Mononuclear Coinage Metals Complexes with Pyrazoles and Imidazoles. Syntheses, Characterizations and Catalytic Applications on MW Peroxidative Oxidation of Alkane catalyzed by [3,5-Dinitropyrazolyl-copper-triphenylphosphane]$_2$

Serena Passarelli

Thesis to obtain the Master of Science Degree in
Chemistry

Supervisors

Prof^a. Maria de Fátima Guedes da Silva

Prof.^{a} Rossana Galassi

Prof^a. Camille Simon Oumarou

Examination Committee

Chairperson: Prof^a. Maria Matilde Soares Duarte Marques

Supervisor: Prof^a. Maria de Fátima Guedes da Silva

Members of the Committee: Doctor Luísa Martins

Doctor Corrado Bacchiocchi

April 2017

Abstract

In this chemistry project many aspects of the chemistry of pyrazoles and imidazoles with coinage metals have been evaluated.

As concerns metallocycles chemistry, the synthesis of trinuclear cyclic silver derivatives with 1-benzylimidazolate as bridging ligand has been obtained (compound **1)**. The successful synthesis of this compound represents an actual achievement as the analogous gold compound has been obtained more than 30 years ago. Compound **1** was characterized by the means of spectroscopic techniques and the X-ray crystal structure determination was performed. The structure showed the formation of a nine-membered cycle, $C_3Ag_3N_3$ that crystallizes in the triclinic space adopting a packing in the crystal unit consisting of a dimer of trimers, joined by intermolecular Ag-Ag bonds with distances of 3.49 and 3.50 Å. Reactions with benzoyl and benzyl chlorides have been performed to investigate the chemical properties of this compound. The reactions did not lead to the formation of the corresponding mononuclear silver carbene derivative, as already observed in the case of the gold analogue.

To understand the reason why these reactions failed, the stability of the silver carbene has been analyzed. Compound [1,3-dibenzyl-imidazolyl-2-yl-silver chloride]$_2$ (compound **3**) was synthesized by reaction of the imidazolium salt (**2**) with Ag_2O. This compound showed a very high stability and the X-ray crystal structure was obtained. This evidence supports our thesis: in the case of the gold(I) derivative, the addition of acyl or alkyl halides leads to an oxidative addition to the gold centers and a consequent reductive elimination with formation of the mononuclear gold(I) carbene derivatives. As for the trinuclear cyclic silver derivatives, their reaction with benzyl and benzoyl chlorides was unsuccessful. The synthesis of mononuclear silver(I) carbene derivatives was also performed with 1,3-dibenzyl-benzoimidazolium chloride (compound **5** and **6**, the corresponding carbene), while the 1,3-dibenzoyl-imidazol-2-yl-silver carbene (compound **8**) was likely formed, but additional efforts in the purification should be made.

The synthesis of mononuclear or trinuclear cyclic coinage metal derivatives with azoles having electron withdrawing groups in their cycles is another aspect studied herein. When pyrazoles contained CF_3 groups in the 3,5 positions, cyclic trinuclear derivatives were obtained with Cu(I), Ag(I) and Au(I). Many attempts were previously performed with the 3,5 dinitropyrazolate analogues with silver, gold and copper. As for trinuclear cyclic derivatives, only the silver compound was obtained while the gold and copper analogues were isolated only by adding PPh_3 as co-ligand. Many synthetic methods were approached and the mononuclear 3,5-[bis(dinitro)pyrazolate Cu(I)triphenylphosphane] (compound **9**), 3,5-[bis(dinitro)pyrazolate Cu(I)triphenylphosphane] (compound **10**), [bis(trifluoromethyl)pyrazolate Cu(I)triphenylphosphane] (compound **11**), and 3,5-[bis(trifluoromethyl)pyrazolate Ag(I)triphenylphosphane] (compound **12**) derivatives were isolated. The X-ray crystal structure determination of compound **9** showed its dinuclear nature, with the two copper centers bridged through the two nitrogen atoms of the pyrazoles in a six membered cycle having a boat conformation. The three-coordination of the copper was then achieved by the PPh_3 ligands, bound to the two Cu(I) atoms showing a paddle like configuration.

Two complexes, [Cu_2(μ-N,N-3,5-$(NO_2)_2$pz)$_2$(PPh_3)$_2$], compound **9**, and the analogous metallocycle with Cu(II) metal centers, [trans-Cu_6(μ-OH)$_6$(μ-3,5-$(CF_3)_2$pz)$_6$], despite the structural differences, were

successfully tested as catalysts on the microwave-assisted neat oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone through a likely radical mechanism, affording considerably high yields (up to 58%) in rather short reaction times (30 min, for$[Cu_2(\mu\text{-}N,N\text{-}3,5\text{-}(NO_2)_2pz)_2(PPh_3)_2]$. The presented catalytic procedure leads to significantly higher yields of cyclohexanol and cyclohexanone than those reported (although for considerably different conditions) for copper complexes with related ligands, such as the C-scorpionate Cu(II) complex $[CuCl_2(TpmOH)_2]$ (TpmOH = 2,2,2-tris(pyrazol-1-yl)ethanol), 7%; copper coordination polymers with pyrazolato-based tectons, 11%, or based on trinuclear triangular $[Cu_3(\mu^3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$ units, 36%. This catalytic protocol (TBHP/MW) is very fast, solvent-free and uses a green energy source.

Resumo

Neste projeto foram avaliados vários aspetos da química de pirazoles e imidazoles com metais de cunhagem.

No que toca à química de metalociclos, conseguiu-se a síntese de derivados de prata trinucleares com 1-benzimidazolato como ligando em ponte (composto **1)**. A síntese bem sucedida deste composto é um resultado inovador, já que apenas tinha sido reportado o composto análogo de ouro, há mais de 30 anos. O composto **1** foi caraterizado por técnicas espetroscópicas e cristalografia de raios-X. Demonstrou-se que a sua estrutura consiste num ciclo de 9 membros, $C_3Ag_3N_3$, que cristaliza no sistema triclínico adotando um empacotamento correspondente a um dímero de trímeros, conetados por ligações Ag-Ag intermoleculares com distâncias de 3.49 e 3.50 Å. Foram efetuadas reações com cloreto de benzoílo e de benzilo para investigar as propriedades químicas do composto. Estas reações não conduziram à formação do carbeno mononuclear correspondente, anteriormente observado para o composto de ouro análogo.

