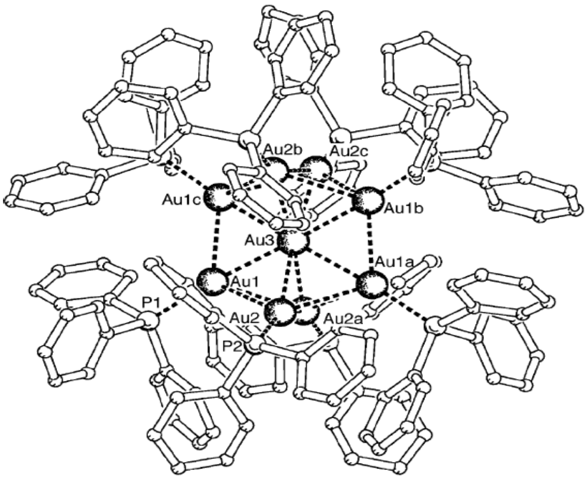
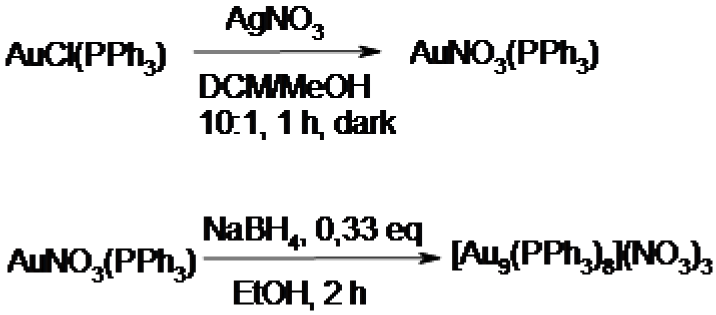


Figure 47: structure of the cluster $[Au_9(PPh_3)_8](NO_3)_3$ [76]

These clusters represents very interesting species, because the lack of a filled superatomic valence shell may lead to an improved reactivity. From literature, the reactivity of this cluster in solution is mediated by the dissociation of an AuL^+ cation, that leaves a coordinatively unsaturated $[Au_8L_7]^{2+}$ species. This species can act as an intermediate in the interconversion $[Au_9L_8]^{3+}$<-->$[Au_8L_8]^{2+}$.[77]

Our group decided to perform the synthesis of the cluster $[Au_9(PPh_3)_8](NO_3)_3$ and subject it to some trials, specifically to attempt a reaction with $[Au_2(di\text{-}NHC)]X_2$ complexes.

The ionic ligand exchange reaction has been performed according to a literature procedure[78], while the reduction has been performed according to another literature procedure [79]. The synthetic strategy is presented in scheme 32.



Scheme 32: synthetic strategy for the preparation of $[Au_9(PPh_3)_8](NO_3)_3$.

Seeing the success of the reaction a scale up of both the ionic ligand exchange and reduction has been performed, yielding a sufficient amount of cluster for some trials. During this scale up a small excess of silver nitrate has been used in the exchange reaction, granting an higher yield. The purity of the product has been confirmed via ^{31}P NMR (figure 48).

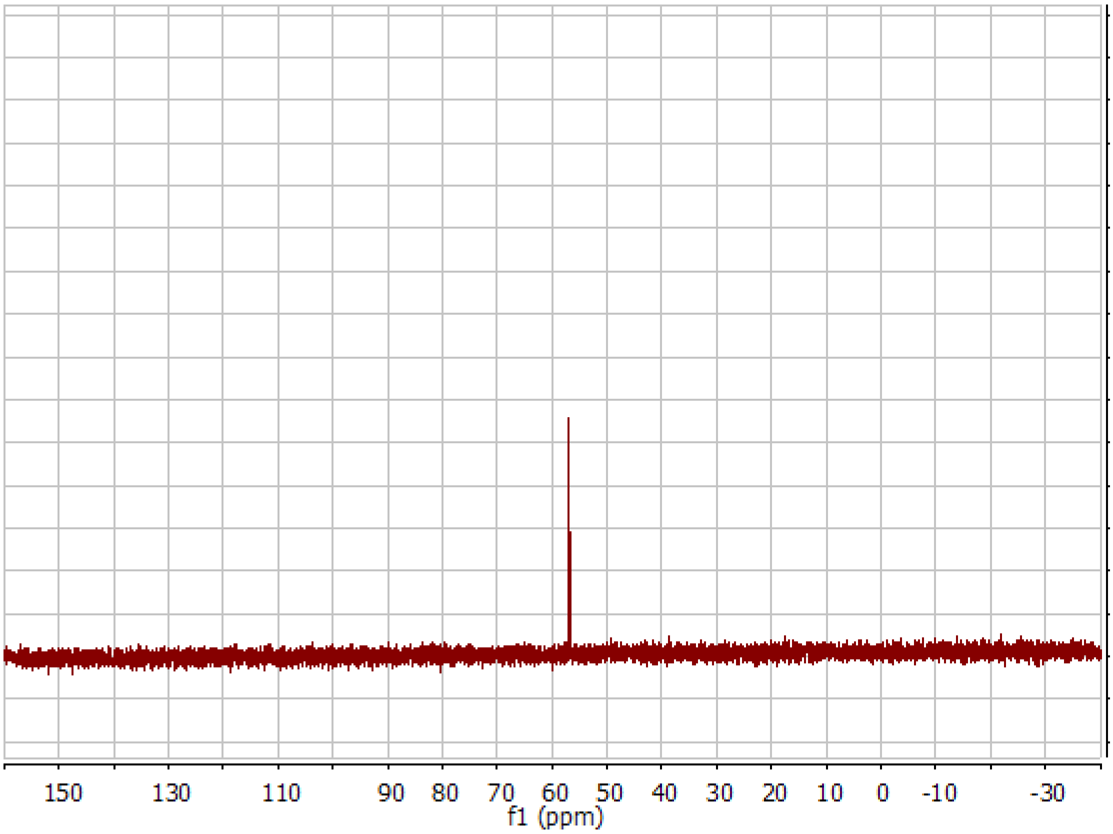
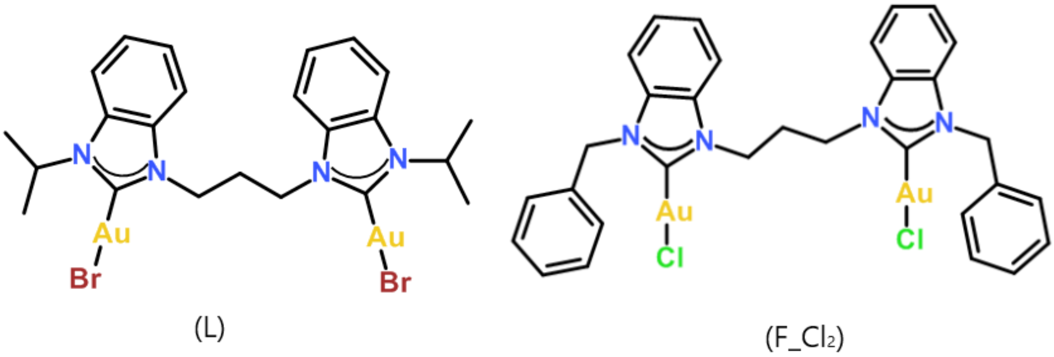


Figure 48: ^{31}P NMR spectrum of $[Au_9(PPh_3)_8](NO_3)_3$, in $CDCl_3$. The cluster is the only species present bearing PPh_3 ligands, and gives a singlet at 56.8 ppm.[79]

Complexes L and F_Cl_2, already available in the lab, have been selected for the reactions. Structures are reported in scheme 33.



Scheme 33: complexes selected for the reactions with the Au_9 cluster.

The cluster has been dissolved in DCM, and the reaction has been carried out dissolving together with it 0,8 equivalent of complex (due to an error in the calculations, the desired quantity was 1 eq.). Withdrawals have been carried out at 3, 24, 48, 72 and 96 h (100 µL each), and have been subjected to ESI-MS analysis.

ESI-MS analysis (figure 49) shows the presence of several peaks of interest for the reaction with complex F_Cl$_2$. The signals of the withdrawals carried out on the reaction with complex L instead don't show any presence of products of ligand exchange or complex addition.
In particular, the interesting signals are, reporting the theoretical m/z ratios:

1267,22 → $[Au_9(PPh_3)_6(di\text{-}NHC)H_3]^{3+}$

1202,84 → $[Au_8(PPh_3)_6(di\text{-}NHC)H_3]^{3+}$

1180,19 → $[Au_8(PPh_3)_4(di\text{-}NHC)_2H_3]^{3+}$

1821,74 → $[Au_8(PPh_3)_6(di\text{-}NHC)H_3Cl]^{2+}$

1787,77 → $[Au_8(PPh_3)_4(di\text{-}NHC)_2H_3Cl]^{2+}$

1690,19 → $[Au_8(PPh_3)_5(di\text{-}NHC)H_3Cl]^{2+}$

1801,28 → $[Au_8(PPh_3)_4(di\text{-}NHC)_2H_3(NO_3)]^{2+}$

1821,74 → $[Au_7(PPh_3)_5(di\text{-}NHC)H_3]^{2+}$

1804,76 → $[Au_8(PPh_3)_6(di\text{-}NHC)H_4]^{2+}$

3184,40 → $[Au_7(PPh_3)_5(di\text{-}NHC)H_3Cl]^{+}$

3150,44 → $[Au_7(PPh_3)_5(di\text{-}NHC)H_4]^{+}$

3211,42 → $[Au_7(PPh_3)_5(di\text{-}NHC)H_3(NO_3)]^{+}$

1705,77→ $[Au_7(PPh_3)_6(di\text{-}NHC)H_3]^{2+}$

1443,16→ $[Au_7(PPh_3)_4(di\text{-}NHC)H_3]^{2+}$

1409,19 → $[Au_8(PPh_3)_3(di\text{-}NHC)]^{2+}$

1540,72 → $[Au_8(PPh_3)_4(di\text{-}NHC)]^{2+}$

1377,24 → $[Au_6(PPh_3)_6]^{2+}$

1246,19 → $[Au_6(PPh_3)_5]^{2+}$

These peaks, more or less intense, seem to suggest the presence of a species with stoichiometry $Au_9(PPh_3)_6(di\text{-}NHC)]^{3+}$ that generates a lot of fragments in ESI-MS conditions, or possesses equilibria in solution.

Interesting is the presence of several Au_7 species with coordinated hydrogen atoms: these species arise in ESI-MS conditions, and it has been demonstrated that in gas phase Au_7 moieties are able to coordinate up to 5 neutral hydrogen atoms.[80]

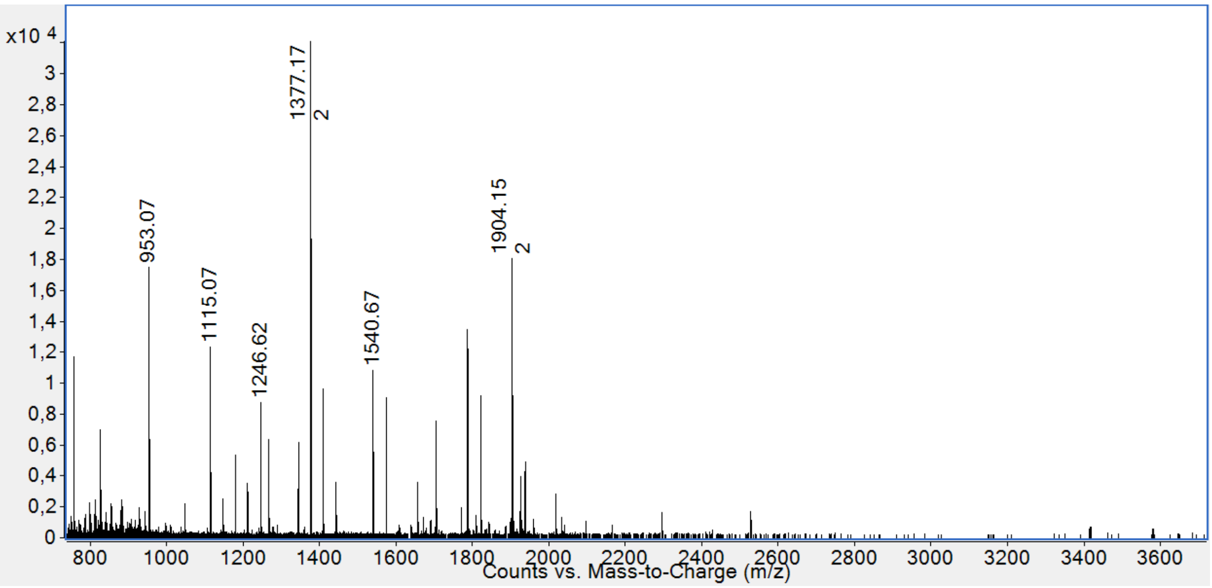


Figure 49: detail of the ESI-MS spectrum of the crude product of the reaction between $[Au_9(PPh_3)_8](NO_3)_3$ and complex F_Cl_2 after 96 h.

The product of the reaction with complex F_Cl_2 has been subjected to ^{31}P NMR, confirming that the cluster had reacted: the cluster reagent, as seen above in figure 48 gives a singlet, while the spectrum of the crude product possesses at least another signal in close proximity, as seen in figure 50. Figure 51 shows the presence of some impurities and other peaks.

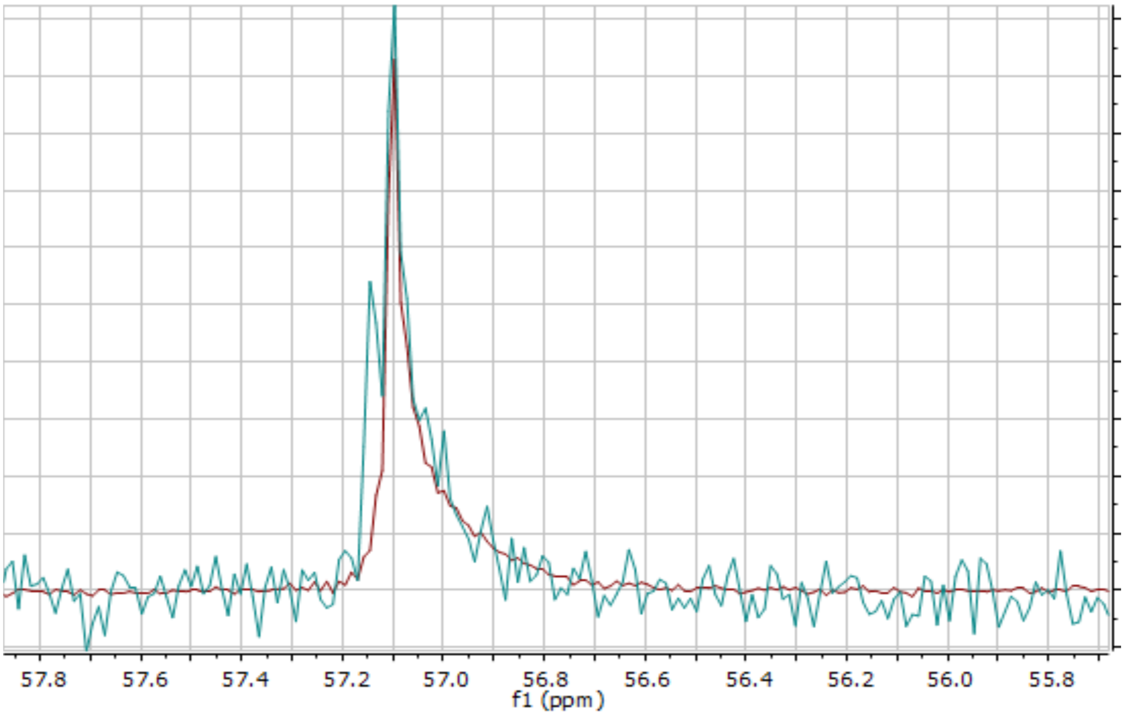


Figure 50: detail of the superimposition of the spectra of the cluster reagent (dark red) and of the crude product of the reaction with complex F_Cl_2 (light blue) in acetonitrile-d3. Other signals (not visible in the reported image) were present at 44,05 and 33,05 ppm, and have been identified later (see below).

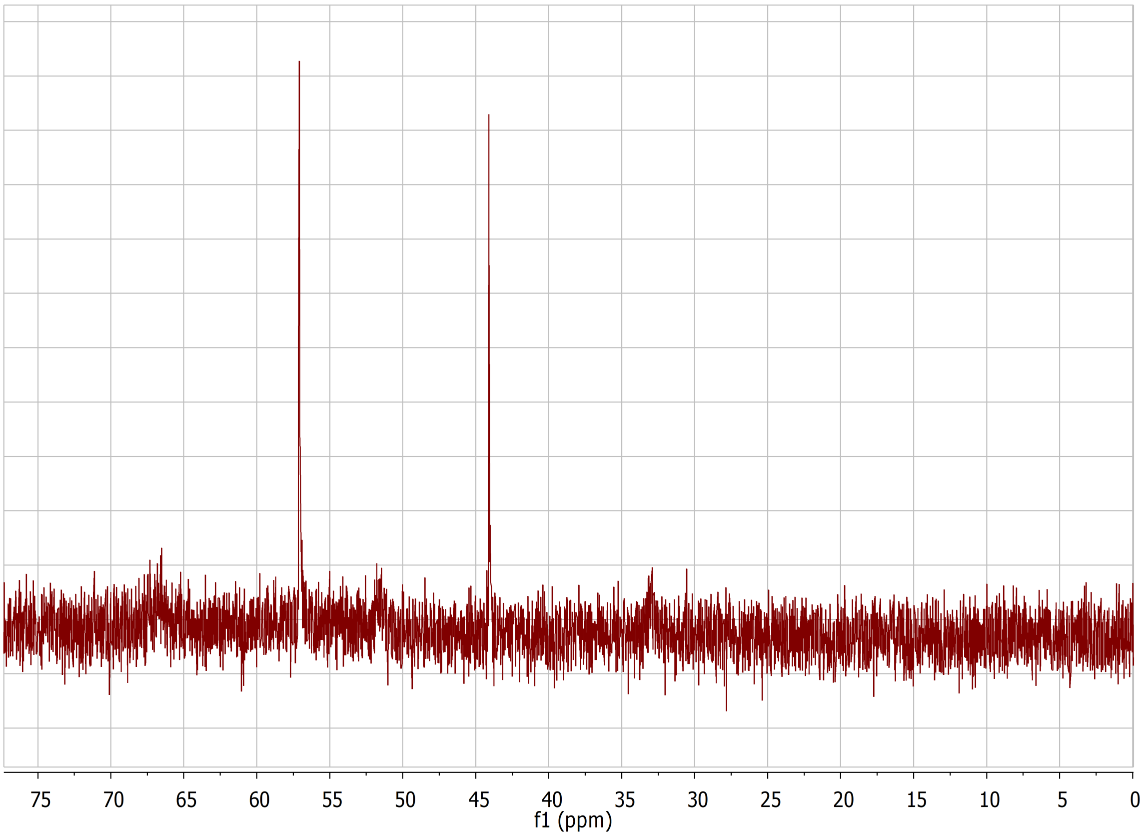


Figure 51: extended vision of the ^{31}P NMR spectrum reported in the previous figure; the peaks at 44,05 and 33,05 ppm are visible, together with some bands around 52 and 67 ppm.