Para compreender as razões deste insucesso foi analisada a estabilidade do carbeno de prata. Sintetizou-se o [1,3-dibenzil-imidazolil-2-yl-Ag Cl]$_2$ (composto **3**) por reação do sal de imidazólio (**2**) com Ag_2O. Este composto, para o qual foi obtida a estrutura de raios-X, demonstrou uma estabilidade elevada. As evidências obtidas são consistentes com a interpretação de que no caso do derivado de ouro(I) a reação com halogenetos de acilo ou alquilo envolve adição oxidativa aos centros de ouro e eliminação redutiva subsequente, com formação dos derivados carbeno mononucleares de ouro(I). Quanto aos derivados cíclicos trinucleares de prata, as reações com os cloretos de benzilo e benzoílo não foram bem sucedidas. Foi também efetuada a síntese de derivados carbeno mononucleares de prata(I) com cloreto de 1,3-dibenzil-benzoimidazólio (composto **5**, sendo **6** o carbeno correspondente). Quanto ao carbeno de 1,3-dibenzoil-imidazol-2-il-prata (composto **8**) aparenta ter sido formado mas são necessários esforços adicionais de purificação.

A síntese de derivados cíclicos mono- ou trinucleares de metais de cunhagem com azoles contendo grupos eletroatratores foi outro aspeto abordado nesta tese. Foram obtidos derivados cíclicos trinucleares de Cu(I), Ag(I) e Au(I) com pirazoles contendo grupos CF_3 nas posições 3,5. Foram anteriormente feitas muitas tentativas com análogos do 3,5-dinitropirazolato e prata, ouro e cobre. No que toca a derivados cíclicos trinucleares, apenas foi obtido o composto de prata, enquanto os compostos análogos de ouro e cobre foram isolados apenas quando se usou PPh_3 como co-ligando. Foram testados vários métodos sintéticos, tendo-se isolado os compostos mononucleares 3,5-[bis(dinitro)pirazolato Cu(I)trifenilfosfano] (composto **9**), 3,5-[bis(dinitro)pirazolato Cu(I)trifenilfosfano] (composto **10**), -[bis(trifluorometil)pirazolato Cu(I)trifenilfosfano] (composto **11**) e 3,5-[bis(trifluorometil)pirazolato Ag(I)trifenilfosfano] (composto **12**). Contudo, a determinação da estrutura cristalina de raios-X do composto **9** demonstrou a natureza dinuclear do composto, com os dois centros de cobre ligados em ponte por dois azotos de pirazoles num ciclo de seis membros com uma conformação em barco. A coordenação do cobre é completada pelos ligandos PPh_3, ligados aos dois cobres numa configuração de tipo prancha.

Apesar das diferenças estruturais, o composto **9**, [Cu_2(μ-N,N-3,5-$(NO_2)_2$pz)$_2$(PPh_3)$_2$], e o seu análogo com centros metálicos Cu(II), [trans-Cu_6(μ-OH)$_6$(μ-3,5-$(CF_3)_2$pz)$_6$], foram testados com sucesso como

catalisadores na oxidação *neat*, assistida por micro-ondas, de ciclo-hexano a uma mistura de ciclo-hexanol e ciclo-hexanona por um mecanismo provavelmente radicalar, que ocorreu com rendimentos razoavelmente elevados (até 58%) em tempos de reação bastante curtos (30 min para o $[Cu_2(\mu\text{-}N,N\text{-}3,5\text{-}(NO_2)_2pz)_2(PPh_3)_2]$. O processo catalítico em questão conduz a rendimentos significativamente superiores aos reportados (embora em condições bastante diferentes) para complexos de cobre com ligandos relacionados com os aqui testados, como por exemplo o complexo C-escorpionato de Cu(II) $[CuCl_2(TpmOH)_2]$ (TpmOH = 2,2,2-tris(pirazol-1-il)etanol), 7%; polímeros de coordenação de cobre com tectões de base pirazolato, 11% ou baseados em unidades trinucleares triangulares $[Cu_3(\mu^3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$, 36%. Este protocolo catalítico (TBHP/MW) é muito rápido, não utiliza solventes e recorre a uma fonte de energia verde.

ACKNOWLEDGMENTS

I would like to thank all the people who have contributed to the development of this master thesis.

- First of all my supervisor Dr.ssa Rossana Galassi, my co-supervisor Dr. Camille Simon Oumarou and Dr.ssa Anna Teresa Ramadori.

- Prof. Martins A.N.C. and Prof. Pombeiro A.J.L of Instituto Superior Técnico of Lisbon, Portugal who performed the preliminary studies on the catalytic activity of compound 9 and [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$.

- Prof.ssa Claudia Graiff of University of Parma, Italy, for the crystallographic characterization of compound **3** and **4**.

Sommario

Index of Figures

Index of Schemes

1. INTRODUCTION

1.2 Metallacycles chemistry.

The interest in coordination chemistry has impressively increased in the last decades. The synthesis, the characterization and the study of specific properties of a great variety of complexes, composed by organic molecules called ligands bonded to metals, have been focused by many laboratories for their potential applicability in a large quantity of fields.[1] One of these research lines in progressively expansion is the family of the metallacycles containing pyrazole and imidazole as bridging ligands.[2] The coinage metals cycles belong to this last class of complexes and they are widely studied for their interesting properties, their structures and their potential applications.[3]

Here the most important examples of copper, silver or gold metallacycles with the above quoted bridging ligands possessing nuclearity from three to eight will be discussed.

The pyrazole heterocycles are considered to be versatile ligands that can interact with the coinage metals in several fashion[4]: neutral monodentate (**A**), anionic monodentate (**B**) or exo/endo (η^2) bidentate (**C** / **D**) (Figure1.1).