At this point the crude product has been subjected to TLC tests to try to find a correct eluent mixture to separate the product from the reagents and other byproducts. The testing however gave an unexpected result: even the pure cluster reagent, used as a comparison to identify its position in the chromatographic run, gave several different spots, despite being pure (as shown by its ^{31}P NMR spectrum). This result excluded the use of chromatographic separation as a mean to purify the product.

A recrystallization was therefore attempted to clean the product, putting it into a vial and dissolving it in DCM, and then placing the vial into a close container with cotton drenched in diethyl ether.

The obtained solid had a very dark red-brown color, and the surnatant was orange. Both fractions have been collected, dried, and subjected to ESI-MS and ^{31}P NMR analysis.

This cross-analysis allowed to determine that the recrystallization was indeed able to clean the product, and allowed also to identify the main impurity, $[Au(PPh_3)_2]^+$, together with a minoritary one, $AuCl(PPh_3)$. The spectrum of the surnatant is reported in figure 52.

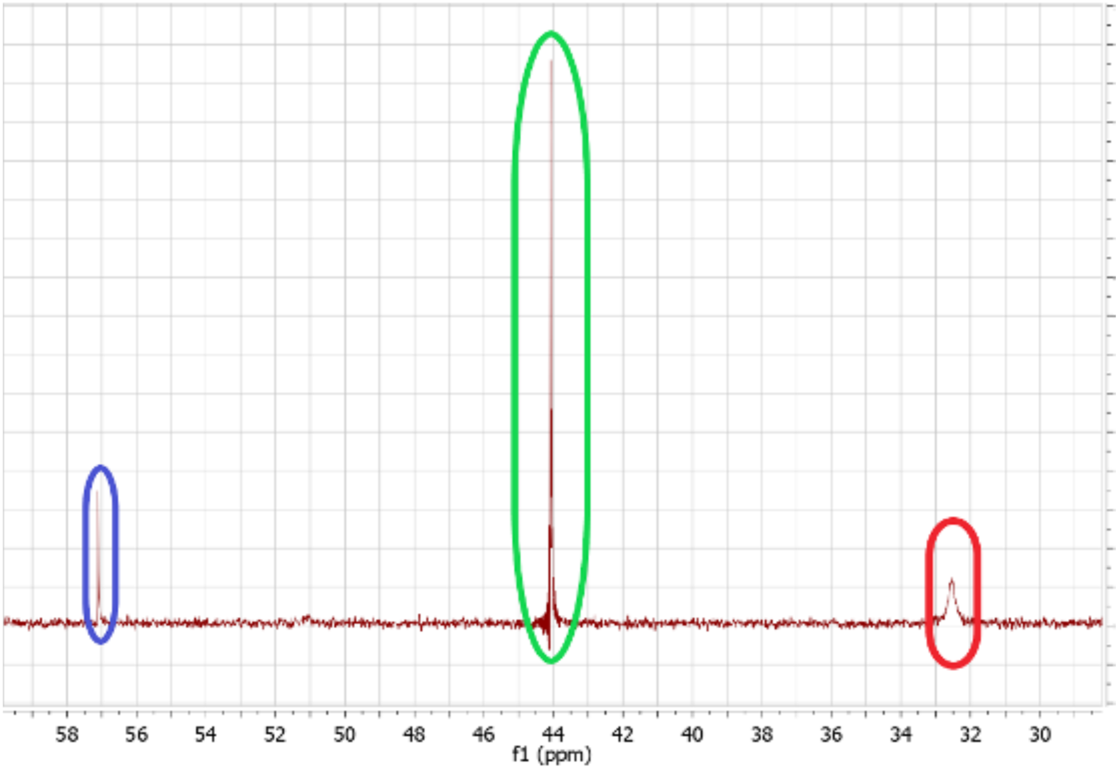


Figure 52:^{31}P NMR spectrum of the surnatant in CD_3CN; identification of impurities: blue = reagent cluster; green = $[Au(PPh_3)_2]^+$, red = $AuCl(PPh_3)$. The identification has been made by comparison with the already obtained spectra for the cluster and searching for the most abundant species containing phosphorus in the mass spectrum for the complexes. It has been later confirmed by literature sources [81].

The main point of interest, however, is another: after the recrystallization process the second peak evident in figure 50, attributed to the product of the reaction, decreased a lot in intensity, while other peaks at 51,5 ppm, 54,5 ppm, 66,5 ppm and 67,5 ppm (see figure 53), nearly invisible before, increased. This suggested that the product had decomposed or transformed into another/other cluster/s.

The recrystallization has been repeated a second time, and a second set of NMR spectra has been recorded. The spectra are totally analogous, with just a small reduction in the amount of impurities. This led to the hypothesis that the previously listed peaks belong all to a singular species, or to different species in rapid equilibrium since they vary coherently in intensity in different spectra. ESI-MS analysis has been performed as well.

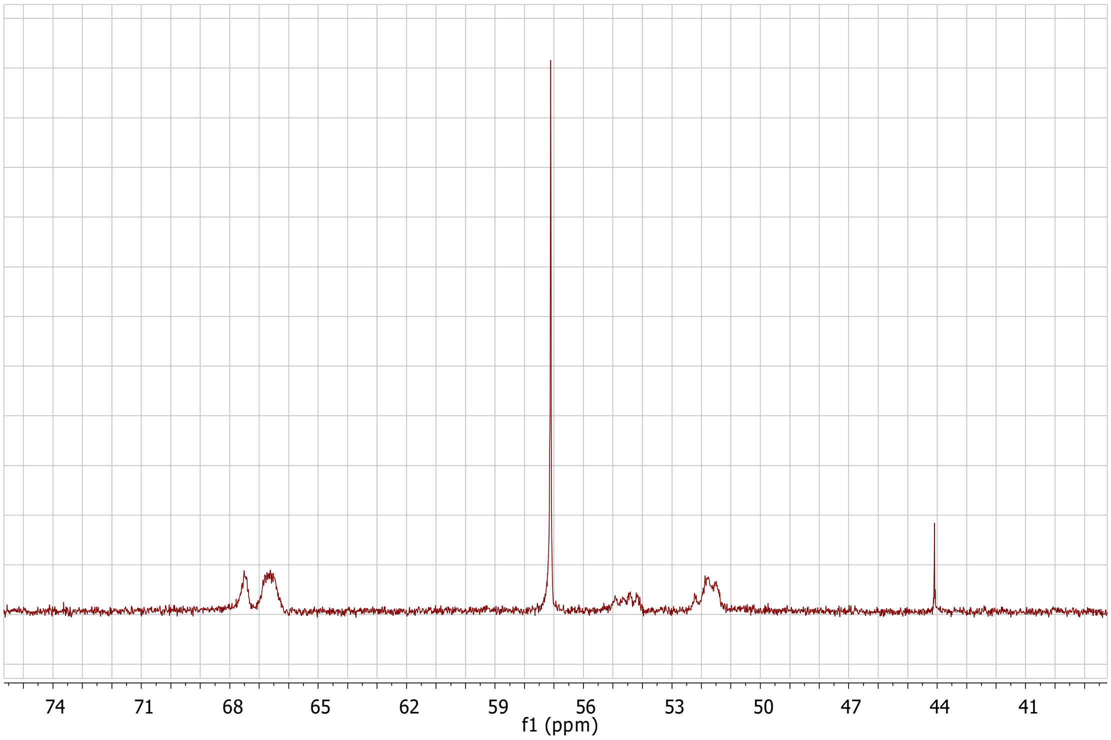


Figure 53: ^{31}P NMR spectrum of the solid obtained by two recrystallizations in CD_3CN.

ESI-MS analysis on the solid obtained from the second recrystallization showed that a lot of peaks that were minoritary in the crude product spectrum increased in relative intensity. Among these signals some are very interesting, and are listed according to the theoretical m/z ratio:

2017,73 → $[Au_{10}(PPh_3)_6(di\text{-}NHC)(Cl)H]^{2+}$

1886,68 → $[Au_{10}(PPh_3)_5(di\text{-}NHC)(Cl)H]^{2+}$

1999,74 → $[Au_{10}(PPh_3)_6(di\text{-}NHC)]^{2+}$

1333,50 → $[Au_{10}(PPh_3)_6(\text{di-NHC})H]^{3+}$

1344,80 → $[Au_{10}(PPh_3)_6(\text{di-NHC})Cl]^{3+}$

1359,80 → $[Au_{10}(PPh_3)_6(\text{di-NHC})Br]^{3+}$ (probably due to impurities in the apparatus)

2130,73 → $[Au_{10}(PPh_3)_7(\text{di-NHC})]^{2+}$

These signals seem to confirm the presence of an Au_{10} species, with a 4+ charge related to its metal core. Isolable Au_{10} clusters, but protected entirely by NHC ligands and halides, have recently been discovered by Crudden et. al., and are very interesting because, at least in that case, they possess a toroidal shape with an unprotected gold atom in the center, that may lead to an increased reactivity.[82]

In order to better comprehend the ms spectrum, ms-ms analysis has been performed on four of the peaks reported in the spectra, namely the ones with m/z = 1267, 1344, 1540, 1801.

This allowed to determine which peaks are originated by fragmentations of the same substance and which are relative to species present in solution, keeping in mind that these species might be present only in ESI conditions.

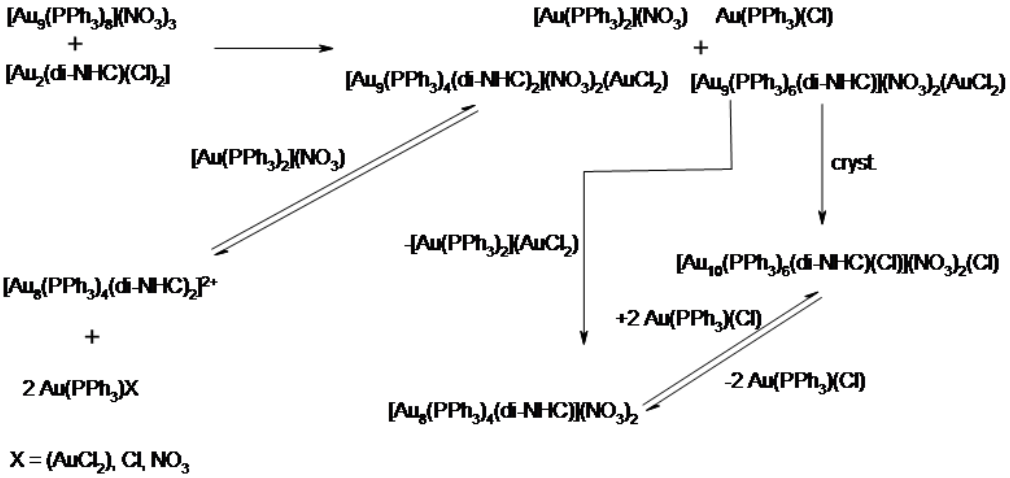
	1267	1344	1540	1801
459,08	🟩	🟩	🟥	🟥
653,24	🟩	🟩	🟩	🟩
721,21	🟩	🟩	🟩	🟩
953,14	🟩	🟩	🟥	🟥
1047,19	🟩	🟩	🟩	🟥
1115,15	🟩	🟩	🟥	🟥
1180,19	🟩	🟩	🟥	🟥
1246,7	🟩	🟩	🟥	🟥
1278,14	🟥	🟥	🟩	🟩
1377,25	🟩	🟩	🟥	🟥
1409,2	🟩	🟩	🟩	🟩
1443,17	🟩	🟩	🟥	🟥
1540	🟩	🟩	🟩	🟩
1547,73	🟩	🟩	🟥	🟥
1639,23	🟥	🟥	🟥	🟩
1670,23	🟥	🟥	🟥	🟩
1703,26	🟥	🟥	🟩	🟥
1705,78	🟩	🟩	🟥	🟥
1770,28	🟥	🟥	🟥	🟩

1801,29	🟩	🟩	🟥	🟩
1821,75	🟩	🟩	🟥	🟥
1835,09	🟥	🟥	🟩	🟩
1844,76	🟩	🟩	🟥	🟥
1917,26	🟩	🟩	🟥	🟥
1938,73	🟩	🟩	🟥	🟥
2033,31	🟩	🟩	🟥	🟥
2091,79	🟩	🟩	🟥	🟥
2097,2	🟥	🟥	🟩	🟩
2359,3	🟥	🟥	🟩	🟩
2618,25	🟥	🟥	🟥	🟩
2881,34	🟥	🟥	🟥	🟩

Table 1: summary of the results of ms-ms analysis. Green = present in the spectrum; Red = absent in the spectrum. Columns represent the ions selected for the analysis, named by their m/z ratio, while rows the peaks present in the ms-ms spectra

Due to the equality between the first two ms-ms spectra (appreciable in the first two columns of table1), it has been demonstrated that the peaks at m/z= 1267 and 1344 are due to the same species, $[Au_{10}(PPh_3)_6(di\text{-}NHC)Cl]^{3+}$, that seems to lose an AuCl fragment in ESI conditions. The other two spectra are different from these two and slightly different from each other, bringing up the possibility of the coexistence of at least 3 species in solution.

The reactions and the supposed equilibria are reported in scheme 34:



Scheme 34: supposed equilibria between species present in solution, derived from the data obtained from ESI-MS, ms-ms analysis and ^{31}P NMR.

^1H NMR has been performed on the whole solid obtained by the recrystallization, and shows the presence of a set of peaks relative to the di-NHC ligand (figure 53, red). These peaks are narrower for what concerns the protons in the lateral parts of the ligand (benzyl CH_2 bridges), while are broader for the protons of the $(CH_2)_3$ bridge, suggesting high flexibility and a relatively rapid rotation around the bond axis in the NMR time scale. Duplication of some of the signals arise, confirming that the ligand is placed into an environment that turns non-diastereoisotopic protons into diastereoisotopic ones, and this is the proof of the bond to the surface of a NC.

In order to support the hypothesis of the presence of several species giving equilibria in solution ^1H and ^{31}P NMR have been performed at 25°C, -20°C and -38°C. Indeed the signals in the spectra became narrower and some splitted (figures 54 and 55).

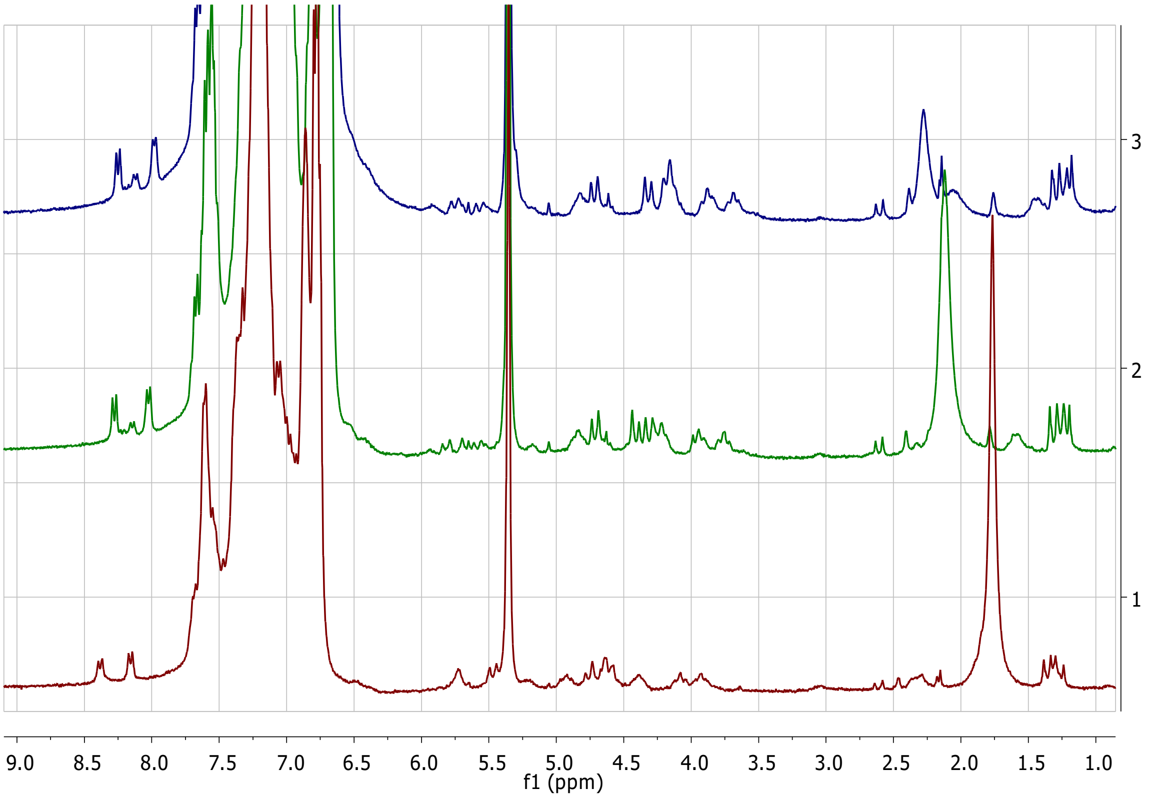


Figure 54: stacked ^1H NMR spectra at 20°C (red), -25 °C (green) and -38 °C (blue). The narrow band at 5,35 ppm is due to non-deuterated DCM, while the large mobile band at 1,75-2,25 ppm is due to the presence of water. The aromatic region of the spectra is very similar in all of them, so it has been cut for the low temperature ones in order to zoom and appreciate the peaks related to the dicarbene ligand.

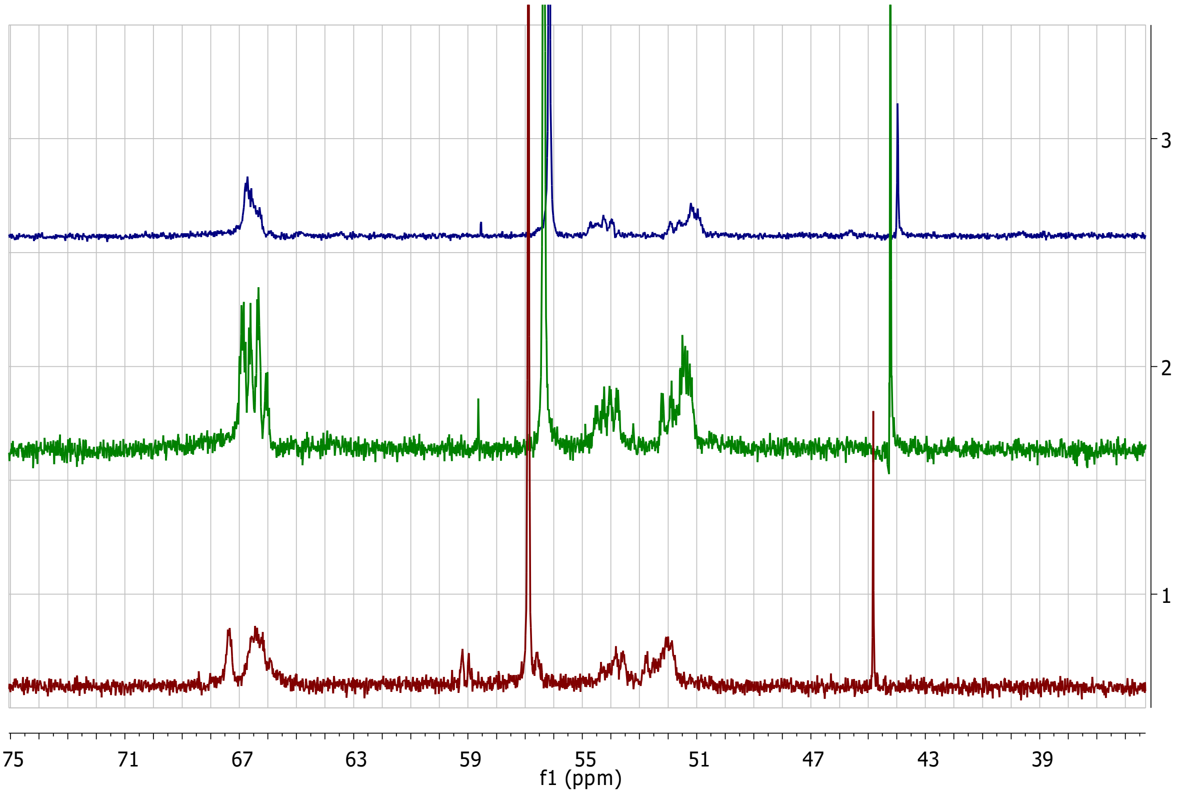


Figure 55: stacked ^{31}P *NMR spectra at 20°C (red), -25 °C (green) and -38 °C (blue). The loss if intensity of the signals in the last spectrum (real or apparent) could be due to decreased solubility or inefficient temperature control.*

As a conclusion, it has been determined that this reaction generates multiple species in equilibrium, and this makes the isolation and characterization of the species very difficult, if not impossible. Due to the supposed equilibria, repeating the recrystallization could lead in principle to the decomposition of Au_{10} species to Au_8 species, since $AuCl(PPh_3)$ is removed, together with $Au(PPh_3)_2^+$.

At this point another trial has been performed, using 4 equivalents of complex F_Cl_2 to check for possible complete ligand exchange. The reaction conditions are completely analogous to the ones reported for the first trial, with the exception of the relative amount of complex. After the reaction was halted, the mixture has been dried and the solid subjected to ^1H and ^{31}P NMR analysis (figures 56 and 57).

NMR analysis gave some useful informations: ^{31}P NMR showed that all the phosphorous present was in a single species, giving a singlet at 33,05 ppm in the spectrum, recorded in CD_3CN. The signal has been attributed to $AuCl(PPh_3)$ using literature sources. [81] ^1H NMR allowed to determine that the dicarbene ligand was present in at least two different species, since at least two different sets of peaks relative to the ligand were present. Both sets of peaks seemingly showed characteristics recalling the bond to a complex structure, such as broadening in one case and duplication and splitting of the signals in the other.

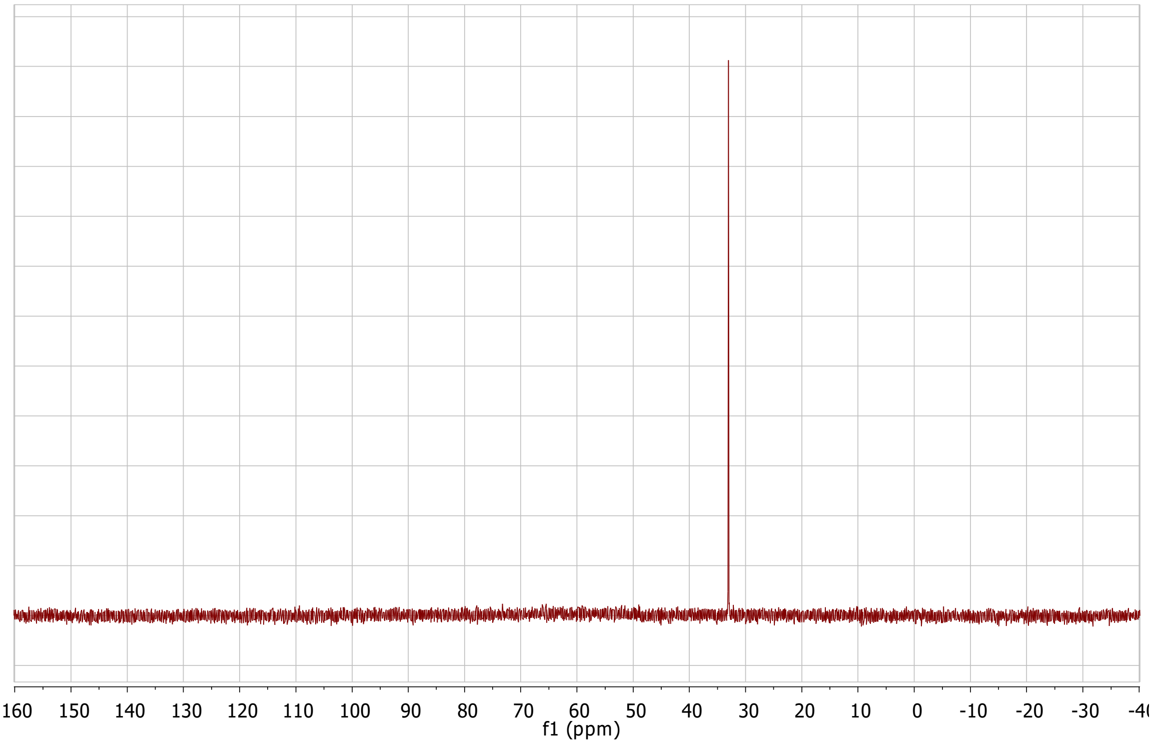


Figure 56: ^{31}*P NMR spectrum recorded in* CD_3CN *on the raw product of the reaction between cluster* $[Au_9(PPh_3)_8](NO_3)_3$ *and 4 equivalents of complex* F_Cl_2.

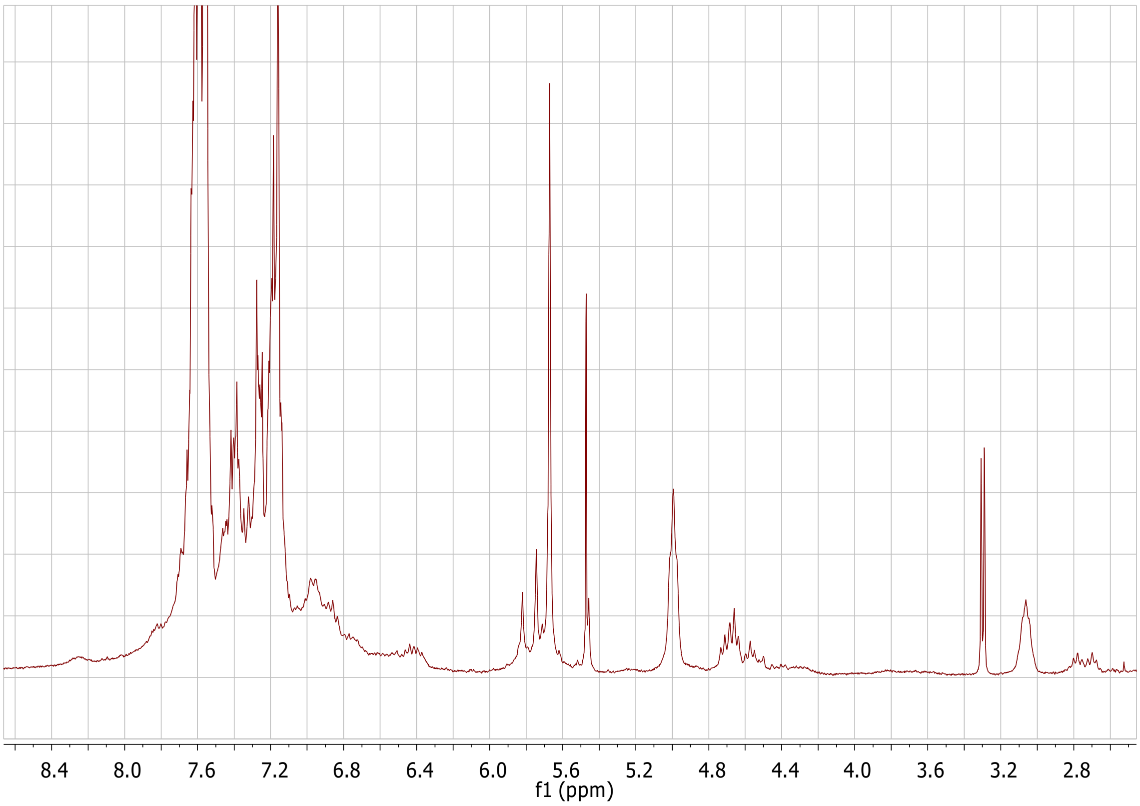


Figure 57: detail of the ^{1}*H NMR spectrum recorded in* CD_3CN *on the raw product of the reaction between cluster* $[Au_9(PPh_3)_8](NO_3)_3$ *and 4 equivalents of complex* F_Cl_2*. The peaks relative to the benzyl* CH_2 *and to the propylene bridge should fall into the 6.5-2,0 ppm range.*

TLC trials have been performed using a DCM/MeOH 9:1 mixture as eluent, and gave a nice separation of five spots. Column chromatography has been performed using the same eluent mixture, and five fractions have been collected. ^{1}H NMR and ^{31}P NMR have been used to check the if some separation had occurred, and the outcome was positive. The first fraction contained mostly $AuCl(PPh_3)$, while the second a mixture of it and cluster species; the third, fourth and fifth probably contained cluster species, and the last one contained probably also the dicationic complex $[Au_2(di\text{-}NHC)_2]^{2+}$, common byproduct of clusters synthesis, since the signals are not broad and not splitted.

ESI-MS analysis shows the presence in the second fraction of mostly $Au(PPh_3)_2^+$, that may originate in ESI conditions from the neutral complex $Au(PPh_3)Cl$, as evidenced by its pattern situated at 721,16 m/z units. The presence of this complex is evident in all fractions, while its amount decreases, indicating an inefficient separation; the last fraction contains a lot of dicationic $[Au_2(di\text{-}NHC)_2]^{2+}$complex, as expected, and this is confirmed by its isotopic pattern at 653,20 m/z units. The second, third and fourth fractions contain a higher amount of cluster species (figures 58 and 59), while the last a lot less.

The main cluster species present are $[Au_{13}(PPh_3)_3(di\text{-}NHC)_3(Cl)_2(X)]^{2+}$ and $[Au_{13}(PPh_3)(di\text{-}NHC)_4(Cl)_2(X)]^{2+}$, where X = Br or Cl. The first species have already been obtained by our group using Au_{11} clusters as starting reagent, in an analogous process. It may be possible that the reaction between the phosphine protected Au_9 cluster and the dinuclear gold complex brings first to the formation of Au_{11} intermediates, that are subsequently converted to Au_{13}.

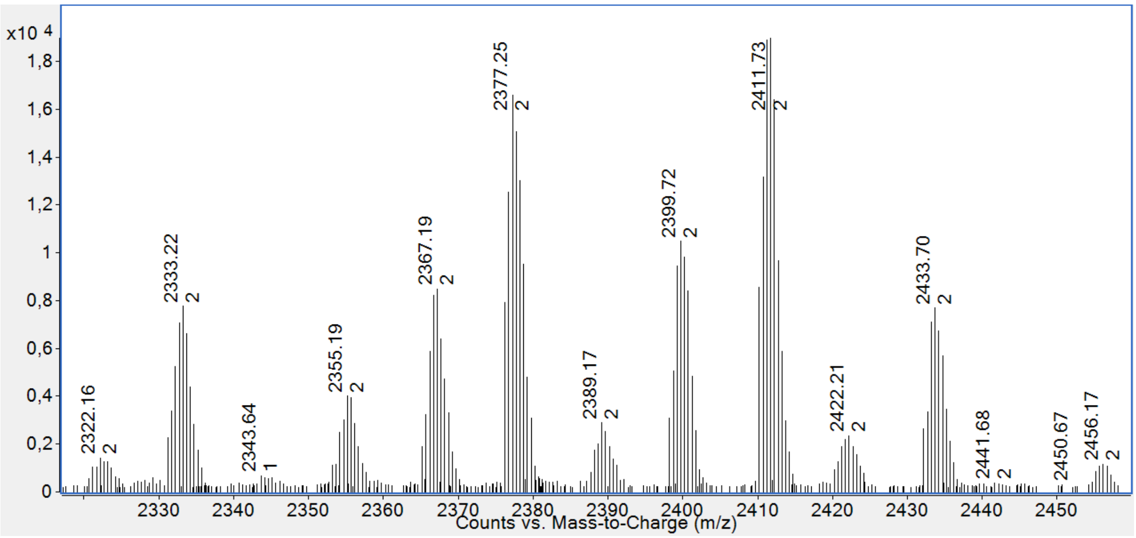


Figure 58: detail of the ESI-MS spectrum of the second fraction eluted from column chromatography. The spectra of the third and fourth fraction don't differ significantly in this region, while in the fifth fraction the cluster species are present in traces amount.

Identified peaks:

2411,73 → $[Au_{13}(PPh_3)_3(di\text{-}NHC)_3(Cl)_3]^{2+}$

2377,25 → $[Au_{13}(PPh_3)(di\text{-}NHC)_4(Cl)_3]^{2+}$

2432,23 → $[Au_{13}(PPh_3)_3(di\text{-}NHC)_3(Cl)_2(Br)]^{2+}$

2399,76 → $[Au_{13}(PPh_3)(di\text{-}NHC)_4(Cl)_2(Br)]^{2+}$

The peaks at 2367,20, 2389,17, 2355,19 and 2333,22 form an analogous pattern, therefore they differ from each other with an analogous trend to the one in the previous four peaks; the whole pattern is shifted from the one before by 89 mass units (44,5 m/z units) to the left (lighter).

Moving towards higher m/z ratios some interesting peaks related to cluster species, that form patterns analogous to the ones just reported, are evident; the detail of the spectrum is reported, and also some peaks that were identified.

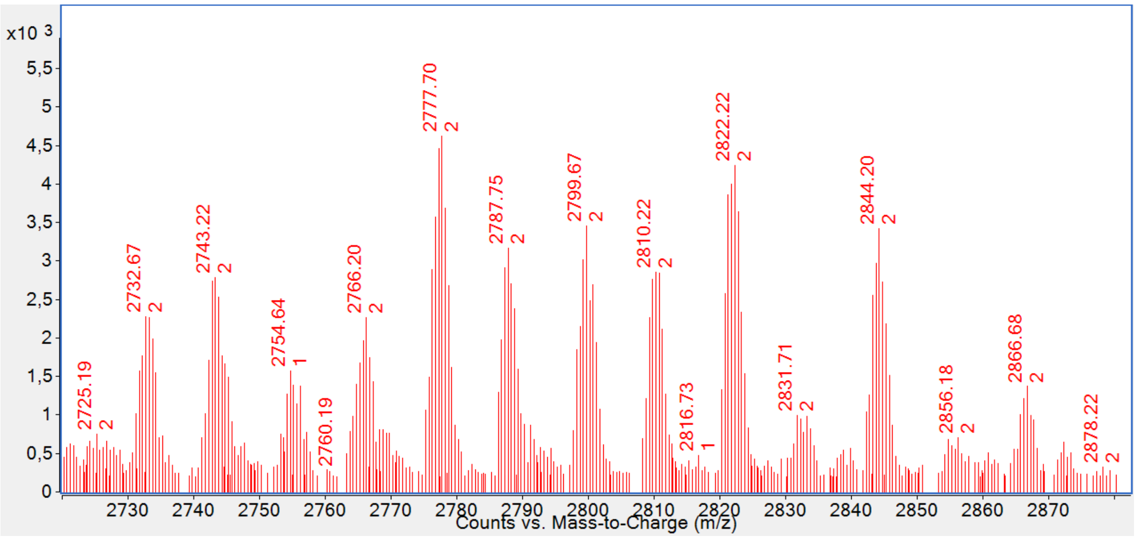


Figure 59: detail of the ESI-MS spectrum of the second fraction eluted from column chromatography. The spectra of the third and fourth fraction don't differ significantly in this region, while in the fifth fraction the cluster species are present in traces amount.

Identified peaks:

2787,74(75) → $[Au_{16}(\text{di-NHC})_5(Cl)_4]^{2+}$

2822,23(22) → $[Au_{16}(PPh_3)_2(\text{di-NHC})_4(Cl)_4]^{2+}$

2844,20 → $[Au_{16}(PPh_3)_2(\text{di-NHC})_4(Cl)_3(Br)]^{2+}$

2810,22 → $[Au_{16}(\text{di-NHC})_5(Cl)_3(Br)]^{2+}$

The presence of these species is only an hypothesis and shouldn't be taken for granted; however the hypothesis is reinforced by the similarity between the isotopic patterns shown in the spectrum above and the simulated isotopic patterns (figures 60 and 61). As an example the simulated and experimental isotopic patterns for the supposed species$[Au_{16}(\text{di-NHC})_5(Cl)_4]^{2+}$ are reported. Some differences are evident, but this may be due to the fact that the region of the spectrum in question is very noisy and the concentration of the species low. Under these conditions the limiting factor may be the processing ability of the software used for the analysis. Indeed trying multiple times to extract the ms spectrum from the chromatogram leads to significant modifications of the isotopic patterns in the same spectrum, and the effect is less evident on peaks related to more concentrated species.

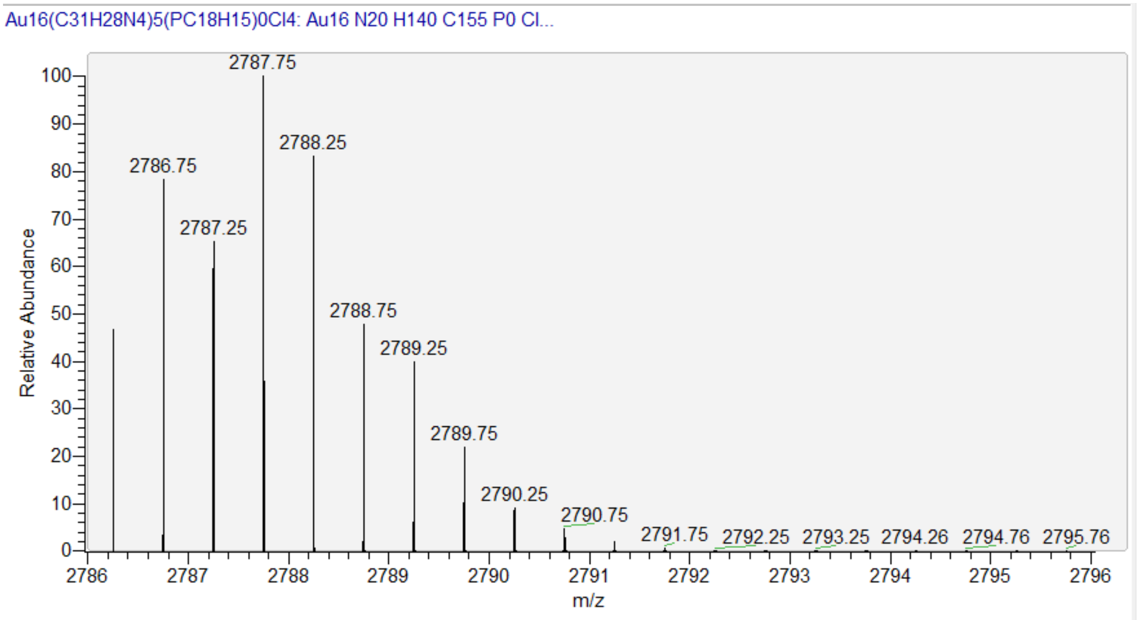


Figure 60: simulated isotopic pattern for the supposed species $[\mathrm{Au}_{16}(\mathrm{di\text{-}NHC})_5(\mathrm{Cl})_4]^{2+}$.