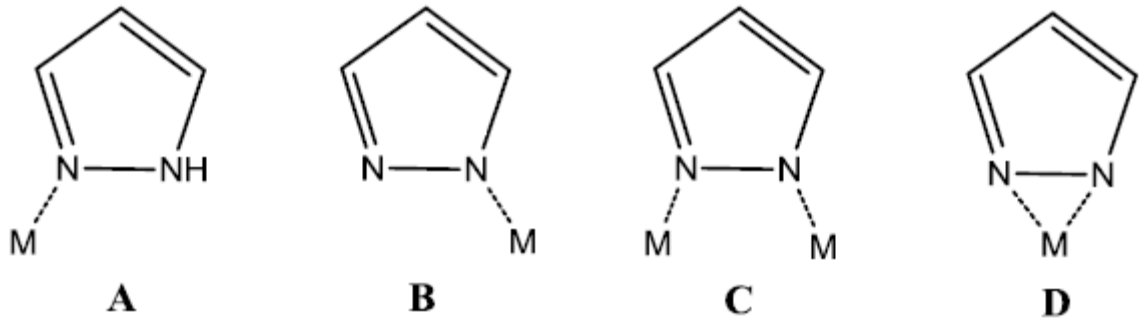


Figure 1.1. *Common coordination modes of the pyrazolyl ligand and the corresponding anionic ligand.*

In the bidentate mode, after deprotonation of the N-H group, pyrazoles are optimal bridging ligands to form metallacycles with different nuclearity such as: dimers, trimers, tetramers, hexamers, etc; (Figure 1.2) depending by the substituents on the ligand and their overall steric hindrance. Substituents at 3- and 5- position modify the steric properties, whereas substituents at the 4-position can mainly influence the electronic properties. Polymers can be also obtained and examples with the coinage metals are reported in literature.[5]

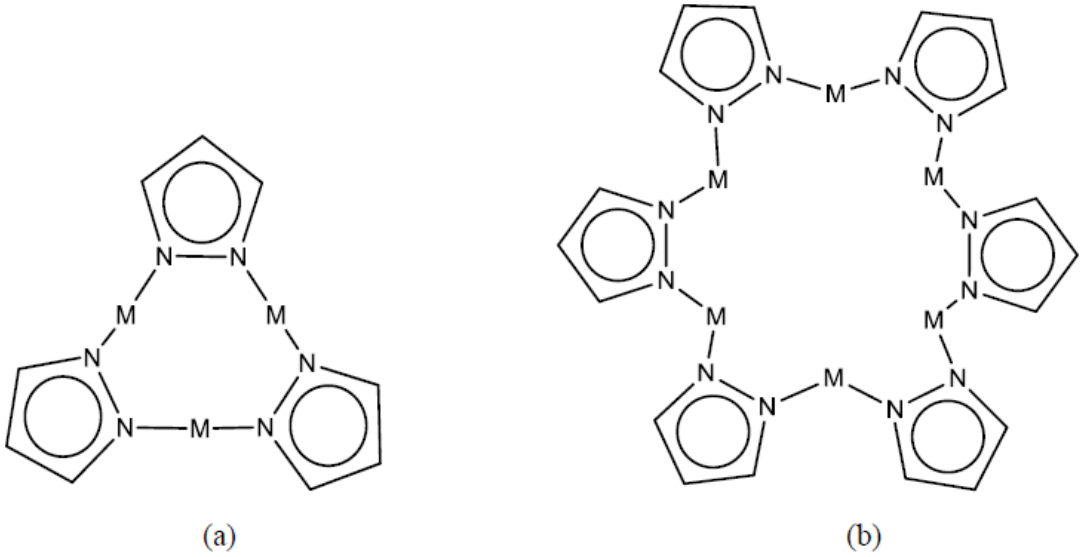


Figure 1.2. *Two framework of pyrazolate metallacycles: trinuclear (a) and hexanuclear (b) metallacycles.*

The imidazole is an aromatic heterocycle sterically and electronically comparable with the pyrazole. In the anionic form imidazole can act as a mondentate ligand to give mononuclear complexes[6], while in the exo-bidentate coordination it can forms polymers[7] or metallacycles.[8] Both type of exo-bidentate coordinations are possible as shown in figure 1.3, involving N,N' or N,C metal binding: the latter is typical in N-substituted imidazoles after deprotonation of the C^2 with a strong base.

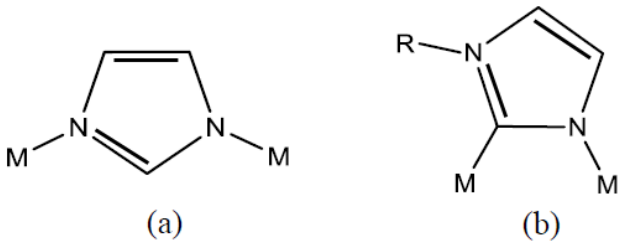


Figure 1.3. *Possible exo-bidendate coordination modes of the imidazolates: (a) N,N' and (b) N,C.*

1.2.1 Trinuclear Copper Complexes.

Trinuclear Cu(I) pyrazolate metallacycles show essentially planar nine-membered M_3N_6 cycle with mild deviations from the planarity, except the trimeric complex $[Cu(\mu\text{-}3,5\text{-}(Ph)_2pz)]_3$ showing a twisted ring with significant deviations from the planarity.[9] These derivatives show intra- and inter-molecular Cu---Cu interactions. In fact, in the crystal lattice trimers can be paired through crystallographic inversion centres with two Cu atoms of a M_3N_6 metallacycle being positioned close to two Cu atoms of the second trimer unit.

Copper(II) ions can also form trinuclear cyclic derivatives but in this case mono- or bi-capped complexes are obtained. The spontaneous self-assembly of $[Cu^{II}(\mu\text{-}4\text{-}R\text{-}pz)]_3$ cycle cores occurs only when unsubstituted pyrazole or 4-substituted pyrazoles (4-R-pzH; R = H, Cl, Br, I, Me, NO_2) are employed, while 3-, 3,5- and 3,4,5-substituted ones favor the synthesis of mononuclear or dinuclear copper(II) species.[10b,11] The X-ray crystal structure determinations of trimer copper(II)pyrazolate complexes always shows the presence of a corrugate nine-membered $[Cu\text{-}N\text{-}N]_3$ framework where the metallacycle can be mono- or bi-capped (Figure 1.4). In the mono-capped structures the Cu atom shows an approximate square-planar geometry, each metal centre is coordinated by two pyrazolato rings, a terminal L ligand (usually Cl or Br) and a μ_3-X bridging anion (X = O^{2-}; HO^-). In the bi-capped structures the Cu atom have a distorted trigonal bypiramidal geometry, each metal centre is coordinated by two pyrazolato rings, a terminal L ligand (Cl or Br) and two μ_3-X bridging anions.