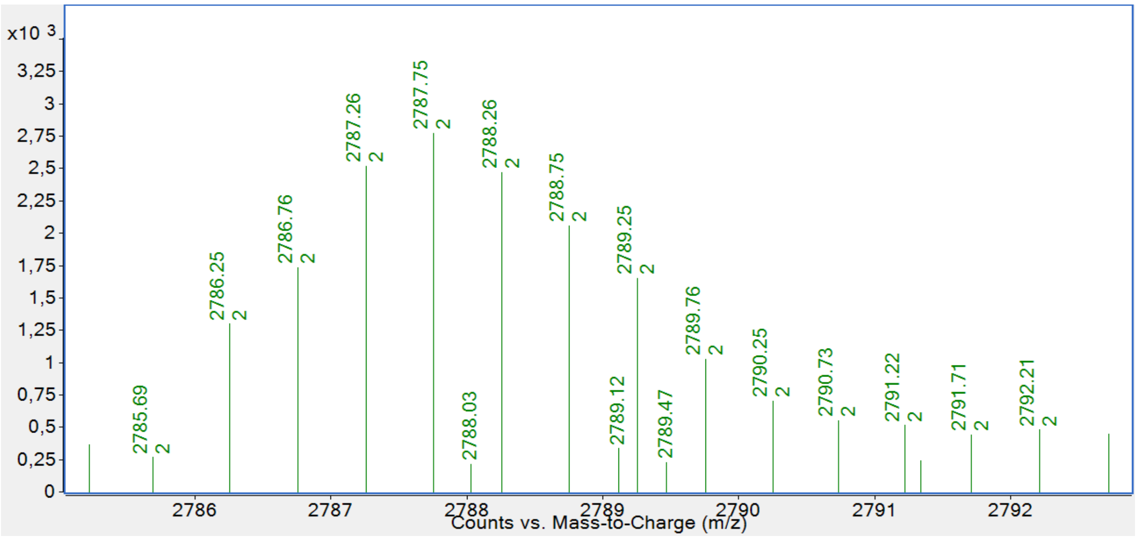


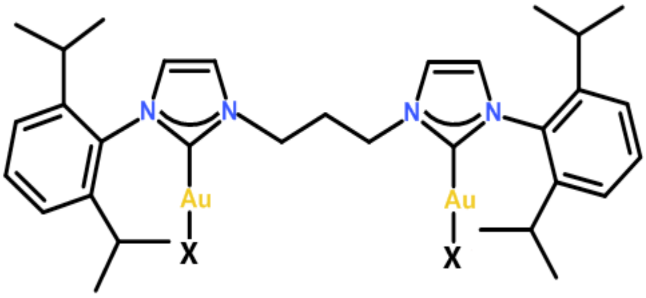
Figure 61: experimental isotopic pattern for the supposed species $[\mathrm{Au}_{16}(\mathrm{di\text{-}NHC})_5(\mathrm{Cl})_4]^{2+}$*. The slight differences in the appearance of the pattern may be due to the fact that the concentration of these species is very low and the region of the spectrum in question very noisy. The processing ability of the software used for the analysis may become the limiting factor under these conditions.*

Determining the structure or the origin of the cluster from its mass spectrum is not possible, but a conclusion that can be drawn for certain is the fact that this species are not superatomic clusters, since 16 gold atoms, 2+ charge and 4 anionic ligands lead to an electron count of 10 in the valence shell.

Chapter 7: Synthesis of AuNCs protected by bulky di-NHC ligands

Preliminary trials on the synthesis of an Au cluster protected by bulky di-NHC ligands

The reduction of two dinuclear complexes bearing a di-NHC ligand with high steric bulk has been attempted. The complexes (named C and C_(OTs)$_2$) are reported in scheme 35.



Scheme 35: structure of the complexes C and C_(OTs)$_2$, where X is, respectively, Br and OTs.

A small amount of complex C_(OTs)$_2$ was already available, and a reduction attempt in DCM/EtOH 4:1 showed a modification of the solution colour from beige to a darker shade of brown, indicating a possible positive outcome. The reduction, performed using NaBH$_4$, has been followed by means of withdrawals and ESI-MS analysis, and generated some low molecular weight clusters (Au$_3$-Au$_4$, figure 62).

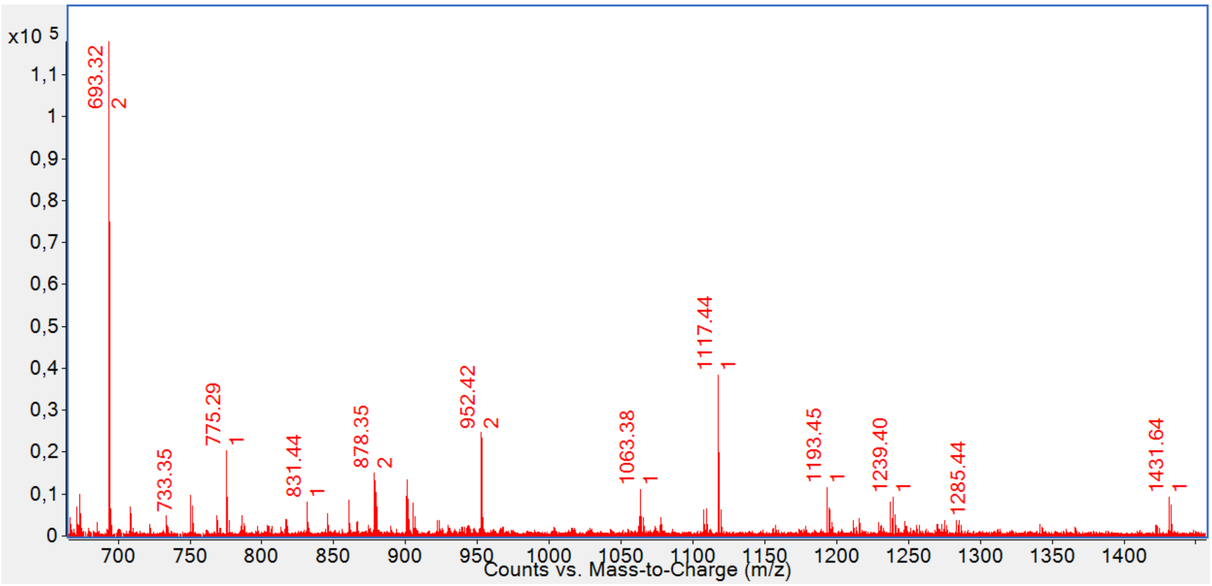
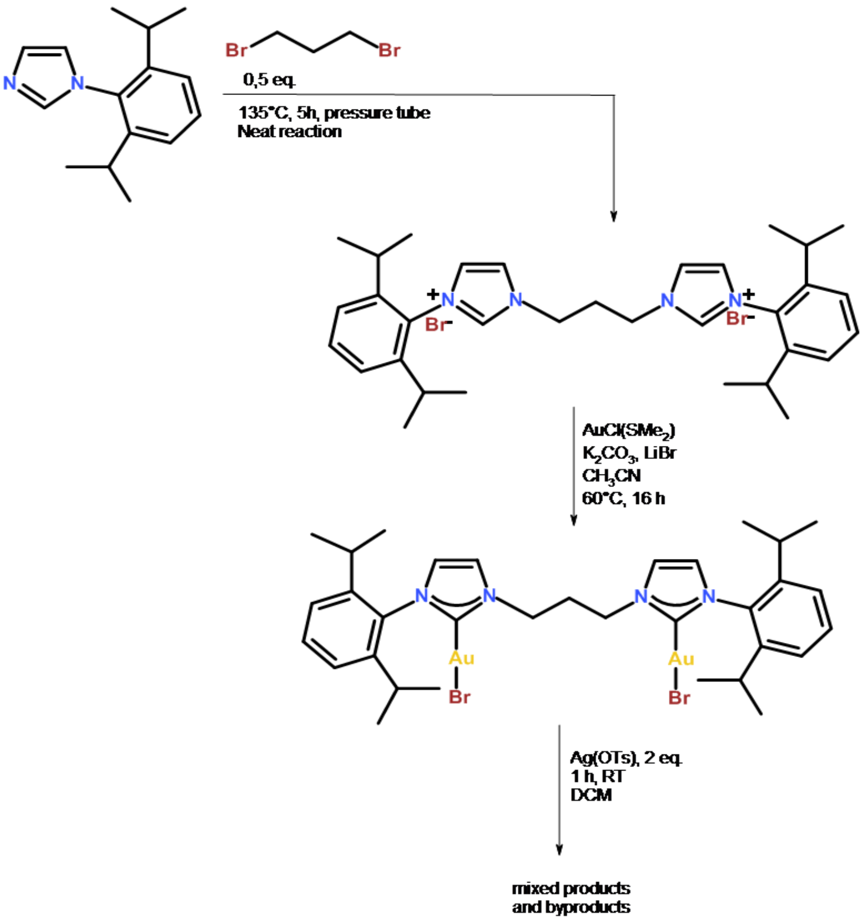


Figure 62: ESI-MS spectrum of the species obtained from the reduction of complex C_(OTs)$_2$.

Complex C was the subject of a reduction attempt in DCM, conducted previously by the group, but it didn't get reduced. Encouraged by the results of the first trial the complex has been synthesized again starting from the corresponding imidazolium salt, obtained by means of a literature procedure, to perform anionic ligand exchange and obtain other complex C_(OTs)$_2$ for additional reductions.[83] ^{1}H NMR spectra are reported in figure 63 and 64 for the salt and complex C respectively. The synthetic strategy is reported in scheme 36. All the following attempts to repeat the synthesis of complex C_(OTs)$_2$ starting from the new batch of complex C and using AgOTs gave an impure product even if the reagent was acceptably pure, as seen from ^{1}H NMR (figure 64). The main problem, evidenced by analogous procedures performed by the research group, is the formation of the dicationic complex [Au$_2$(di-NHC)$_2$]$^{2+}$. Due to this outcomes the reduction of the complex bearing tosylate anions as ligands has not been repeated. Other members of the group have recently been able to conclude that when the anionic ligand exchange is performed by slow addition of an Au complex solution to the silver tosylate solution, this problem is reduced or even minimized.



Scheme 36: synthetic strategy for the synthesis of complex C_(OTs)$_2$. The last step was revealed to be problematic, giving an impure product, as discussed in the chapter.

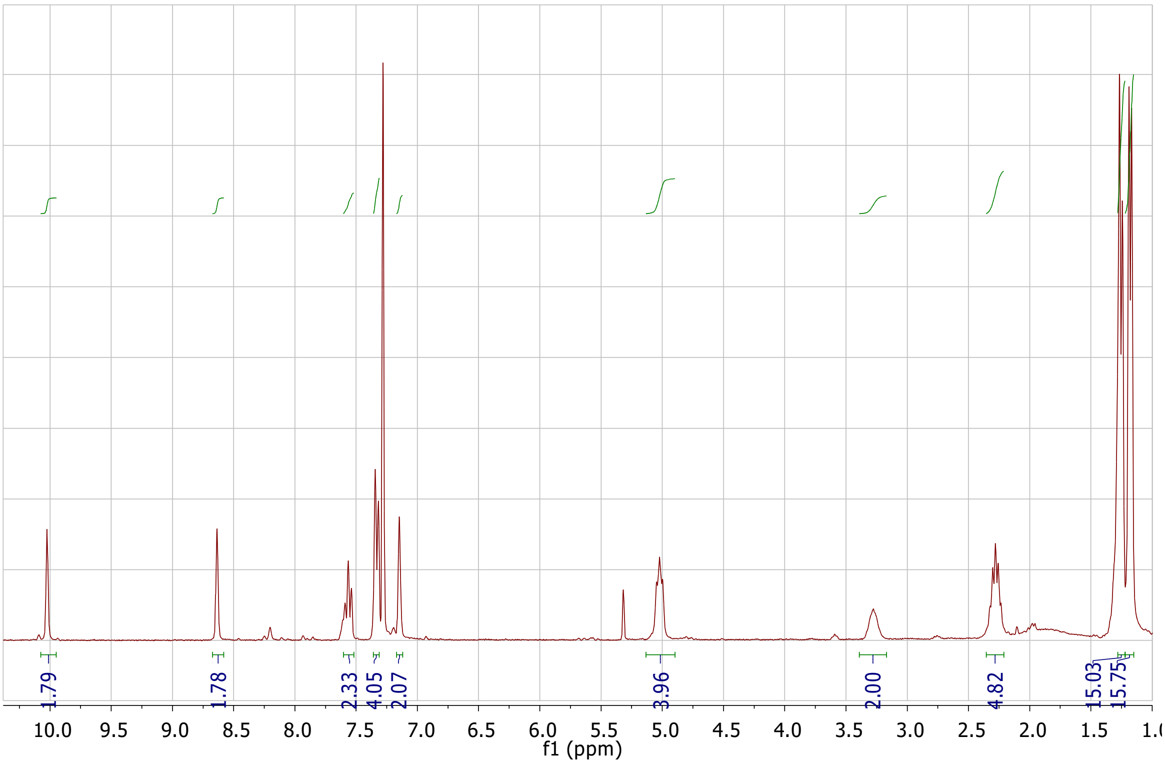


Figure 63:^{1}H NMR spectrum of the bis-imidazolium salt in CDCl$_3$, ligand precursor used for the synthesis of complex C; the signal at 5,30 ppm to DCM, and the one at 7,26 ppm to chloroform. The integrals are slightly different from the theoretical ones for the presence of some impurities.

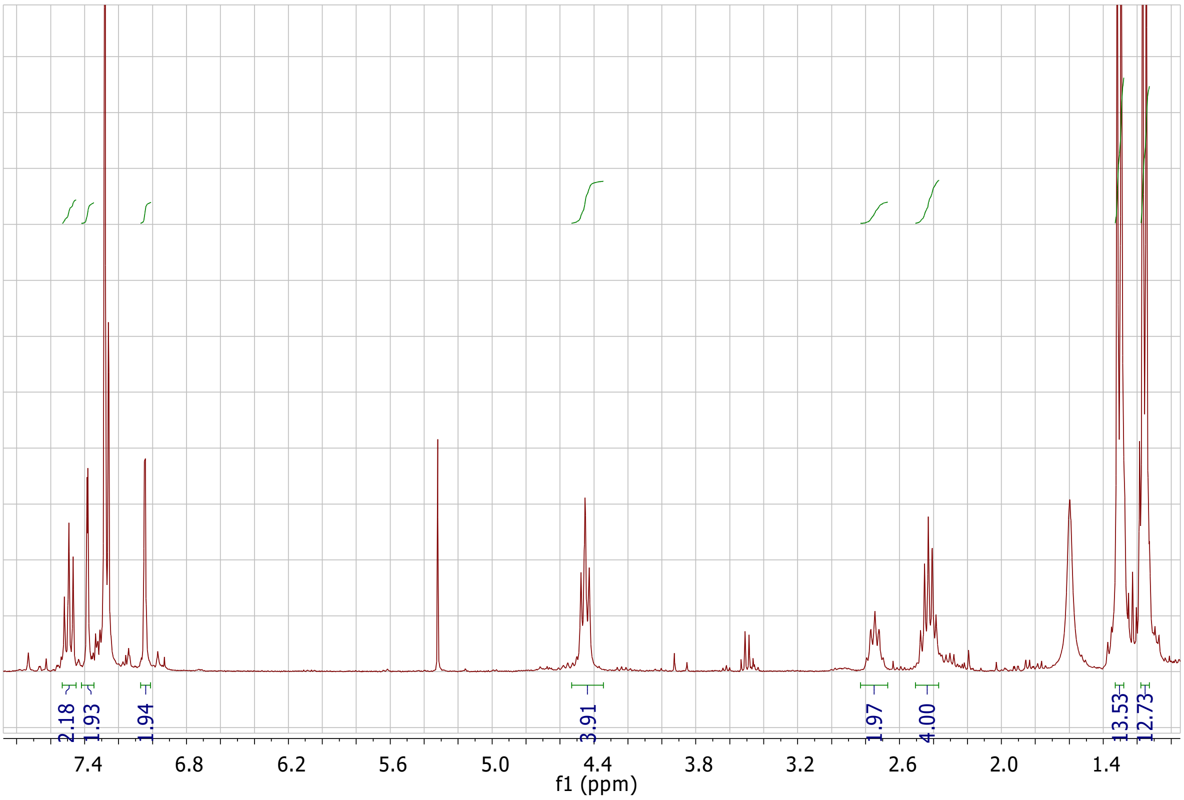


Figure 64: ^{1}H NMR spectrum of complex C; the signal at 1,56 ppm is attributed to water, the quartet at 3,50 ppm is attributed to diethyl ether, the singlet at 5,30 ppm to dichloromethane and the singlet at 7,26 ppm at chloroform; this last signal covers the second peak of a doublet relative to the protons of the aromatic diisopropylphenyl rings.

Concurrently, during a clean up, some residues of complex C present in a vial have been suspended in ethanol, and a high excess of $NaBH_4$ has been dropped inside. The suspension rapidly turned into a clear, dark brown solution, indicating the possible presence of cluster species. The reaction has therefore been followed by means of withdrawals, and ESI-MS analysis on the product shows the presence of some relatively small cluster species, not identified for lack of time (figure 65).

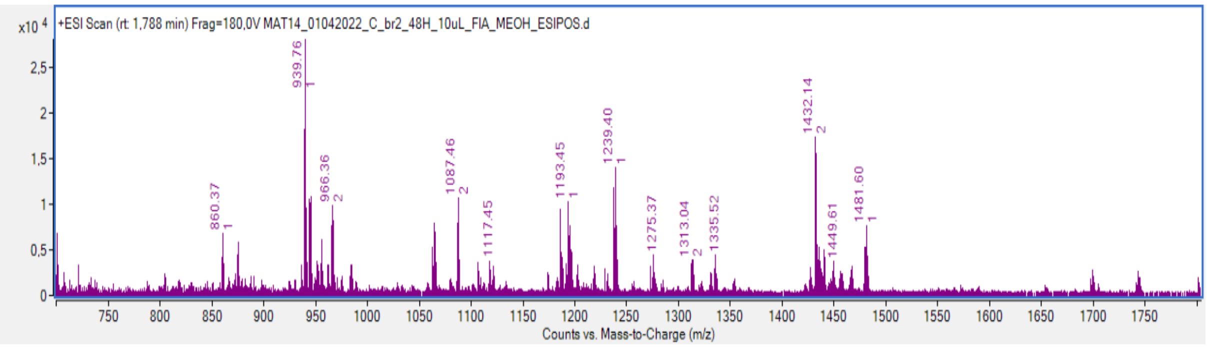


Figure 65: ESI-MS spectrum of the product obtained by the reduction of complex C in EtOH with a large excess of $NaBH_4$, after 48 hours.

This last reaction is interesting, since it shows clearly that bulky ligands lead to the formation of smaller clusters[69], that may have sterically protected free metal atoms on the surface and therefore possess useful properties such as enhanced catalytic activity. It may be useful to repeat the synthesis using a reproducible procedure and rationalize the results.

Chapter 8: Conclusions

The thesis project has involved the attempted or successful synthesis of pre-ligand imidazolium and bisimidazolium salts, several Au complexes, and their attempted or successful conversion into nanoclusters by means of direct reduction and stoichiometric co-reduction. The project has also included reactions between $Au_2(di\text{-}NHC)X_2$ complexes and phosphine-protected clusters.

For what concerns the research on the synthesis of an NHC ligand with enhanced π-accepting properties, the attempts performed to synthesize the precursor imidazolium salt 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(halide) or 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(triflate) gave only failures. The last performed reaction involving silver triflate, however, seems interesting to develop further since it is a very clean synthesis, and the only downside seems to be the instability of the benzyl triflate obtained *in-situ*. Using a better solvent than DCM for the reagents may be the key to obtain the desired product, allowing a faster reaction and avoiding decomposition of benzyl triflate.
The optimization of the synthesis of Au_{13} clusters has given mixed results in the preliminary parts of the project, followed personally. In particular, the optimal conditions to obtain as a major product the cluster $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$ have been determined, while the ones to obtain the clusters $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ and $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$ could not be determined due to the poor reproducibility of the syntheses.
The testing of hydrazine monohydrate as a reducing agent for the synthesis of nanoclusters allowed to obtain the first hexa-aurated methanium dication protected by di-NHC ligands; in the literature only examples with mono-NHC ligands are present[73][75]. The use of this reducing agent together with KOH is very interesting for the synthesis of these species, that in the literature are synthesized by means of a complex two-step procedure using uncommon reagents. The disadvantage of the hydrazine reduction synthesis is in its low yield and in the difficult separation of the product from the wide array of byproducts that form during the reaction. Further optimization of the synthesis to increase the yield with modifications of the reaction conditions is certainly a road to travel for the novelty and simiplicity of the methodology and the novelty of the product itself.
For what concerns the trials performed on the cluster $[Au_9(PPh_3)_8](NO_3)_3$, they highlighted the possibility of synthesizing cluster of different nuclearity starting from it and putting it in

contact with $[Au_2(di\text{-}NHC)X_2]$ complexes bearing appropriate ligands.

Attempts at performing monosubstitution (0,8 eq. of complex) led to the formation of different species in equilibrium, and recrystallization brought to obtain an Au_{10} heteroleptic species, supposedly in equilibrium with an Au_8 heteroleptic species through loss of complex. Repeating the recrystallization multiple times could lead to obtain a novel Au_8 cluster, since, as shown in the previous discussion, the procedure removes the complex that supposedly allows the two species to be in equilibrium.

The attempt to perform complete ligand exchange led to the clear formation of cluster $[Au_{13}(di\text{-}NHC)_3(PPh_3)_3(Cl)_3]^{2+}$, already obtained by our research group starting from $[Au_{11}(PPh_3)_8(Cl)]^{2+}$, together with $[Au_{13}(di\text{-}NHC)_4(PPh_3)(Cl)_3]^{2+}$ and other cluster species of similar mass not yet identified. It also led to the formation of heavier cluster species with assumed molecular formula $[Au_{16}(di\text{-}NHC)_5(Cl)_4]^{2+}$ and $[Au_{16}(PPh_3)_2(di\text{-}NHC)_4(Cl)_4]^{2+}$. This species are very interesting since no reports of clusters of such nuclearity protected by NHC ligands are available in the literature. Optimization of the reaction conditions to allow for the synthesis in higher yield of these species is certainly an interesting perspective.

The tests on the reduction of complex C and $C\_(OTs)_2$ have shown a strong effect of the solvent on the ability to obtain AuNCs; ethanol allows to obtain small cluster species, not identified for lack of time, whereas the reduction attempts performed in DCM/EtOH mixtures give even smaller clusters or no clusters at all. Further and more methodical investigation on these reactions may be conducted to rationalize the results.

Chapter 9: Experimental

Details about the experiments and characterizations

In the synthesis of air- or moisture sensitive compounds inert conditions have been created in the reaction apparatus by means of three argon-vacuum cycles, or by flushing Ar using the Schlenk apparatus and an adapter in cases where this last procedure wasn't feasible (ex. pressure tubes).

In synthetic procedures requiring a temperature higher than room temperature an oil bath with a thermometer connected to a hot plate have been used to control the temperature. When temperatures below 0°C were necessary, a cold bath obtained using acetone and liquid nitrogen has been created in a dewar, and the temperature has been controlled with an apposite termometer.

^{1}H and ^{31}P NMR characterization has been performed using non anhydrous deuterated solvents. Chemical shifts are reported in ppm, and the signals (when attributable) are indicated using the number of nuclei, the multiplicity and the position of the nuclei.

Legend for the multiplicity: s = singlet; d = doublet; t = triplet; q = quintet; h = heptet; b indicates a broad signal when placed near the multiplicity, if appreciable or known, m indicates a multiplet deriving by multiple signals or from the presence of a second order spectrum.

Solvent signals have been attributed according to a literature article.[84]

The NMR spectrometer used is a Bruker Avance 300 MHz, (^{31}P: 121 MHz, ^{13}C: 75 MHz). The spectra have been analyzed using MestreNova 6.0.

ESI-MS characterization (positive mode) has been performed using Flow Injection Analysis (FIA) coupled with an Agilent 1260 Infinity II LC System and an Agilent 6545 LC/Q-TOF mass analyser. The spectra have been analyzed using Agilent MassHunter Qualitative Analysis 10.0 and Thermo Scientific Xcalibur 4.2 for, respectively, visualization of the spectra and simulation of isotopic patterns.

UV-Vis spectra have been recorded using an Cary 100 Bio UV-Visible Spectrophotometer.

Solvents and reagents

In the following tables (2-5) the solvents and reagents used during the thesis period are listed.

Solvents	Formula	MW (g/mol)	d (g/ml)	Supplier
Acetone	CH_3COCH_3	58,08	0,784	Sigma Aldrich
Acetone (dry)	CH_3COCH_3	58,08	0,784	VWR Chemicals
Acetonitrile	CH_3CN	41,05	0,786	Sigma Aldrich
Acetonitrile (dry)	CH_3CN	41,05	0,786	Sigma Aldrich
Acetonitrile (d3)	CD_3CN	44,07	0,844	Sigma Aldrich
Chloroform	$CHCl_3$	119,38	1,490	Sigma Aldrich
Chloroform (d)	$CDCl_3$	120,38	1,500	Sigma Aldrich
Dichloromethane	CH_2Cl_2	84,93	1,330	Sigma Aldrich
Dichloromethane (d2)	CD_2Cl_2	86,94	1,362	Sigma Aldrich
Dichloromethane (dry)	CH_2Cl_2	84,93	1,330	Sigma Aldrich

Diethyl ether	$(CH_3CH_2)O$	74,12	0,713	Sigma Aldrich
N,N-Dimethyl formamide	$C_3H_7O_2N$	73,09	0,944	Sigma Aldrich
Dimethyl sulfoxide	CH_3SOCH_3	78,13	1,100	Sigma Aldrich
Dimethyl sulfoxide (d6)	CD_3SOCD_3	84,17	1,190	Sigma Aldrich
Ethanol	CH_3CH_2OH	46,07	0,789	Sigma Aldrich
n-Hexane	C_6H_{14}	86,18	0,655	Sigma Aldrich
Methanol	CH_3OH	32,04	0,792	Sigma Aldrich
Tetrahydrofuran	C_4H_8O	72,11	0,889	Sigma Aldrich

Table 2: solvents used during the thesis project

Commercial reagent	**Formula**	**MW (g/mol)**	**d (g/ml)**	**Supplier**
Benzyl alcohol	$C_6H_5CH_2OH$	108,14	1,04	J.T. Baker
Benzyl bromide	$C_6H_5CH_2Br$	171,04	1,44	Sigma
Benzyl chloride	$C_6H_5CH_2Cl$	126,58	1,1	Sigma Aldrich

Commercial reagent	**Formula**	**MW (g/mol)**	**d (g/ml)**	**Supplier**
1-benzylimidazole	$C_{10}H_{10}N_2$	158,2	-	Sigma Aldrich
benzimidazole	$C_7H_6N_2$	118,14	-	Sigma Aldrich
1,8-bis(dimethylamino)naphthalene	$C_{14}H_{18}N_2$	214,31	-	Sigma Aldrich
Chloro(dimethyl sulfide)gold (I)	$AuCl(SC_2H_6)$	294,55	-	Strem Chemicals Inc.
Chloro(triphenyl phosphine)gold (I)	$AuCl(PC_{18}H_{15})_3$	494,71	-	Sigma Aldrich
1,3-dibromopropane	$C_3H_6Br_2$	201,9	1,98	Fluka AG, Buchs SG
1,3-dichloropropane	$C_3H_6Cl_2$	112,99	1,19	Sigma Aldrich
4,5-dicyanoimidazole	$C_5H_2N_4$	118,1	-	Sigma Aldrich
Hydrazine Monohydrate	$N_2H_4{\cdot}H_2O$	50,06	1,03	Fluka SG
Hydrobromic Acid (48%)	HBr	80,91	1,49	Sigma Aldrich
Lithium Bromide	LiBr	86,85	3,46	J.T. Baker

Commercial reagent	**Formula**	**MW (g/mol)**	**d (g/ml)**	**Supplier**
Lithium Chloride	LiCl	42,39	2,07	J.T. Baker
Methyl Iodide	CH_3I	141,94	2,28	Sigma Aldrich
Potassium Carbonate (anhydrous)	K_2CO_3	138,21	2,43	Carlo Erba
Potassium Hexafluorophosphate	KPF_6	184,06	2,75	-
Potassium Hydroxide (90%)	KOH	56,11	2,12	Sigma Aldrich
Potassium Iodide	KI	166	3,12	Sigma Aldrich
Silver Nitrate	$AgNO_3$	169,87	4,35	Sigma Aldrich
Silver Oxide	Ag_2O	231,74	7,14	Sigma Aldrich
Silver p-toluenesulfonate	$(CH_3C_6H_4SO_3)Ag$	279,06	-	-
Silver trifluoromethane--sulfonate	$Ag(CF_3SO_3)$	256,94	-	Sigma Aldrich
Sodium borohydride	$NaBH_4$	37,83	1,07	Sigma Aldrich
Sodium Iodide	NaI	149,89	3,67	J.T. Baker

Commercial reagent	**Formula**	**MW (g/mol)**	**d (g/ml)**	**Supplier**
Sodium Sulfate (anhydrous)	Na_2SO_4	142,04	2,66	Carlo Erba
Trifluoromethane- -sulfonic anhydride	$(CF_3SO_2)_2O$	282,14	1,68	Sigma Aldrich
Triphenylphosphine	$(PC_{18}H_{15})$	262,29	1,1	-
2,4,6-tri-tert-butyl-N-methyl aniline	$C_{19}H_{33}N$	275,47	-	Sigma Aldrich
2,6-di-tert-butyl-pyridine	$C_{13}H_{21}N$	191,31	0,89	Sigma Aldrich
Sand	-	-	-	Sigma Aldrich
Silica Gel, 60 ang. pore size, 70-230 mesh	SiO_2	60,08	2,65	Sigma Aldrich

Table 3: commercial reagents used during the thesis project. The supplier is indicated except in the case of compounds stored in containers different from the original, that could not be found.

Available reagent	**Formula**	**MW (g/mol)**	**d (g/ml)**
1,1'-dibenzyl-3,3'-propylene-di-(imidazolium)bis-(bromide)[83]	$[C_{23}H_{26}N_4](Br)_2$	518,29	-
Complex L[68]	$C_{23}H_{28}N_4Au_2Br_2$	914,24	-
1,1'-dibenzyl-3,3'-propylene-di-	$[C_{31}H_{30}N_4](Br_2)$	618,41	-

Available reagent	Formula	MW (g/mol)	d (g/ml)
(benzimidazolium)bis-(bromide) [85]			
1,1'-diisopropyl-3,3'-propylene-di-(imidazolium)bis-(bromide) [86]	$[C_{15}H_{26}N_4](Br_2)$	422,21	-
1-(2,6-Diisopropylphenyl)imidazole[87]	$C_{15}H_{20}N_2$	228,34	-
Complex F_Cl$_2$[68]	$C_{31}H_{28}N_4Au_2Cl_2$	921,43	-
Complex C_(OTs)$_2$[88]	$C_{33}H_{44}N_4 Au_2(SO_2C_6H_4CH_3)_2$	1201,07	-

Table 4: Non-commercial reagents that were already available in the lab during the thesis project. References are relative to the followed procedures, that in some cases have been readapted for the synthesis of different compounds with respect to the ones seen in the article.

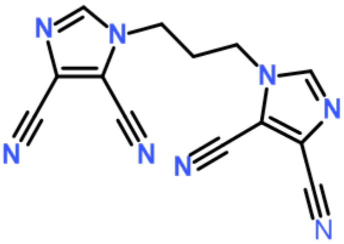
Synthesized reagent and procedure	Formula	MW (g/mol)	d (g/ml)
Benzyl iodide[62]	$C_6H_5CH_2I$	218,04	1,75 (lett.)
1,3-bis(4,5-dicyanoimidazole) propane[54]	$C_{13}H_8N_8$	276,26	-
1,1'-dibenzyl-3,3'-propylene-di-	$[C_{23}H_{26}N_4](Cl)_2$	429,39	-

Synthesized reagent and procedure	**Formula**	**MW (g/mol)**	**d (g/ml)**
(imidazolium)bis-(chloride)[19]			
complex H[68]	$C_{23}H_{24}N_4Au_2Br_2$	910,21	-
complex H_Cl$_2$[68]	$C_{23}H_{24}N_4Au_2Cl_2$	821,31	-
1,3-dibenzylbenzimidazolium chloride	$[C_{21}H_{19}N_2]Cl$	334,85	-
Complex G[68]	$C_{21}H_{18}N_2AuCl$	530,81	-
Complex M[68]	$C_{15}H_{24}N_4Au_2Br_2$	814,12	-
Complex F[68]	$C_{31}H_{28}N_4Au_2Br_2$	1010,33	-
(Triphenylphosphine)Nitrate Gold(I) [78]	$Au(PC_{18}H_{15})NO_3$	521,26	-
Cluster $[Au_9(PPh_3)_8](NO_3)_3$ [79]	$Au_9(PC_{18}H_{15})_8(NO_3)_3$	4057,04	-
1,1'-di(2,6-diisopropylphenyl)-3,3'-propylene-di-(imidazolium)bis-(bromide)[83]	$[C_{33}H_{46}N_4]Br_2$	658,56	-
Complex C[68]	$C_{33}H_{44}N_4Au_2Br_2$	1050,48	-

Table 5: Reagents that have been synthesized during the thesis project, starting from commercial ones or reagents already available in the lab. References are relative to the followed procedures, that in some cases have been readapted for the synthesis of different compounds with respect to the ones seen in the article. Where references are missing, the synthesis is novel.

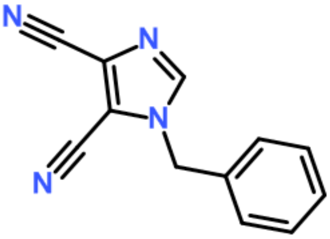
Attempted syntheses of the electron-withdrawing NHC (pre)ligand

Synthesis of 1,3-bis(4,5-dicyanoimidazole)propane



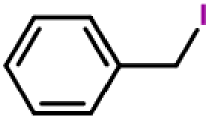
2,54 g (21,5 mmol) of 4,5-dicyanoimidazole and 3,17 g (22,9 mmol) of potassium carbonate have been added into a three-necks round bottom flask together with a stirring bar. The necks have been closed with two silicon plugs and a condenser, and the last capped with a vacuum tap. Three Ar-vacuum cycles have been performed on the content of the flask, and then 50 ml of dry acetonitrile have been added using a 50 ml syringe, followed by 1,16 ml (2,31 g, 11,4 mmol) of 1,3-dibromopropane, using a 5 ml syringe. The reaction has been heated to reflux (90°C) using an oil bath, and has been kept stirring for 24 h. The reaction apparatus then has been cooled down removing it from the oil bath and the content of the flask has been vacuum-filtered. The solid has been washed with 3 aliquots of 3 ml of acetonitrile. The acetonitrile has been evaporated under vacuum and the resulting yellowish oil has been redissolved in acetonitrile and precipitated using diethyl ether, giving an ivory colored solid.
Yield: 2,64 g (87%); ^{1}H NMR (DMSO-d_6): 8,38 (s, 2H, NCHN), 4,30 (m, 4H, NCH_2), 2,48-2,33 (m, 2H, CH_2). For complete characterization, see article [54].

Attempted synthesis of 1-benzyl-4,5-dicyanoimidazole



1,00 g (8,5 mmol) of 4,5-dicyanoimidazole and 1,17 g (8,5 mmol) of potassium carbonate have been added into a three-necks round-bottom flask together with a stirring bar. The necks have been closed with two silicon plugs and a vacuum tap. Three Ar-vacuum cycles have been performed on the content of the flask, and then 10 ml of dry DMF have been added with a 10 ml syringe, followed by 1,00 ml (1,44 g, 8,4 mmol) of benzyl bromide using a 1 ml syringe. The reaction has been left stirring for 24 hours and a withdrawal of 0,5 ml has been performed to check its degree of completion via proton NMR. The analysis revealed no conversion. After this check the reaction has been heated up to 70°C and has been left stirring for other 24 hours. The reaction mixture has been dried under vacuum and heating using the Schlenk apparatus. The product has been dissolved in DCM and vacuum-filtered, and the solid has been washed with 3 aliquots of 3 ml of DCM. The solvent has been removed under vacuum with the rotary evaporator, leaving a white solid, that has been transferred into a vial. ^{1}H NMR confirms the very low conversion of the reagent to product.

Synthesis of benzyl iodide



A stirring bar has been placed into a three-necks round bottom flask, followed by 0,5302 g (3,5 mmol) of NaI. The necks have been closed with two silicon plugs and a vacuum tap. Three Ar-vacuum cycles have been performed on the flask. 7,0 ml of dry acetone have been added through one of the plugs, using a 10 ml syringe, followed by 0,41 ml (0,45 g, 3,5 mmol) of benzyl chloride, using a 1 ml syringe. The reaction mixture quickly turned yellow. After stirring for 18 hours, a withdrawal has been performed, dried and analyzed via ^{1}H NMR to check the conversion (erroneously assigned at 95%), and the reaction has been halted.
Yield (^{1}H NMR): 63% ^{1}H NMR (DMSO-d_6): 4.60 (s, 2H), 7.21-7.39 (m, 3H), and 7.39-7.41 (d, 2H). For ^{13}C NMR characterization, see article [89]

Attempted synthesis of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(chloride)

0,1999 g of 1,3-bis(4,5-dicyanoimidazole)propane have been added to a pressure tube. The tube has been flushed with Ar for 10 minutes, and then 0,21 ml of benzyl chloride have been added using a 1 ml syringe. A stirring bar has been dropped inside and the cap has been screwed on top. The reaction has been heated up to 130°C using an oil bath, and has been left stirring for 24 h. The mixture turned slowly yellow, and after 24 hours has been allowed to cool. The surnatant has been separated from the solid and dissolved in diethyl ether, giving a white precipitate. The solid still present in the tube has been washed with diethyl ether. Both solids have been dried, and part of each has been dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. Both of the spectra were consistent with the one of the reagent, confirming that no reaction had happened.