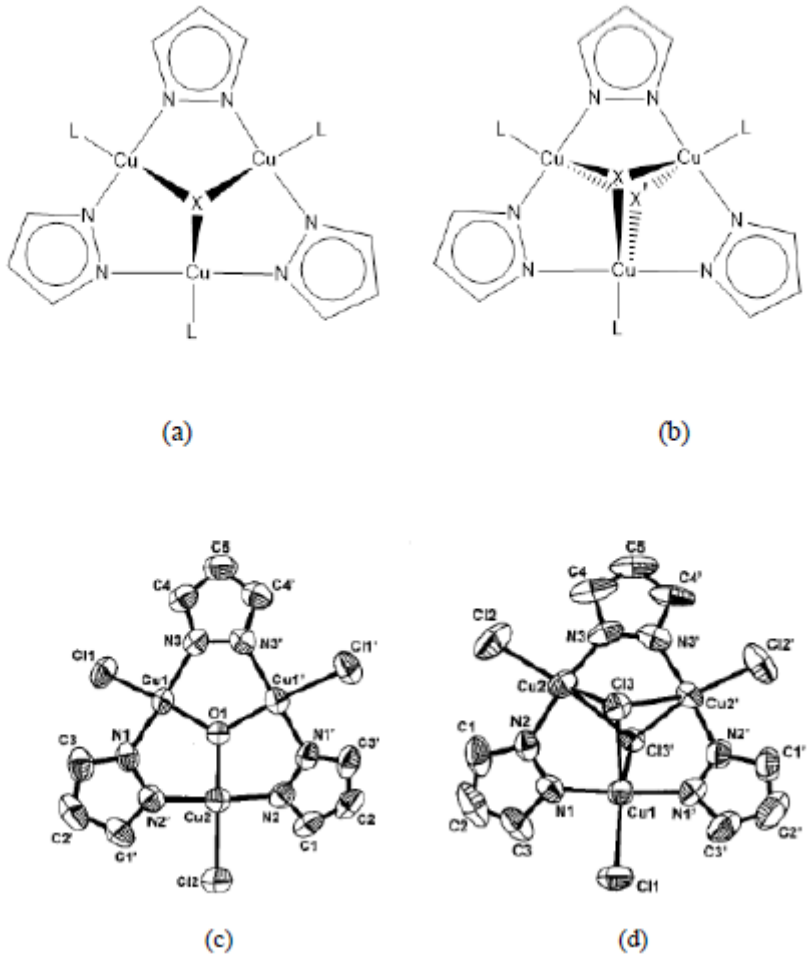


Figure 1.4: *Top: Possible structures of the copper(II) trinuclear metallacycles: (a) mono-capped and (b) bi-capped. Bottom: ORTEP plots of the trinuclear complexes* $[Cu_3(\mu_3\text{-}O)(\mu\text{-}pz)_3Cl_3]$ *(c) and* $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}pz)_3Cl_3]$ *(d) highlighting the two possible structures (a) and (b).*

1.2.3 Trinuclear silver complexes.

The trinuclear metallacycles are the most important and the first example, structurally characterized by power diffraction, is the complex $[Ag(\mu\text{-}pz)]_3$.[5a]

The X-ray data of the all silver metallacycles reported above show a trinuclear cyclic structure with essentially planar nine-membered Ag_3N_6 cycles and very often these derivates show intra and inter-molecular Ag---Ag interactions. An example can be the complex $[Ag(\mu\text{-}3\text{-}(CF_3),5\text{-}(CH_3)pz)]_3$. In its crystal packing neighboring pairs of these trinuclear units are linked by two equal and relatively short Ag---Ag contacts (3.3553 Å) across a crystallographic inversion center. The dimer of trimers interacts further with their neighbors via additional Ag---Ag links (3.4263 Å), forming extended stepladder-shaped columns (Figure 1.5).

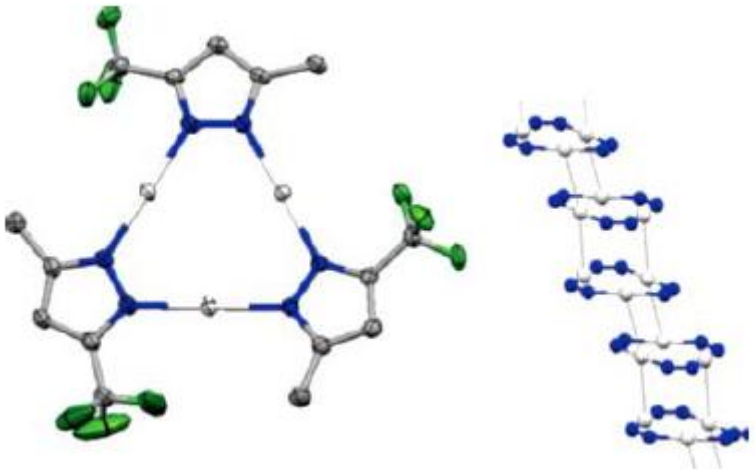


Figure 1.5. *Molecular structure of $[Ag(\mu\text{-}3\text{-}(CF_3),5\text{-}(CH_3)pz)]_3$ (hydrogen atoms have been omitted for clarity) and the extended chains of $[Ag(\mu\text{-}3\text{-}(CF_3),5\text{-}(CH_3)pz)]_3$ formed via Ag---Ag contacts (all except nitrogen and silver atoms have been omitted for clarity).*

Unlike the copper metallacycles, it is interesting to note that the presence of two bulky substituents on the pyrazolyl ring, such as in the complex $[Ag(3\text{-}(C_3F_7),5\text{-}(^t\text{Bu})pz)]_3$ gives the typical trinuclear unit (Figure 1.6). These trinuclear units pack in a staggered fashion (i.e., with a lateral slippage), forming zig-zag chains that do not feature any intertrimer Ag---Ag contacts (the closest separation is at 5.376 Å). The nine-membered Ag_3N_6 metallacycle in $[Ag(\mu\text{-}3\text{-}(C_3F_7),5\text{-}(^t\text{Bu})pz)]_3$ shows also a significant deviation from planarity and it appears that this ring twisting is caused primarily by the intertrimer steric interactions of the two large substituents.