Attempted syntheses of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(bromide)

1) 0,999 g of 1,3-bis(4,5-dicyanoimidazole)propane have been added to a two-necks round bottom flask, equipped with a silicon plug and a condenser closed by a vacuum

tap. Three Ar-vacuum cycles have been performed on the apparatus to grant inert atmosphere. 20 ml of dry acetonitrile have been added by means of a 20 ml syringe, followed by 0,36 ml of benzyl bromide, using a 1,00 ml syringe. Using an hot plate and an oil bath the reaction mixture has been heated up to reflux. The reaction has been left stirring for 48 hours, the acetonitrile turned slightly yellow and a white solid was present on the bottom during the whole reaction. After 48 hours the apparatus has been allowed to cool, the condenser disconnected and the solid has been separated by means of vacuum filtration and washed several times with diethyl ether. The surnatant has been reduced in volume to 2 ml, then 20 ml of diethyl ether have been added. A small amount of white solid precipitated. Both solids have been dried, partially dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. Both of the spectra were consistent with the one of the reagent, confirming that no reaction had happened. The reagent has been recovered and a second reaction, using the same amount of 1,3-bis(4,5-dicyanoimidazole)propane and 0,48 ml of benzyl bromide, has been performed, this time mantaining the reflux conditions for 120 h. Similar results were achieved.

2) 0,2999 g of 1,3-bis(4,5-dicyanoimidazole)propane have been added to a pressure tube. The tube has been flushed with Ar for 10 minutes, and then 1,10 ml of benzyl bromide have been added using a 2 ml syringe. A stirring bar has been dropped inside and the cap has been screwed on top. The reaction has been heated up to 120°C and after 24 hours up to 130°C using an oil bath, and has been left stirring for 48 h. The mixture slowly turned yellow. After 48 hours the reaction has been halted. The surnatant has been separated from the solid and dissolved in diethyl ether, giving a white precipitate. The precipitate has been decanted using a centrifuge. The solid still present in the tube has been washed with diethyl ether. Both solids have been dried, and part of each has been dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. The spectrum of the solid residue was consistent with the one of the reagent, while the one on the precipitated solid didn't contain organic components, probably deriving from some soluble inorganic impurities, confirming that no reaction had happened.

3) 0,2992 g of 1,3-bis(4,5-dicyanoimidazole)propane have been added to a pressure tube. The tube has been flushed with Ar for 10 minutes, and then 0,53 ml of benzyl bromide and 2,00 ml of dry DMF have been added using a 1,00 ml and 5,0 ml syringe

respectively. A stirring bar has been dropped inside and the cap has been screwed on top. The reaction has been heated up to 140°C using an oil bath, and has been left stirring for 48 h. The mixture quickly turned yellow and then after one day was black. After 48 hours the mixture has been cooled and has been transferred into a round bottom flask. The solvent has been removed under vacuum using the Schlenk apparatus, leaving a black oil. The oil has been washed with 5 ml of diethyl ether 3 times, and part of it has been dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. The spectrum showed the presence of deshielded protons that could have been consistent with an imidazolium salt, therefore a work up has been attempted. The oil has been dissolved in 3 ml of DCM and precipitated using 20 ml of acetone. A black oily precipitate formed, and has been decanted by centrifugation. The surnatant has been removed via filtration, the solid has been washed with acetone and dried under vacuum. The solid has been dissolved in DCM and precipitated using diethyl ether. The obtained oil has been dried using the rotary evaporator, giving an oily black solid. The solid has been dissolved in methanol, giving a white precipitate, removed via vacuum filtration. The brown solution has been dried using the rotary evaporator, yielding an oily black solid. Each drying step has been followed by proton NMR analysis on a sample of the oil. After the last step, seeing no signal coherent with the functionalization of the imidazole nitrogen, the work-up has been halted.

Attempted syntheses of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(iodide)

1) The crude reaction mixture of the benzyl iodide synthesis has been filtered through a PTFE syringe filter directly into a pressure tube filled with Argon.Due to an error in determining the yield in the previous reaction, 0,50 g of 1,3-bis(dicyanoimidazole)propane have been added together with a stirring bar, and then the cap has been screwed on top. The reaction has been left stirring for 24 hours at 90°C in an oil bath. A withdrawal has been performed after cooling, dried, dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. No signals relative to a potential product have been detected, therefore the reaction has been halted.

2) The reaction mixture of the previous synthesis has been dried using a heatgun. Once the benzyl iodide and the 1,3-bis(dicyanoimidazole)propane had been dried, the tube was closed and placed in an oil bath. The mixture has been heated up to 150°C and has

been left stirring for 24 h, becoming dark brown, and after that it has been cooled down to room temperature. Part of the solid has been dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. Extremely low signals relative to the presence of product have been detected, therefore the reaction has been discarded.

Attempted syntheses of 1,1'-dibenzyl-3,3'-propylene-di-(4,5-dicyanoimidazolium)bis-(trifluoromethanesulfonate)

1) 3 Å molecular sieves have been dried under heating and vacuum for 2 hours. A vial has been subjected to three Ar-vacuum cycles. 105 µl of benzyl alcohol have been transferred into the vial, together with 2 ml of dry DCM, and the dry molecular sieves have been added. A two-necks round bottom flask (A) has been equipped with a vacuum tap and a silicon plug. A stirring bar has been dropped inside and the flask has been subjected to 3 Ar-vacuum cycles, and then 5 ml of dry DCM have been added using a 5 ml syringe. A three-necks round bottom flask has been equipped with a gooch funnel, closed by a silicon plug, a vacuum tap and another silicon plug (B). A stirring bar has been dropped inside and the flask has been subjected to 3 Ar-vacuum cycles. 0,139 g of 1,3-bis(dicyanoimidazole)propane have been added into flask (B), together with 5 ml of dry acetone. 168 µl of trifluoromethanesulfonic anhydride have been added using a 250 µl syringe in flask(A). The mixture has been stirred for 5 minutes and then has been cooled down to about -80°C using an acetone/liquid nitrogen bath. The benzyl alcohol solution has been transferred into the flask (A) using a capillary and the vacuum provided by the Shlenk apparatus, then 0,214 g of 1,8-bis(dimethylamino)naphthalene have been added in Ar counterflow. The mixture has been allowed to stir for 15 minutes, becoming orange, and then has been transferred into flask (B) through the gooch funnel using a capillary and the vacuum granted by the Schlenk apparatus. The mixture has been left stirring for 90 hours, becoming dark red, and a withdrawal has been carried out at the 18 hour mark, dried and subjected to ^{1}H NMR analysis to check if the reaction was working. Some peaks consistent with the presence of product were detected in this spectrum and also in one recorded after the reaction (90 h). However these peaks were less intense after 90 h, indicating a possible decomposition.

A work-up has been attempted: the solvent has been evaporated under vacuum, giving an oil. The oil has been dissolved in acetone and precipitated in n-hexane, giving an oil again. The hexane has been removed and the oil dried under vacuum, then redissolved in acetone and precipitated in DCM. Each drying step has been followed by proton NMR analysis, no separation has been achieved.

2) The previous reaction has been repeated on the scale of 1,067 g of 1,3-bis(dicyanoimidazole)propane, mantaining the same proportions of solvents and duplicating the relative quantities of other reagents (2,053 g of 1,8-bis(dimethylamino)naphthalene, 3,22 ml of trifluoromethanesulfonic anhydride, 2,00 ml of benzyl alcohol, 40 ml of dry acetone, 55 ml total of DCM). A withdrawal has been carried out at the 48 hour mark, dried and subjected to a work up. The solvent has been evaporated under vacuum, and the resulting solid has been washed with n-hexane. The solid has been dissolved in acetone and DCM has been added to it. A yellow solid precipitated from the red solution and has been washed with 3 aliquots of 1 ml of DCM. The obtained solid has been dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis to check if the reaction was working. The NMR spectrum showed peaks consistent with the presence of reagent, a monosubstituted product (DMSO-d_6: 4,38 (t), 2H (NCH_2), 4,48 (t), 2H (NCH_2), 8,39 (s), 1H (NCHN) 9,95 (s), 1H (NCHN)) and a small fraction of disubstituted product (DMSO-d_6: 4,57 (t) 4H, NCH_2, 10,00 (s) 2H (NCHN)), however aromatic signals were very low in intensity, indicating the presence of a not identified non-benzyl substituent. After this the reaction has been heated up to 40°C for 24 h. Following withdrawal and proton NMR analysis (same procedure as before) showed the reduction in intensity of the peaks listed above. The reaction has been halted and after solvent removal and many DCM washing an oil remained at the bottom of the flask. Subjecting the oil to the same work up listed above didn't produce the same result as before, and the deriving proton NMR spectrum was much more complex than the previous one. Several solvents (MeOH, EtOH, DCM, acetone, water) were employed to try to separate some components from the mixture, but traces or small amount of both product and reagent were found in every fraction using proton NMR.

3) The previous reaction has been repeated on the scale of 0,367 g of 1,3-bis(dicyanoimidazole)propane, using 2,6-di-tert-butyl pyridine as a base (0,56 ml of 2,6-di-tert-butyl pyridine, 0,44 ml of trifluoromethanesulfonic anhydride, 0,27 ml of benzyl alcohol, 18 ml of dry acetone, 5,25 ml total of DCM). The reaction still turned

orange and then red despite the change of base, but was way less dark than in the previous case.
The reaction has been followed by means of withdrawals at 19, 33 and 57 h, all subjected to the same work up listed in point 2) and to ^1H NMR analysis. The first two withdrawals showed a situation very similar to the one of the early withdrawals of the previous reactions, while the last showed an abrupt lowering in intensity of the peaks of the products. Due to this the reaction has been halted.

4) 2,00 ml of benzyl alcohol have been dried using 3 Å molecular sieves overnight. 0,502 g of N-methyl-2,4,6-tri-tert-butyl aniline have been added together with 0,251 g of 1,3-bis(4,5-dicyanoimidazole)propane and a stirring bar to a pressure tube, that has been flushed with Ar for 15 minutes. After that the benzyl alcohol has been added and the mixture has been allowed to stir, closing the cap. Using an acetone-liquid nitrogen bath the temperature has been dropped to -15°C. The cap has been opened and 0,40 ml of trifluoromethanesulfonic anhydride have been quickly added to the mixture, then the cap has been quickly screwed back on top. The mixture has been left stirring at 100°C using an oil bath for heating, and slowly turned brown. At 3 h and 16 h two withdrawals were carried out, dissolved in DMSO-d_6 and subjected to ^1H NMR analysis. The second analysis showed the presence of an intense peak at 9.95 ppm, together with two broad bands at 4.80 to 4.40 ppm and 5.77 to 5.62 ppm, consistent with the expected values for the protons of the lateral CH_2 of the propylene bridge and benzylic CH_2 protons of the product respectively. The reaction has been halted and the reaction mixture has been allowed to cool, giving a brown paste. The content of the tube has been dissolved in acetone and transferred in a round-bottom flask. The content of the flask has been dried using the rotary evaporator and washed with DCM and diethyl ether. The ether washing gave a brown oily solid. Another washing has been attempted using methanol, without success (all soluble). The solid has been dried, dissolved in DMSO-d_6 and subjected to ^1H NMR analysis. The analysis revealed the presence of three broad bands in the regions diagnostic for a substitution product (4,65-4,30 ppm, 5,77-5,62 ppm 10,00-9,87 ppm). The analysis confirmed the total absence of 1,3-bis(4,5-dicyanoimidazole)propane, and the presence of impurities consistent with benzyl groups. To separate the products from the residue of anilinium salt an extraction has been carried out using a K_2CO_3/MeOH solution and hexane. The mixture unfortunately turned orange, indicating the dimerization of the product caused

by the deprotonation, and this has been confirmed by ^1H NMR analysis (absence of signals at around 10 ppm, shift of the signals at 4,65-4,30 ppm to 4,00-3.65 and of the signals at 5,77-5,62 to around 7,2 ppm, together with aromatic signals).

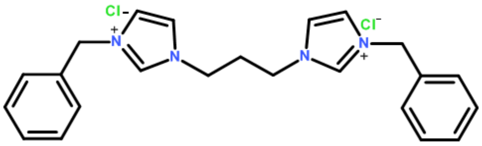
5) 1,3-bis(4,5-dicyanoimidazole)propane and silver trifluoromethanesulfonate have been dried using the Schlenk apparatus for 8 hours. Two three necks round-bottom flask, closed with 2 silicon plugs and a vacuum tap have been subjected to three Ar-vacuum cycles after addition, respectively, of 0,050 g of 1,3-bis(4,5-dicyanoimidazole)propane and 0,093 g of silver trifluoromethanesulfonate. 5 ml of dry DCM have been added in the flask containing the silver triflate, and strong stirring has been employed to try to dissolve the reagent. The reagent, however, kept its dispersed state and has been transferred using a capillary in the flask containing the 1,3-bis(4,5-dicyanoimidazole)propane. The mixture has been kept under stirring for 15 minutes and then 40 μl of benzyl chloride have been added. The reaction has been left stirring at room temperature for 24 hours. After that a sample has been taken, dried, dissolved in DMSO-d_6 and subjected to ^1H NMR analysis. The analysis confirmed that no conversion had happened and the reaction has been halted.

A pressure tube has been flushed with Ar for 15 minutes. 0,100 g of 1,3-bis(4,5-dicyanoimidazole)propane have been added, together with 0,186 g of silver trifluoromethanesulfonate and a stirring bar. 2 ml of dry DCM mixed with 80 μL of benzyl chloride have been added on top and the cap has been screwed back on. A suspension formed, the reaction has been heated up to 50 °C using an oil bath and has been left stirring for 24 hours. After the reaction the content of the tube has been transferred into a round-bottom flask and has been dried using the rotary evaporator. A sample has been taken, dried, dissolved in DMSO-d_6 and subjected to ^1H NMR analysis, confirming a partial conversion with formation of the monosubstituted product (DMSO-d_6: 4,38 (t), 2H (NCH_2), 4,48 (t), 2H (NCH_2), 9,96 (s), 1H (NCHN)). The reaction has been repeated doubling the amount of benzyl triflate (0,372 g of silver trifluoromethanesulfonate, 160 μL of benzyl chloride) and heating it up to 100 °C. It has also been left stirring for 120 h, to counter the low solubility of the reagents. Despite the harsher reaction conditions the results were almost the same, with just a slightly higher conversion, appreciable from ^1H NMR analysis.

Optimization of the synthesis of Au_{13} NCs

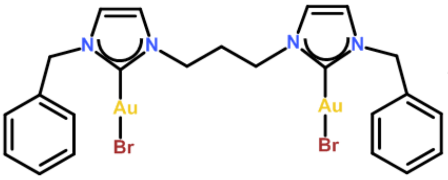
Complex H has been prepared from the corresponding imidazolium salt, already available. [68] Complex H_Cl_2 has been prepared from the imidazolium salt[68], obtained starting from 1-benzylimidazole, adapting the procedure reported in article [19].

Synthesis of 1,1'-dibenzyl-3,3'-propylene-di-(imidazolium)bis-(chloride)



2,012 g (12,7 mmol) of 1-benzylimidazole have been added to a two-necks round bottom flask, together with 0,60 ml (0,714 g, 6,3 mmol) of 1,3-dichloropropane (1 ml syringe), 25 ml of THF (20 ml syringe, 2 additions) and a stirring bar. The flask has been closed with a silicon plug and a condenser, closed on top by another silicon plug. The reaction mixture has been heated to reflux using an oil bath, and it has been left stirring for 144 hours. After that the solvent has been completely removed under vacuum using the Schlenk apparatus. The residue has been washed with 20 ml of DCM, and the resulting white solid has been filtered, transferred into a vial and dried under vacuum. Yield: 2,01 g (75%); (^{1}H NMR ($CDCl_3$): 2,86 (2H, q, $CH_2\mathit{CH_2}CH_2$), 4,67 (4H, t, $\mathit{CH_2}CH_2\mathit{CH_2}$), 5,42 (4H, s, Ph-$\mathit{CH_2}$), 7,03-7,08 (2H, s, imi-H_1), 7,30-7,38 (6H, m, Ph-H), 7,38-7,43 (4H, m, Ph-H), 8,22-8,26 (2H, s, imi-H_2), 10,56 (2H, s, NCHN). For complete characterization, see article [90].

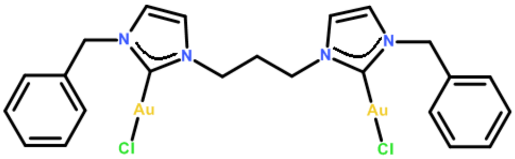
Synthesis of complex H:



123,3 mg (0,42 mmol) of AuCl(SMe_2), 107,3 mg (0,22 mmol) of 1,1'-dibenzyl-3,3'-propylene-di-(imidazolium)bis-(bromide), 88,5 mg (1,02 mmol) of LiBr, 622 mg (4,50 mmol) of K_2CO_3 and a stirring bar have been transferred into a two-necks round bottom flask. The two necks have been closed with a vacuum tap and a silicon plug. Three Ar-vacuum cycles have been performed on the solid reagents. 20 ml of dry acetonitrile have been added using a 20 ml syringe. The reaction has been heated up to 60 °C using an oil bath, and it has been left stirring for 16 hours. The content of the flask has then been vacuum filtered while still warm. The obtained solution has been transferred into a round-bottom flask and reduced to about 2 ml using the rotary evaporator. 50 ml of diethyl ether have been added to precipitate the product, in the form of a white powder. The ether has been removed and the solid has been dried and transferred into a vial. The synthesis has been repeated three times, the maximum and minimum yield have been reported.

Yield: 106,2 mg-119,4 mg (59%-67%); ^{1}H NMR ($CDCl_3$): 2,52 (2H, q, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$), 4,29 (4H, t, $\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$), 5,47 (4H, s, Ph-$\mathit{CH_2}$), 6,94 (2H, d, imi-$H_1$), 7,06 (2H, d, imi-$H_2$) 7,36-7,40 (10H, m, Ph-H). ^{13}C NMR ($CDCl_3$): 30,5 ppm ($\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$), 47,3 ppm ($\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$) 55,5 ppm (Ph-$\mathit{CH_2}$-N), 120,0 ppm (imi-C), 121,9 ppm (imi-C), 128, 6 ppm (Ph *CH*), 128,9 ppm (Ph *CH*), 129,3 ppm (Ph *CH*), 135,2 ppm ($\mathrm{(CH)_2}\mathit{C}\mathrm{-CH_2}$), 175,0 ppm ($\mathrm{NR_2}$-*C*-$\mathrm{NR_2}$). Elemental analysis: C: 30,70% (theor. 30,35%); H: 2,65% (theor. 2,65%); N 5,95% (theor. 6,16%)

Synthesis of complex H_Cl$_2$



145,5 mg (0,49 mmol) of AuCl(SMe_2), 106,2 mg (0,28 mmol) of 1,1'-dibenzyl-3,3'-propylene-di-(imidazolium)bis-(chloride), 52,4 mg (1,23 mmol) of LiCl, 761 mg (5,51 mmol) of K_2CO_3 and a stirring bar have been transferred into a two-necks round bottom flask. The two necks have been closed with a vacuum tap and a silicon plug. Three Ar-vacuum cycles have been performed on the solid reagents. 25 ml of dry acetonitrile have been added using a 20 ml syringe (2 additions). The reaction has been heated up to 60 °C using an oil bath, and it has been left stirring for 16 hours. The content of the flask has then been vacuum filtered while still warm. The obtained solution has been transferred into a round-bottom flask and reduced to about 2 ml using the rotary evaporator. 50 ml of diethyl ether have been added to precipitate the oily product. The ether has been removed, the procedure repeated again and the resulting yellowish solid has been dried under heating and transferred into a vial. The synthesis has been repeated three times, the maximum and minimum yield have been reported.

Yield: 115,4-180,1 mg (54%-83%*).^{1}H NMR ($CDCl_3$): 2,52 (2H, q, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$), 4,28 (4H, t, $\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$), 5,45 (4H, s, Ph-$\mathit{CH_2}$), 6,93 (2H, d, imi-$H_1$), 7,06 (2H, d, imi-$H_2$) 7,36-7,39 (10H, m, Ph-H). *wet with solvent. For complete characterization, see article [86].

Preliminary synthesis of Au$_{13}$ clusters using complex H

10,0 mg of complex H have been added into two vials together with 1,9 mg of AuCl(SMe_2) and a stirring bar. The complexes have been dissolved into 1,8 ml of DCM/MeOH 4:1 mixture, and placed under stirring. A solution of $NaBH_4$ in ethanol has been prepared in a third vial (1,00 ml, 10,0 mg/ml) and 50 and 100 µl of it have been added dropwise into the

complexes solution. Immediately a very finely divided black precipitate started to form, and the solution started assuming a pale orange color, and after some time it turned red. The reaction has been left stirring for 72 hours and withdrawals have been carried out at 3h, 24 h, 48 h and 72 h. The withdrawals and the whole reaction mixture have been subjected to a work up (listed below) and the solids obtained by the withdrawals have been redissolved in DCM and subjected to ESI-MS analysis.
ESI-MS: $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$:1500,51 (theor: 1500,50).

15,6 mg of complex H have been added into a vial together with 3,3 mg of $AuCl(SMe_2)$ and a stirring bar. The complexes have been dissolved into 3 ml of DCM/MeOH 4:1 mixture, and placed under stirring. A solution of $NaBH_4$ in ethanol has been prepared in a second vial (1 ml, 14,9 mg/ml) and 328 μl of it have been added dropwise into the complexes solution. Immediately a very finely divided black precipitate started to form, and the solution started assuming an orange color. The reaction has been left stirring for 72 hours and withdrawals have been carried out at 3h, 24 h, 48 h and 72 h. The solution turned brown over this time. The withdrawals and the whole reaction mixture have been subjected to a work up (listed below) and the solids obtained by the withdrawals have been redissolved in DCM and subjected to ESI-MS analysis.
ESI-MS: $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$:1479,17 (theor: 1479,17).

Work-up: The solutions have been filtered using a syringe and a 0,2 μm porosity PTFE syringe filter. The vials have been washed with 1 ml of DCM and the filter itself has been washed with 1 ml of DCM (for the withdrawals one singular washing with 0,5 ml). 5 ml of water have been added to the vial (1 ml for the withdrawals). The vial has been agitated to provide a good mixing and the two layers have been left to separate. The acqueous layer has been removed using a Pasteur pipette, and dry sodium sulfate has been used to remove the last water remaining. Using a Pasteur pipette and some cotton the solution has been subjected to gravity filtration to remove the sodium sulfate. The sulfate and the filter have been washed with 3 ml (0,6 ml for the withdrawals) of DCM. The solvent has been removed under vacuum and the resulting solid has been dissolved in 3 ml of acetone (1 for the withdrawals). The resulting solution has been subjected to another syringe filtration and the original vial and the filter have been washed with 2 ml of acetone (0,5 for the withdrawals). The solvent has been dried under vacuum.

Synthesis of cluster $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$

The previous procedure has been repeated using 39,8 mg of complex H, 8,0 mg of $AuCl(SMe_2)$ and 394 µl of a 10,0 mg/ml solution of $NaBH_4$ in ethanol. The work up has been repeated and the product has been recrystallized from DCM and diethyl ether vapours.
Yield: 6,0 mg (15%), ESI-MS: $[Au_{13}(di\text{-}NHC)_5(Br)_2]^{3+}$: 1500,81 (theor: 1500,81)

Synthesis of cluster $[Au_{13}(di\text{-}NHC)_5(Br)(BH_4)]^{3+}$

The previous procedure has been repeated using 40,6 mg of complex H, 7,7 mg of $AuCl(SMe_2)$ and 1,3 ml of a 15,2 mg/ml solution of $NaBH_4$ in ethanol. The work up has been repeated and the product has been recrystallized from DCM and diethyl ether vapours.
Yield: 9,4 mg (23%) ESI-MS: 1479,18 (theor: 1479,17).

Preliminary synthesis of Au_{13} *clusters using complex* H_Cl_2

39,9 (1) and 39,6 (2) mg of complex H_Cl_2 have been added into two vials together with 8,6 (1) mg and 8,7 (2) mg of $AuCl(SMe_2)$ and a stirring bar, respectively. The complexes have been dissolved into 7 ml of DCM/MeOH 4:1 mixture, and placed under stirring. A solution of $NaBH_4$ in ethanol has been prepared in a third vial (1 ml, 15,0 mg/ml) and 61 µl of it have been added dropwise into the solution (1), while 306 µl into solution (2). Immediately a very finely divided black precipitate started to form. After 3 hours the reaction (1) had formed a gold mirror on the surface of the vial, and has been halted and subjected to work up (see preliminary synthesis with complex H). Reaction (2) has been left stirring for 48 hours, turning black. After this the reaction has been halted and subjected to the work up (see preliminary synthesis with complex H). Samples have been taken and analyzed using ESI-MS. Reaction (2) formed also cluster $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$.
ESI-MS: $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ m/z = 1457,54; $[Au_{13}(di\text{-}NHC)_5(Cl)(BH_4)]^{3+}$ m/z = 1464,19 $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ m/z = 1471,18

Attempted optimization of the synthesis of cluster $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$

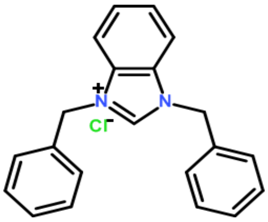
32,0 mg of complex H have been added into a vial together with 6,9 mg of $AuCl(SMe_2)$ and a stirring bar. The complexes have been dissolved into 5,6 ml of DCM/MeOH 4:1 mixture, and placed under stirring. A solution of $NaBH_4$ in ethanol has been prepared in a second vial (1 ml, 14,9 mg/ml) and 246 µl of it have been added dropwise into the complexes solution. Immediately a very finely divided black precipitate started to form, and the solution started assuming an orange color. The reaction has been left stirring for 96 hours and withdrawals have been carried out at 3h, 24 h, 48 h, 72 h and 96 h. The solution turned brown and then black over this time. The withdrawals and the whole reaction mixture have been subjected to a work up (see preliminary synthesis with complex H) and the solids obtained by the withdrawals have been redissolved in DCM and subjected to ESI-MS analysis. ESI-MS confirms the presence of a mixture of clusters $[Au_{13}(di\text{-}NHC)_5(Cl)(BH_4)]^{3+}$ and $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$.

ESI-MS: $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ absent; $[Au_{13}(di\text{-}NHC)_5(Cl)(BH_4)]^{3+}$ m/z = 1464,51 $[Au_{13}(di\text{-}NHC)_5(BH_4)_2]^{3+}$ m/z = 1471,16

Testing of new reducing agents - hydrazine

Complex L was already available. Complex M and F have been prepared from the corresponding imidazolium salt.[68] Complex G has been prepared from the corresponding imidazolium salt[68], prepared starting from benzimidazole using a novel synthetic approach.

Synthesis of imidazolium salt 1,3-dibenzylbenzimidazolium chloride



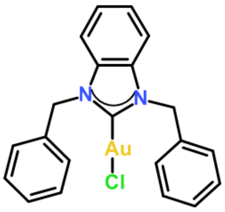
1,00 g of benzimidazole (8,47 mmol) has been added to a three-necks round-bottom flask together with a stirring bar. The flask has been closed with two silicon plugs, a condenser and a vacuum tap on top of it. Three Ar-vacuum cycles have been performed on the solid reagent. 16,0 ml of dry acetonitrile have been added through one of the plugs using an hamilton syringe, followed by 1,95 ml of benzyl chloride (16,94 mmol). The reaction has been left stirring at reflux for 16 hours, then the reaction has been cooled to room temperature and 0,585 g of potassium carbonate have been added in Ar counterflow to the reaction mixture. The reaction has been left stirring for additional 24 hours at reflux.

The solvent has been removed using the vacuum dryer and 5 ml of DCM have been added to dissolve the imidazolium salt. The mixture has been filtered under vacuum and the solid has been washed with 3 additional aliquants of 2 ml of DCM. The filtrate has been dried under vacuum and the white solid transferred into a vial.

Yield 1,98 g (70%); ^{1}H-NMR: (DMSO-d6): 5,79 ppm (4H, s, Ph-CH_2-N); 7,35-7,48 ppm (6H, m, *p-* + *m-* Ph); 7,50-7,56 ppm (4H, m, *o*-Ph); 7,64 ppm (2H, m, bimi CH-

CH-*CH*-CH); 7,97 ppm (2H, dd, bimi *CH*-CH-CH-*CH*); 10,10 ppm (1H, s, NR_2-*CH*-NR_2). For complete characterization, see article [32].

Synthesis of chloro(N,N-dibenzylbenzimidazol-2-ylidene)gold(I) (G)

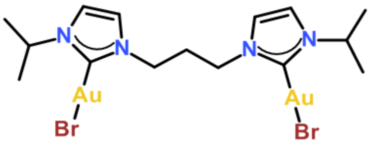


0,100 g (0,34 mmol) of $AuCl(SMe_2)$ have been added to a three-necks round-bottom flask together with 0,1136 g (0,34 mmol) of 1,3-dibenzylbenzimidazolium chloride, 0,5160 g (3,7 mmol) of potassium carbonate and 0,090 g (2,12 mmol) of lithium chloride. The flask has been closed with two silicon plugs, a condenser and a vacuum tap on top of it. Three Ar-vacuum cycles have been performed on the solid reagents. 12,0 ml of dry acetonitrile have been added through one of the plugs using an hamilton siringe.

The reaction has been left stirring at reflux for 3 hours, then the pink precipitate has been filtered under vacuum and washed five times with DCM. The filtrate has been dried under vacuum, redissolved in 2 ml of DCM, transferred into a vial and precipitated with diethyl ether. The white solid has then been washed two additional times with diethyl ether.

Yield:164,2 mg (91%); ^{1}H-NMR: 5,78 ppm (4H, s, Ph-*CH_2*-N); 7,28-7,47 ppm (14 H, m, bimi-H + Ph-H). Complete characterization available in article [32]

Synthesis of dibromo(1,3-di(N-isopropylimidazol-2-ylidene)propane) digold(I) (M)



0,0525 g of $AuCl(SMe_2)$ (0,179 mmol) have been added to a three-necks round-bottom flask together with 0,0303 g of 1,3-di(N-isopropylimidazol)propane (0,090 mmol) 0,2707 g of potassium carbonate (1,96 mmol) and 0,0393 g of lithium bromide (0,453 mmol). The flask has been closed with two silicon plugs and a vacuum tap. Three Ar-vacuum cycles have been performed on the solid reagents. 9,0 ml of dry acetonitrile have been added through one of the plugs using an hamilton siringe. The reaction has been left stirring for 16 hours at 60°C, obtained by means of a hot plate and an oil bath. The reaction mixture has been vacuum-filtered and the solid washed three times with 3 ml of acetonitrile. The filtrate has been collected and dried under vacuum, then it has been dissolved in 1 ml of DCM and precipitated using 40 ml of hexane, obtaining an higroscopic oil, dissolved in methanol and dried under vacuum four times to obtain a solid.

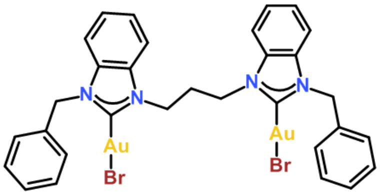
Yield: 41,3 mg (56,3%) ^{1}H-NMR ($CDCl_3$): 1,51 ppm (12H, d, *CH_3*CH*CH_3*); 2,54 ppm

(2H, q, CH_2-CH_2-CH_2); 4,23 ppm (4H, t, CH_2-CH_2-NR_2); 5,05 ppm (2H, h, CH_3CHCH_3); 7,08 ppm (2H, d, $CH_2NRCHCH$); 7,14 ppm (2H, d, CHNR*CH*CH).

^{13}C-NMR ($CDCl_3$): not performed yet.

Elemental analysis: results pending

Synthesis of dibromo(1,3-di(N-benzylbenzimidazol-2-ylidene)propane) digold(I) (F)

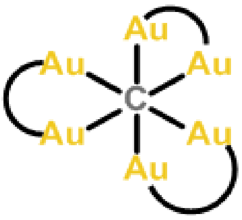


0,0798 g of AuCl(SMe_2) (0,27 mmol) have been added to a three-necks round-bottom flask together with 0,0777 g of 1,3-di(N-benzylbenzimidazol)propane (0,126 mmol) 0,4086 g of potassium carbonate (2,96 mmol) and 0,0642 g of lithium bromide (0,738 mmol). The flask has been closed with two silicon plugs and a vacuum tap. Three Ar-vacuum cycles have been performed on the solid reagents. 6,0 ml of dry acetonitrile have been added through one of the plugs using an hamilton siringe. The reaction has been left stirring for 16 hours.

The reaction mixture has been vacuum-filtered and the solid washed three times with 3 ml of acetonitrile. The solid has been collected and then 1 ml of chloroform has been added to dissolve the product. The resulting solution has been vacuum-filtered again, transferred in vial, then the solvent has been removed and the solid washed three times with diethyl ether (3 ml) and dried again.

Yield: 74,5 mg (58,5%); ^{1}H-NMR ($CDCl_3$): 2,82 ppm (2H, q, CH_2-CH_2-CH_2); 4,72 ppm (4H, t, CH_2-CH_2-NR_2); 5,79 ppm (4H, s, Ph-CH_2-N); 7,30-7,44 ppm (14 H, m, Ph-H + bimi-H); 7,44-7,52 ppm (2H, m, Ph-H + bimi-H); 7,55-7,63 ppm (2H, m, Ph-H + bimi-H). For the complete characterization see article [19]

Attempted synthesis of cluster $[CAu_6(di\text{-}NHC)_3]^{2+}$ (di-NHC = 1,3-di(N-isopropylimidazol-2-ylidene)propane



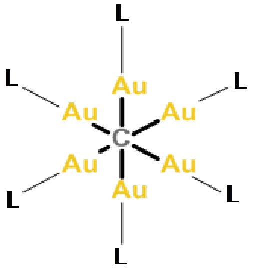
0,0199 g of complex M (0,0244 mmol) have been dissolved into 1 ml of DCM/MeOH 4:1 mixture into a vial, and a stirring bar has been dropped inside. 12 µL of hydrazine monohydrate (0,0123 g, 0,245 mmol) have been diluted into 4 ml of DCM into a second vial. 0,1573 g of 90% purity KOH (2,53 mmol) have been dissolved into 1 ml of MeOH into a third vial.

The solution of hydrazine has been added slowly to the complex solution, kept under stirring. Immediately the solution assumed a blue-gray colour and a black precipitate started forming. Then the KOH solution was added to the reaction mixture, and a yellow-orange colour started slowly forming. The reaction has been left stirring for 96 h, and 100 µL withdrawals were performed at 3, 24, 48 and 72 hours.

Each withdrawal and the reaction product have been subjected to the following work-up: the solution has been evaporated to dryness in a vial, then DCM has been added (0,5 ml for the withdrawals, 7 ml for the whole batch). The vial has been sonicated and the solution has been filtered using a siringe PTFE filter into another vial (10 ml round-bottom flask for the whole batch). The solution has then been evaporated, yielding an orange solid. Repeated two times, the second without withdrawals.

ESI-MS: 987,21 (theor: 987,20).

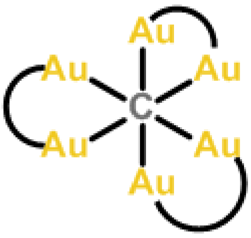
Synthesis of cluster $[CAu_6(NHC)_6]^{2+}$ *(NHC = N,N-dibenzylbenzimidazol-2-ylidene)*



The synthesis is totally analogous to the previous one, except for the quantities: 0,0198 g of complex G (0,0373 mmol), 19 µL of hydrazine monohydrate (0,389 mmol), 0,2372 g of KOH (90%, 3,81 mmol), DCM/MeOH 4:1 mixture (6 ml in total). Repeated a second time with doubled amounts of solvent/reagents.

ESI-MS: 1491,86 (theor: 1491,84)

Synthesis of cluster $[CAu_6(\text{di-NHC})_3]^{2+}$ *(di-NHC = 1,3-di(N-isopropylbenzimidazol-2-ylidene)propane*



The synthesis is totally analogous to the previous two, except for the quantities: 0,0398 g of complex L (0,044 mmol), 21 µL of hydrazine monohydrate (0,43 mmol), 0,3056 g of KOH (90%, 4,9 mmol), DCM/MeOH 4:1 mixture (12 ml in total). Repeated three times in total, the last two without withdrawals. Subsequently, after optimization, the reaction has been repeated two additional times doubling the amount of hydrazine (0,86 mmol, 42 µL).

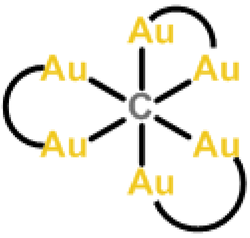
ESI-MS: from 1137,22 to 1137,37 in different spectra (theor: 1137,25).

The cluster has been purified by means of column chromatography using in order DCM/Acetone 8:1, DCM/MeOH 8:1 and pure MeOH in a gradient elution. A purification by means of multiple recrystallizations from DCM/Diethyl ether has been attempted on the last two syntheses.

^{1}H NMR: 1,75 ppm (36 H, d, $\mathit{CH_3}\mathrm{CH}\mathit{CH_3}$); 2,71 ppm (6H, qb, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$); 4,67 ppm (12H, tb, $\mathit{CH_2}\mathrm{CH_2}\mathit{CH_2}$); 5,44 ppm (6H, hb, $\mathrm{CH_3}\mathit{CH}\mathrm{CH_3}$); 7,34-7,68 ppm (24H, m, bimi-

H).

Attempted synthesis of cluster $[CAu_6(di\text{-}NHC)_3]^{2+}$ *(di-NHC = 1,3-di(N-benzylbenzimidazol-2-ylidene)propane*



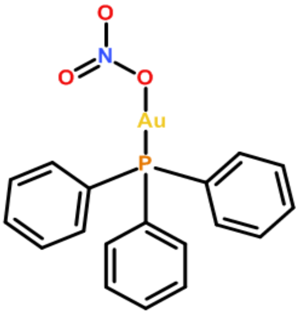
The synthesis is totally analogous to the previous three, except for the quantities: 0,0200 g of complex F (0,0198 mmol), 10 µL of hydrazine monohydrate (0,20 mmol), 0,1234 g of KOH (90%, 1,98 mmol), DCM/MeOH 4:1 mixture (6 ml in total).
ESI-MS: 1281,26 (theor: 1281,25).