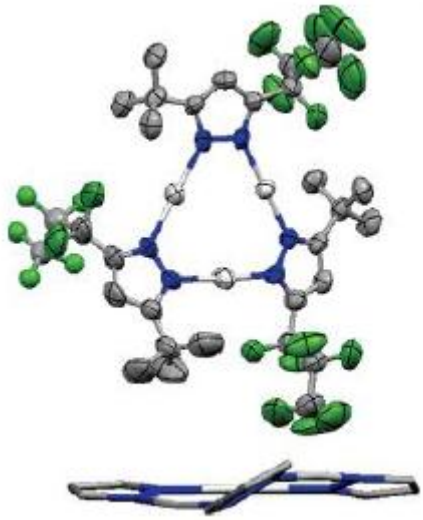


Figure 1.6. *Molecular structure of [Ag(μ-3-(C_3F_7),5-(^{t}Bu)pz)]$_3$ (hydrogen atoms have been omitted for clarity) and a side view showing the twisted Ag_3N_6 core (pyrazolyl ring substituents have been omitted for clarity).*

As concerns the trinuclear silver metallacycles with the imidazolates as bridging ligands, an example was reported by Burini et al. in 1989. The synthetic method to obtain the complex [Ag(μ-C,N-1-benzyl-imidazolate)]$_3$ consists in the reaction between Me_2SAgNO_3 and the 1-benzyl-2-lithium-imidazolate, after deprotonation of the C^2 in the corresponding 1-benzyl-imidazole with an alkyl lithium.[8b]

1.2.4 Trinuclear gold complexes.

Trimeric pyrazolate gold(I) metallacycles are well known and they have the general formula [Au(μ-pz)]$_3$ (pz=pyrazolate or variously substituted pyrazolates).

Trinuclear nine-membered rings formed by gold(I) ions with exobidentate monoanionic ligands, are generally slightly irregular and puckered unless the metallacycle is imposed by intramolecular crystallographic symmetry. Gold-gold intramolecular interactions are always present and the complexes exhibit a roughly D_{3h} symmetry. Crystal structures of these trinuclear complexes show individual complexes, dimers, supramolecular columnar packing or more complex supramolecular aggregates. Dimers and supramolecular structures are held together by aurophilic intermolecular gold-gold interactions. Bulky substituents on the ligands can prevent intermolecular metal-metal interactions or the formation of supramolecular architectures.

The molecular structure of [Au(μ-3,5-(CF_3)$_2$pz)]$_3$ was reported by Bonati et al. and it was the first trinuclear gold(I) metallacycle with a N-Au-N environment, structurally characterized[12] (Figure 1.7). The nine-membered ring is rather irregular and non-planar, with the Au-N average distance of 1.93(1)A˚. Among the three coinage metal complexes with the same ligand, metal–nitrogen distances are longest in the silver and shortest in the copper system. These M–N bond length values agree with the trend expected based on covalent radii of the coinage metals. The long intermolecular Au---Au

distance of 3.998(2)Å rules out any interaction between the trinuclear units due to the bulky substituents on the pyrazolate rings.

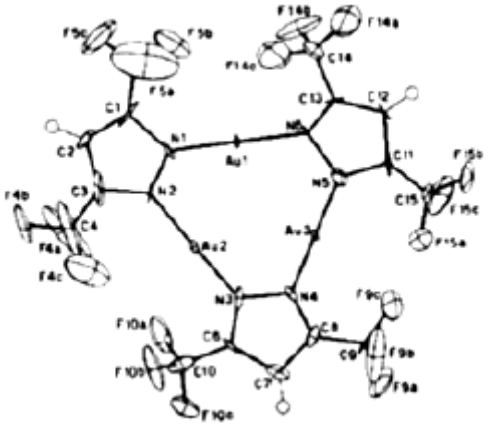


Figure 1.7. *View down c axis of the molecular structure of complex [μ-N,N-3,5-$(CF_3)_2$pzAu]$_3$.*

A similar structure to [Au(μ-3,5-$(CF_3)_2$pz)]$_3$ has been found for complex [Au(μ-3,5-$(Ph)_2$pz)]$_3$ with phenyl substituents on the pyrazolate rings.[13] The nine-membered ring is regular and planar with long Au---Au distances >7.567Å that exclude any intermolecular interaction.

Some trinuclear gold pyrazolates have been described to produce room-temperature columnar mesophases.[14] These complexes have long chain substituents in the 3,5 positions of the pyrazolate ring. X-ray powder diffraction measurements have demonstrated that the supramolecular columnar arrangement is present in the crystalline solids as well as in the mesomorphic phase. The X-ray crystal structure of complex [Au(μ-3,5-(4-MeOPh)$_2$pz)]$_3$, which has an anisole unit on the pyrazolates, yields a unit cell that contains two independent trinuclear units. They are slightly different in the twist about the central metallacycle core and more markedly in the relative conformations of the phenyl substitutents.[15]

A more complex supramolecular architecture has been discovered for the complexes [Au(μ-pz)]$_3$, and [Au(μ-4-(Me)pz)]$_3$.[45]

The molecular structure of [Au(μ-pz)]$_3$ consists of the usual nine-membered ring with Au-N distances and N-Au-N angles in the range of 1.992(6)-2.014(6)Å and 176.9(3)°-178.9(3)°, respectively. Intramolecular aurophilic gold-gold interactions are present with Au···Au distances 3.372(1)-3.401(1)Å. This complex forms a two-dimensional network by self-assembly of the trinuclear metallacycles through intermolecular aurophilic interactions. Each [Au(μ-pz)]$_3$ forms a dimer such as those found in other cyclic trinuclear complexes, with two gold-gold interactions. Moreover, each dimer interacts with four other dimers through single Au---Au contacts to form a net (Figure 1.8).

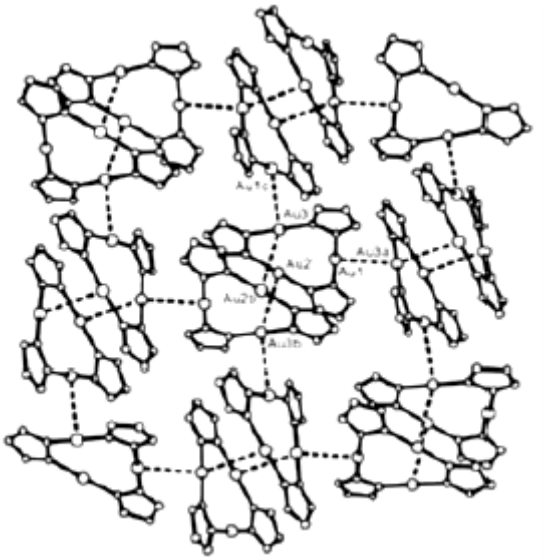


Figure 1.8. *Two-dimensional structure of $[Au(\mu\text{-}pz)]_3$, intermolecular Au···Au interactions of less than 3.6 Å are shown as broken lines.*

In figure 1.9 it is reported the intricate supramolecular network formed by complex $[Au(\mu\text{-}4\text{-}Me\text{-}pz)]_3$. The sixteen cyclic trinuclear complex aggregate is generated by an inversion center located at the center of the Au10-Au11-Au10a-Au11a parallelogram forming a chain of trinuclear metallacycles with side arms. The bond distances, the angles and the gold-gold interactions are consistent with those of $[Au(\mu\text{-}pz)]_3$ and other gold pyrazolate trimers.