Etching of $[CAu_6(di\text{-}NHC)_3]^{2+}$ *(di-NHC = 1,3-di(N-benzylbenzimidazol-2-ylidene)propane*

The crude product of the previous reaction has been dissolved in 6 ml of DCM/MeOH 4:1. 0,5 mL of concentrated HBr (48%, 1,49 g/ml) have been mixed with 0,63 ml of distilled water, and 0,5 ml of the resulting solution have been added to the cluster solution (around 100 equivalents of HBr with respect to the starting complex). The colour shifted overnight from orange to bright red. The dispersion has been extracted with water three times (20 ml), then dried using sodium sulfate and filtered. The resulting clear red solution has been dried under vacuum, yielding a red solid. A sample of the solid has been dissolved in DCM and analyzed via ESI-MS.
ESI-MS: 1667,52 (theor: 1667,52): $[Au_{13}(di\text{-}NHC)_5Br_2]^{3+}$; 2541,73 (theor: 2541,74): $[Au_{13}(di\text{-}NHC)_5Br_2]^{3+}Br^-$; 2680,17 (theor: 2680,18): $[Au_{13}(di\text{-}NHC)_5Br_2]^{3+}(AuBr_2)^-$; 2004,52 (theor: 2004,52): $[Au_{13}(di\text{-}NHC)_5Br_2]^{3+}\cdot[Au_2(di\text{-}NHC)Br_2]$; 1986,54 (theor 1986,54) : $[Au_{13}(di\text{-}NHC)_5Br_2]^{3+}\cdot[Au_2(di\text{-}NHC)(Br)(CN)]$.

Trials on a peculiar cluster: $[Au_9(PPh_3)_8](NO_3)_3$

Synthesis of Nitrate(triphenylphosphine)gold (I)



10,3 mg (0,06 mmol) of silver nitrate have been added to 0,3 ml of MeOH into a vial. The vial has been covered with aluminum foil to avoid photodecomposition. A stirring bar has been dropped inside and the solution has been left stirring for 45 minutes, until all the solid had dissolved. 30,0 mg (0,06 mmol) of $AuCl(PPh_3)$ have been added to a vial and dissolved in 3 ml of DCM. A stirring bar has been dropped inside. The vial has been covered with aluminum foil. The silver nitrate solution has been added to the complex solution using a pipette. Immediately a white-gray precipitate started to form. The solution has been left stirring for 1 hour, and then it has been filtered using a PTFE syringe filter (0,2 μm) into another vial. The volume of the solution was reduced to about 0,5 ml using the Schlenk apparatus and then 6 ml of hexane have been added to precipitate the product. The surnatant has been removed using a pipette and the solid has been dried using the Schlenk apparatus. Yield: 22,3 mg (71%); ^{1}H NMR: 7,60-7,48 ppm (Lett: 7,59-7,48 ppm).

The synthesis has been repeated three additional times using 60,0 mg (0,12 mmol) (1) and 210,1 mg (0,43 mmol) (2-3) of complex, 20,7 mg (0,12 mmol) (1) and 78,4 mg (0,46 mmol) (2-3) of silver nitrate, and scaling the solvents accordingly: 0,6 ml MeOH + 6 ml DCM (1) and 2,1 ml of MeOH + 21 ml of DCM (2-3). The amount of solvents used in the work-up procedure has been scaled as well. The syntheses 2 and 3 involved the use of a round-bottom flask as the reaction vessel. The slight excess of silver nitrate in the last two attempts proved very beneficial in terms of yield in larger scale.
Yields (1): 41,3 mg (65%) (2): 211,8 mg (96%) (3): 201,9 mg (91%).

Synthesis of cluster $[Au_9(PPh_3)_8](NO_3)_3$

211,8 mg of $Au(PPh_3)(NO_3)$ have been dissolved in 16 ml of EtOH (added using a syringe) under stirring granted by a stirring bar. A solution of $NaBH_4$ in ethanol has been prepared, dissolving 5,4 mg of $NaBH_4$ in 10 ml of EtOH. All this solution has been added slowly to the complex solution. The solution immediately turned bright orange and became darker as the addition progressed, giving black-orange colour at the end of the addition. The mixture has been left stirring for 2 hours. After that, the solution has been filtered using a syringe PTFE filter (0,2 μm) and transferred into a round-bottom flask. The starting vessel and the filter have been washed with 2 aliquants of 3 ml of EtOH. The ethanol has been removed using a rotary evaporator, and the orange-red solid has been redissolved in 10 ml of DCM. The solution has been filtered again with the same procedure, the flask and the filter washed with two aliquants of 3 ml of DCM. The solution has been transferred into a vial and the solvent has been removed using the Schlenk apparatus. The solid has been partially dissolved in 3 ml of THF, 15 ml of hexane have been added and then the solvent mixture has been discarded. This procedure has been repeated two additional times, yielding a green-brown powderous solid. The solid has been dried, dissolved in EtOH and crystallized two times using a layer of diethyl ether. The product is a green solid.

Yield: 121,3 mg (66%); ^{31}P NMR: δ=57,1 ppm (CD_3CN), (s), δ=56,8 ppm ($CDCl_3$) (s) .

^{1}H NMR: (CD_3CN):δ= 7,72-7,52 (m); 7,47-7,30 (m); 7,30-7,17 (m); 7,12-6,98 (t); intensity ratio: 4:1:2:1. MS analysis has been ruled out as a mean of identification because the cluster fragments and its molecular peak is not visible.

The synthesis has been repeated a second time using 201,9 mg of starting complex and scaling the quantities accordingly.

Yield: 105,4 mg (60%); ^{31}P NMR: δ=57,1 ppm (CD_3CN), (s).

Attempted reaction of $[Au_9(PPh_3)_8](NO_3)_3$ *with complex L*

25,0 mg of $[Au_9(PPh_3)_8](NO_3)_3$ have been dissolved together with 5,8 mg of complex L into 8 ml of DCM in a round bottom flask. A stirring bar has been dropped inside. The reaction has been left stirring for 96 hours and 100 µl withdrawals have been performed at 3, 24, 48, 72 and 96 hours. The solvent has been removed using a rotary evaporator and the solid stored in the fridge. ESI-MS analysis has been performed on the withdrawals. No peaks of interest have been detected, therefore the reaction has been discarded.

Reaction of $[Au_9(PPh_3)_8](NO_3)_3$ *with 1 eq. of complex* F_Cl_2

25,0 mg of $[Au_9(PPh_3)_8](NO_3)_3$ have been dissolved together with 5,4 mg of complex F_Cl_2 into 8 ml of DCM in a round bottom flask. A stirring bar has been dropped inside. The reaction has been left stirring for 96 hours and 100 µl withdrawals have been performed at 3, 24, 48, 72 and 96 hours. The solvent has been removed using a rotary evaporator and the solid stored in the fridge. ESI-MS analysis has been performed on the withdrawals, and allowed to determine that after 48 hours the substance present in the reaction mixture didn't evolve.

ESI-MS (48-96 h): 1267,22 $[Au_9(PPh_3)_6(\text{di-NHC})H_3]^{3+}$; 1202,84 $[Au_8(PPh_3)_6(\text{di-NHC})H_3]^{3+}$; 1180,19 $[Au_8(PPh_3)_4(\text{di-NHC})_2H_3]^{3+}$; 1821,74 $[Au_8(PPh_3)_6(\text{di-NHC})H_3Cl]^{2+}$; 1787,77 $[Au_8(PPh_3)_4(\text{di-NHC})_2H_3Cl]^{2+}$; 1690,19: $[Au_8(PPh_3)_5(\text{di-NHC})H_3Cl]^{2+}$; 1801,28: $[Au_8(PPh_3)_4(\text{di-NHC})_2H_3(NO_3)]^{2+}$;1821,74: $[Au_7(PPh_3)_5(\text{di-NHC})H_3]^{2+}$;1804,76: $[Au_8(PPh_3)_6(\text{di-NHC})H_4]^{2+}$; 3184,40: $[Au_7(PPh_3)_5(\text{di-NHC})H_3Cl]^{+}$; 3150,44: $[Au_7(PPh_3)_5(\text{di-NHC})H_4]^{+}$; 3211,42: $[Au_7(PPh_3)_5(\text{di-NHC})H_3(NO_3)]^{+}$; 1705,77: $[Au_7(PPh_3)_6(\text{di-NHC})H_3]^{2+}$; 1443,16: $[Au_7(PPh_3)_4(\text{di-NHC})H_3]^{2+}$; 1409,19: $[Au_8(PPh_3)_3(\text{di-NHC})]^{2+}$; 1540,72:

$[Au_8(PPh_3)_4(di\text{-}NHC)]^{2+}$; 1377,24: $[Au_6(PPh_3)_6]^{2+}$; 1246,19: $[Au_6(PPh_3)_5]^{2+}$

Two recrystallizations from DCM/Diethyl ether vapours have been performed, and each one has been followed by drying, ^{31}P NMR and ESI-MS analysis of both the solid and the precipitate obtained evaporating the solvent, after separation from the solid itself.
^{31}P NMR: (CD_3CN) 67,8-67,4 ppm (m); 67,0-66,2 ppm (m); 57,1 ppm: (s) $[Au_9(PPh_3)_8](NO_3)_3$; 55,2-54,0 ppm (m); 52,3-51,3 ppm (m); 44,0 ppm: (s) $[Au(PPh_3)_2]^+$.
ESI-MS: all precedent peaks + increase in intensity or creation of the following peaks: 2017,73: $[Au_{10}(PPh_3)_6(di\text{-}NHC)(Cl)H]^{2+}$; 1886,68: $[Au_{10}(PPh_3)_5(di\text{-}NHC)(Cl)H]^{2+}$; 1999,74: $[Au_{10}(PPh_3)_6(di\text{-}NHC)]^{2+}$; 1333,50: $[Au_{10}(PPh_3)_6(di\text{-}NHC)H]^{3+}$; 1344,80: $[Au_{10}(PPh_3)_6(di\text{-}NHC)Cl]^{3+}$; 1359,80: $[Au_{10}(PPh_3)_6(di\text{-}NHC)Br]^{3+}$(probably due to impurities in the apparatus); 2130,73: $[Au_{10}(PPh_3)_7(di\text{-}NHC)]^{2+}$

Reaction of $[Au_9(PPh_3)_8](NO_3)_3$ with 4 eq. of complex F_Cl$_2$

25,1 mg of $[Au_9(PPh_3)_8](NO_3)_3$ have been dissolved together with 21,7 mg of complex F_Cl$_2$ into 8 ml of DCM in a round bottom flask. A stirring bar has been dropped inside. The reaction has been left stirring for 96 hours and 100 μl withdrawals have been performed at 3, 24, 48, 72 and 96 hours. The solvent has been removed using a rotary evaporator and the solid has been dissolved into CD_3CN and subjected to ^{31}P NMR and ^1H NMR analysis.
^{31}P NMR: 33,1 ppm: $AuCl(PPh_3)$; ^1H NMR: 7,95-6,65 ppm (m); 6,65-6,33 ppm (m); 5,78 ppm (2H, d, N-CH_2-Ph); 5,67 ppm (2H, s, N-CH_2-Ph); 5,46 ppm (m); 4,99 ppm (4H, t, N-*CH_2*-CH_2); 4,75-4,49 (5H, m, N-*CH_2*-CH_2 + 1H); 3,30 ppm (d); 3,06 ppm (2H, q, CH_2-*CH_2*-CH_2); 2,84-2,64 ppm (2H, dq, CH_2-*CH_2*-CH_2).
After this the deuterated solvent has been removed and the solid crystallized using DCM/diethyl ether vapours; the obtained solid has been dried, redissolved in CD_3CN and subjected to the same analysis, giving no significant differences in the spectra.
The deuterated solvent has been removed and the solid dissolved in 0,5 ml of DCM/MeOH 9:1. Column chromatography has been performed using the same eluent mixture, giving five fractions, analyzed by means of ESI-MS. The fractions 2, 3 and 4 contained cluster species mixed with $AuCl(PPh_3)$, that in ESI conditions is converted to $[Au(PPh_3)_2]Cl$.
ESI-MS: 2411,73: $[Au_{13}(PPh_3)_3(di\text{-}NHC)_3(Cl)_3]^{2+}$;2377,25: $[Au_{13}(PPh_3)(di\text{-}NHC)_4(Cl)_3]^{2+}$; 2432,23: $[Au_{13}(PPh_3)_3(di\text{-}NHC)_3(Cl)_2(Br)]^{2+}$; 2399,76: $[Au_{13}(PPh_3)(di\text{-}NHC)_4(Cl)_2(Br)]^{2+}$; 2787,74: $[Au_{16}(di\text{-}NHC)_5(Cl)_4]^{2+}$; 2822,23: $[Au_{16}(PPh_3)_2(di\text{-}NHC)_4(Cl)_4]^{2+}$;

2844,20: $[Au_{16}(PPh_3)_2(di\text{-}NHC)_4(Cl)_3(Br)]^{2+}$; 2810,22: $[Au_{16}(di\text{-}NHC)_5(Cl)_3(Br)]^{2+}$

The first fraction contained mostly $[Au(PPh_3)_2]Cl$, derived from $AuCl(PPh_3)$:

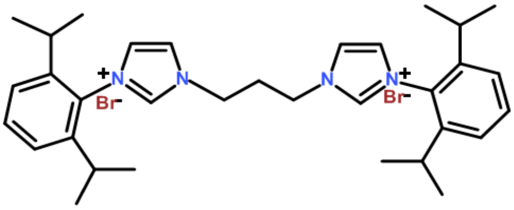
^{31}P NMR: 33,05 ppm (s) (CD_3CN): $AuCl(PPh_3)$; ESI-MS: m/z = 721,16: $[Au(PPh_3)_2]^{2+}$

The fifth fraction contained mostly $[Au(PPh_3)_2]Cl$, derived from fragmentation and complex $[Au_2(di\text{-}NHC)_2]^{2+}$:

ESI-MS: m/z = 721,16: $[Au(PPh_3)_2]^{2+}$; 653,20: $[Au_2(di\text{-}NHC)_2]^{2+}$; ^{31}P NMR: no signals.

Attempted synthesis of AuNCs protected by bulky di-NHC ligands

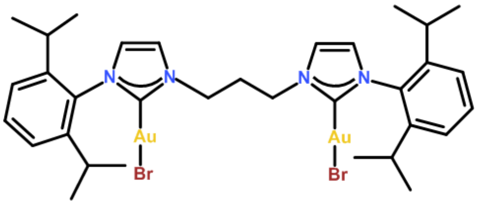
Synthesis of 1,1'-di(2,6-diisopropylphenyl)-3,3'-propylene-di-(imidazolium)bis-(bromide)



0,5031 g of 1-(2,6-diisopropylphenyl)imidazole (2,20 mmol) have been added into a pressure tube together with 0,11 ml (0,218 g, 1,08 mmol) of 1,3-dibromopropane. The cap has been screwed on top and the mixture has been heated up to 135°C for 5 hours. A brown solid precipitated and the whole reaction mixture (wet solid) has been dissolved in the smallest possible quantity of DCM. The solution has been transferred into a round-bottom flask and diethyl ether has been added to precipitate the product, a sand-like solid. The ether has been removed, and the solid dried using the rotary evaporator.

Yield: 0,5043 g (71%). ^{1}H NMR ($CDCl_3$): 1,17 ppm (d, 12H, CH_3-CH-*CH_3*); 1,24 ppm (d, 12H, *CH_3*-CH-CH_3); 2,30 ppm (h, 4H, CH_3-*CH*-CH_3); 3,26 ppm (q, 2H, CH_2-*CH_2*-CH_2); 4,99 ppm (t, 4H, *CH_2*-CH_2-*CH_2*); 7,18 ppm (s, 2H, N*CH*); 7,34 ppm (m, 4H, Ph-H); 7,57 ppm (t, 2H, Ph-H); 8,62 ppm (s, 2H, N-*CH*); 9,92 ppm (s, 2H, NR_2-*CH*-NR_2). For complete characterization, see article [83].

Synthesis of complex C



100,0 mg (0,152 mmol) of 1,1'-di(2,6-diisopropylphenyl)-3,3'-propylene-di-(imidazolium)bis-(bromide) have been added, together with 89,4 mg (0,304 mmol) of $AuCl(SMe_2)$, 66,0 mg of LiBr and 462,3 mg of K_2CO_3 in a three necks round-bottom flask. The flask has been closed with two silicon plugs and a vacuum tap; three Ar-vacuum cycles have been performed on the content of the apparatus, and then 15 ml of dry acetonitrile have been added using a 20 ml syringe. The reaction has been heated up to 60°C and has been left stirring for 16 hours. The mixture has been vacuum-filtered on a gooch funnel and the solid has been washed with three aliquants of 2 ml of acetonitrile. The filtrate has been transferred into a round-bottom flask and has been dried using the rotary evaporator. The obtained light-brown solid has been dissolved in DCM and precipitated using Hexane, yielding a green-brown oily solid. The oily solid has been dried under vacuum until it became a powderous green-brown solid.

Yield: 107, 8 mg (68%); ^{1}H NMR ($CDCl_3$): 1,13 ppm (d, 12H, CH_3-CH-*CH_3*); 1,28 ppm (d, 12H, *CH_3*-CH-CH_3); 2,41 ppm (h, 4H, CH_3-*CH*-CH_3); 2,72 ppm (q, 2H, CH_2-*CH_2*-CH_2); 4,43 ppm (t, 4H, *CH_2*-CH_2-*CH_2*); 7,02 ppm (d, 2H, N-*CH*); 7,25 ppm (d, 4H, Ph-H)*; 7,36 ppm (d, 2H, N-*CH*); 7,47 ppm (t, 2H, Ph-H). For complete characterization see article [68].

*partially covered by the solvent residual signal

Attempted synthesis of complex C_(OTs)$_2$

20,2 mg (0,019 mmol) of complex C have been dissolved into 2 ml of dry DCM in a vial, giving a brown solution; the vial has been covered with aluminum foil, and under stirring, exactly 10,6 mg of Ag(OTs) have been added. A gray solid precipitates out immediately, and the solution turns orange. The reaction has been left stirring for 1 hour, and then the mixture has been filtered using a 0,2 μm syringe filter into another vial. The solvent has been removed using the Schlenk apparatus until the volume was about 0,2 ml, and then the solution has been transferred into 5 ml of hexane. A brown solid should precipitate.

The reaction has been repeated three times, two as indicated and the other scaling up all quantities by three times. Only in one case the solid precipitated, while in the others a brown oil formed and slowly decomposed to give a black precipitate. ^{1}H NMR however shows the presence of more than one species, one is probably dicationic complex.

Yields: 50,2 mg (74%, from 60,6 mg, impure oil) ; 11,2 mg (50%, from 20,2 mg, impure solid); N/A. (decomposition).

Reduction of complex C_(OTs)$_2$

2,5 mg of complex C_(OTs)$_2$ have been dissolved in 4 ml of DCM in a vial. A stirring bar has been dropped inside. 4,1 mg of $NaBH_4$ have been added into 4 ml of ethanol in a second vial, and one ml of the resulting solution has been added dropwise to the complex's solution. The reaction has been left stirring for 48 hours, and withdrawals have been carried out at 3, 24 and 48 hours. The withdrawals have been dried, dissolved in DCM and subjected to ESI-MS analysis.

ESI-MS: 693,32: $[Au_2(\text{di-NHC})_2]^{2+}$; 792,39: $[Au_3(\text{di-NHC})_2(H)]^{2+}$; 1343,09: [$Au_6$(di-

NHC)$_3$(BH$_3$)]$^{2+}$ (very low amount); 804,89: [Au$_3$(di-NHC)$_2$(BH$_3$)$_2$]$^{2+}$.

Reduction of complex C

about 5 mg of complex C have been suspended in 2 ml of ethanol in a vial. A stirring bar has been dropped inside. About 10-12 mg of NaBH$_4$ have been added, and the dispersion turned into a brown clear solution. The reaction has been left stirring for 48 hours, and withdrawals have been carried out at 3, 24 and 48 hours. The withdrawals have been dried, dissolved in DCM and subjected to ESI-MS analysis.

ESI-MS: no peaks have been identified

Chapter 10: References

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