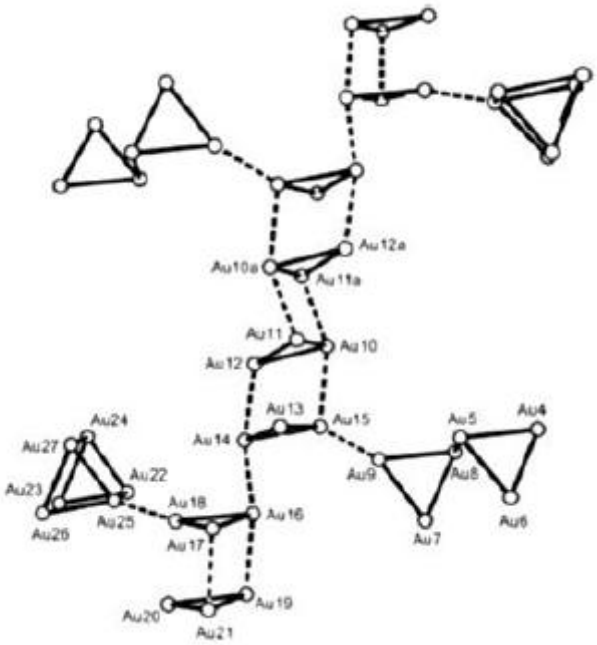
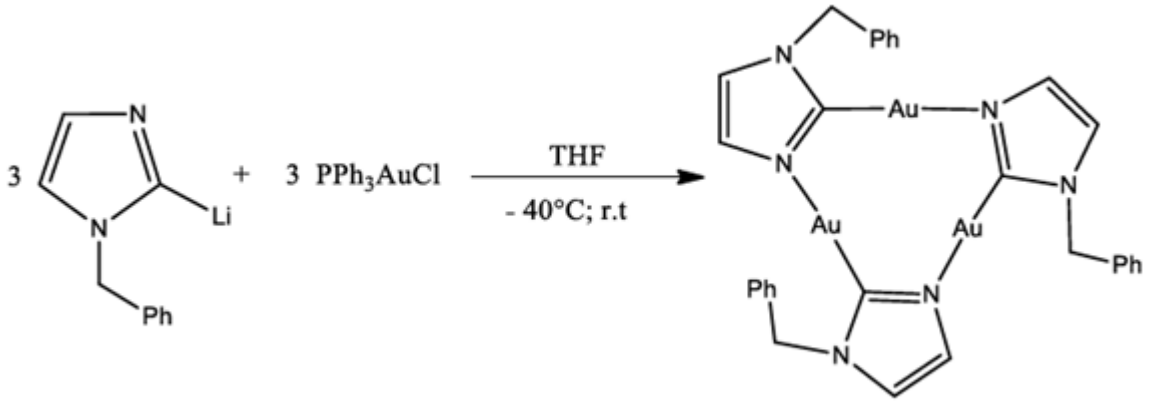


Figure 1.9. *View of the self-association of sixteen trimers in $[Au(\mu\text{-}4\text{-}(Me)pz)]_3$. C, N atoms are omitted for clarity. Intramolecular Au---Au contacts are shown as solid lines, intermolecular Au···Au interactions of less than 3.6 Å are shown as broken lines.*

A family of trinuclear gold(I) complexes, having a C-Au-N environment, was described in which the bridging ligand between gold atoms is an alkyl-2-imidazolate anion (alkyl group = CH_3 or CH_2Ph).[8b] A typical reaction is carried out at -40°C in THF solution using Vaughan's method[16] (Scheme 1.1), but in this case the crude brown solid was extracted overnight at room temperature with hexane.



Scheme 1.1

Recently the crystal structure of [Au(μ-N^3,C^2-bzim)]$_3$ has been reported[8c] and it shows the presence of dimer of trimer units. The complex adopts a semi-prismatic conformation with one long (3.558 Å) and two short (3.346 Å) intertrimer aurophilic distances (Figure 1.10) .

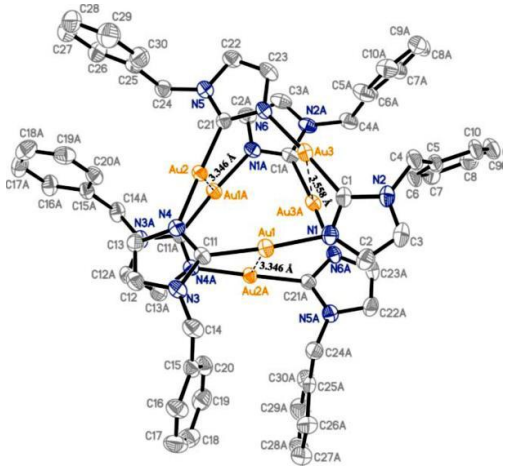


Figure 1.10. *Crystal structure of [Au(μ-N^3,C^2-bzim)]$_3$ showing a dimer-of-trimer repeat unit.*

1.3 Oxidative addition to polynuclear Gold(I) compounds.

Trimeric pyrazolate and imidazolate gold(I) complexes can undergo oxidative-addition reactions of halogens at the metal centers giving mixed-valence Au_2^{I}/Au^{III} metallacycles. Both steric and electronic factors influence the reactivity of the gold atoms in these compounds. In fact one metal center appears to be oxidized to give mixed-valence Au_2^{I}/Au^{III} metallacycles[17]. Surprisingly, aqua regia also fails to give complexes beyond the Au_2^{I}/Au^{III} oxidation state for the pyrazolates. Thus an unusual stability of the $d^{10}d^{10}d^{8}$ configuration for the trinuclear gold complexes is observed. The electronic communication between the gold atoms may be the origin of this effect. The oxidation of the first gold atom may improve the π-acceptor ability of the two ligands coordinated to it so that they decrease sufficient electron density from the remaining two Au^{I} atoms and prevent their oxidation. No changes in the gold-ligand bond lengths are observed. When complex $[Au(\mu\text{-}3,5\text{-}(Ph)_2pz)]_3$ is reacted with aqua regia halogenation at the 4-position of the pyrazolate rings occurs causing the formation of $[Au(\mu\text{-}3,5\text{-}(Ph)_2\text{-}4\text{-}(Cl)pz)]_3Cl_2$. The crystal structure of this complex shows that there is no statistically significant difference between the Au^{I}-N and the Au^{III}-N bond lengths, which range from 1.98(3) to 2.05(2) Å[18c], just as it had been seen in the structure of $[Au(\mu\text{-}3,5\text{-}(Ph)_2pz)]_3Cl_2$ (Figure 1.11) .[18c] Complex $[Au(\mu\text{-}C(OMe)=N(Me)]_3$ seems to be unique in the family of the trinuclear gold(I) metallacycles, in fact, it is the only one that gives the stepwise addition of halogens, resulting in the formation of either mixed-valence or completely oxidized trinuclear gold complexes (Scheme 1.2). The X-ray structures of these derivatives were reported [18g] many years later after their synthesis.[18a]

Oxidative-addition with halogens was also investigated for complex $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$. This substrate behaves similarly to most of the trinuclear gold(I) complexes since it adds Iodine at only one gold center to yield $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3I_2$.[17] It consists of discrete trinuclear complexes with the gold atoms bridged by three l-benzylimidazolate groups. The coordination about Au(2) and Au(3) is nearly linear, while Au(1) has nearly a square planar arrangement. The Au-C, Au-N, and Au-I bond lengths are similar to those found in the analogous carbeniate derivatives.

A different behavior of complex $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$ was observed when it was reacted with other reagents capable of oxidative-addition such as alkyl or acyl halides. In these cases the products were characterized by X-ray crystal structure[18d,f] or by ^{197}Au Mössbauer investigation.[17] Moreover, an oxidation was observed when complex $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$ reacted with Me_3SiI (Au^{I}/Au_2^{III}) or $SOCl_2$ (Au_3^{III}).[18d,17]

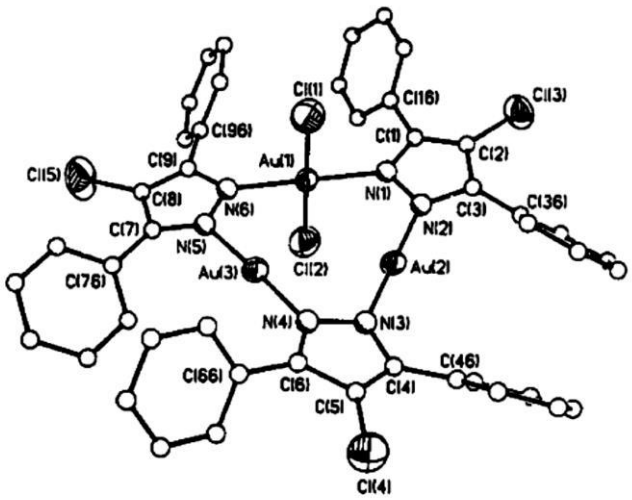
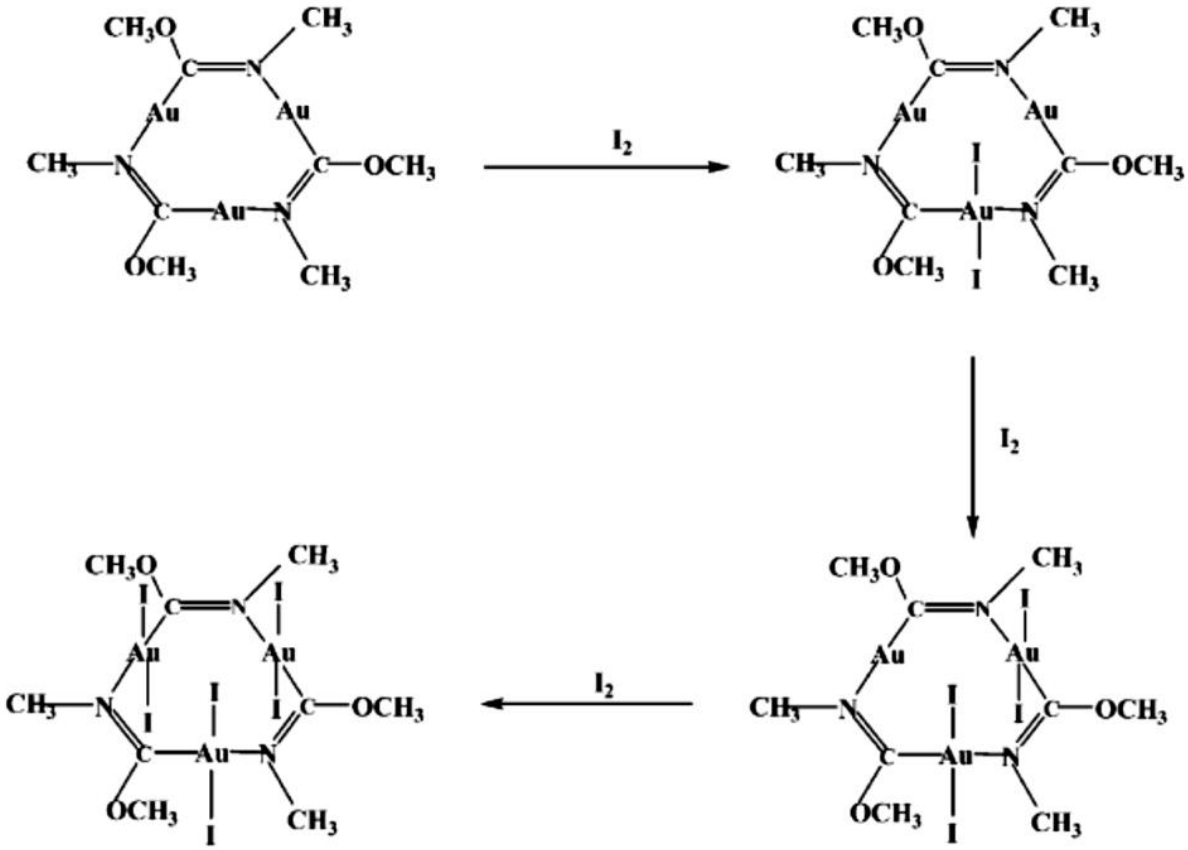


Figure 1.11. *a view of the molecular structure of complexes [Au(μ-3,5-(Ph)$_2$pz)]$_3$Cl$_2$ carbon nitrogen atoms are of arbitrary clarity.*



Scheme 1.2

Oxidative addition to polynuclear gold(I) complexes depends on several factors. Firstly, on the structure: for example the oxidation of dinuclear gold(I) ylide complexes with X_2 (I_2, Br_2 or Cl_2) or CH_3I

may give a transannular addition with formation of an Au^{II}-Au^{II} bond[19] whereas when three gold atoms are in a triangular array in a nine-membered ring, oxidation may occur at the three centers independently and the formation of metal-metal bonds is not observed.[19a]

Secondly, on the bridging ligands: for example trimeric derivatives of Pyrazole [20]react with only one molecule of iodine to give a mixed-valence $Au^{III}/2Au^{I}$ compound,[18b,21] while the trimeric derivative $[AuC(OMe)=NMe]_3$ undergoes a stepwise addition with only one, two or three molecules of alogen.[18a]

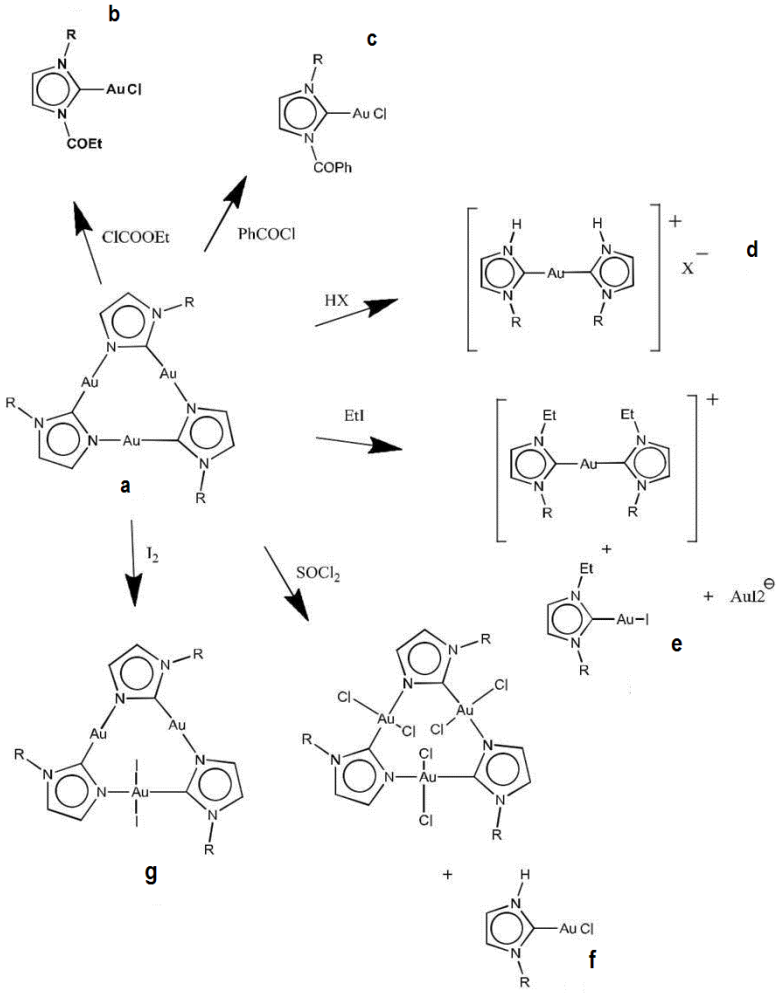
Thirdly, on the reaction condition: for examples treatment of $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ with aqua regia affords a dinuclear gold (III) derivative $[[Cl_2Au(\mu\text{-}(3,5\text{-}Ph_2\text{-}4\text{-}Cl\text{-}pyrazolato\text{-}N,N'))]_2]$ [22a] or a trinuclear mixed-valence $Au^{III}/2Au^{I}$ compound $[[Au(\mu\text{-}(3,5\text{-}Ph_2\text{-}4\text{-}Cl\text{-}pz))_3]$ [18c] depending on the reaction time.

The behaviour of trinuclear gold(I) compound, $[Au(\mu\text{-}Rim\text{-}N^3,C^2)]_3$ where Rim is 1-benzylimidazole, have been investigated towards several reagents capable of oxidative addition (Schema 1.3).

All the sample except **d** were obtained by reaction of the cyclic trimeric compound **a** with the appropriate reagent (ClCOOEt, PhCOCl, EtI, HX, $SOCl_2$ or I_2). The final products **f** and **g** retain the cyclic structure of compound **a** and they are the result of the oxidative addition to the metal.[18d]

In the other cases the reactions take another pathway and the trimeric complexes **a** undergoes cleavage to give the carbene complexes **b**,**c**, **e**.[18d]

The carbene complex **d** was obtained by treating the intermediate of reaction of Lithium benzylimidazolate with Ph_3PAuCl in acidic media.[8b]



Scheme 1.3

1.4 NHC chemistry.

Carbenes are defined as neutral compounds containing a carbon atom with only six valence electrons located two in each bond with the adjacent atom, plus two non-bonding electrons often represented as :CR_2.

Öfele and Wanzlick first pioneered the metalation of imidazol-2-ylidenes, better known as N-heterocyclic carbenes (NHCs), from imidazolium salts in 1968.[23,24] Lappert and coworkers followed this work with the investigation of N-heterocyclic carbene complexes synthesized from electron-rich olefins.[25,26] However, it was not until the isolation of the first free carbene by Arduengo, in 1991, that significant interest was given to the area.[27]

Complexes of N-heterocyclic carbenes with virtually every transition metal and many main group elements have been reported.[23,32] N-Heterocyclic carbenes bind to both hard and soft metals making

it a very versatile ligand system. NHCs bond to metals primarily through σ-donation of the carbene lone pair to the metal; however, recent evidence suggests that some degree of backdonation may occur.[33,34] The bond strength of Nheterocyclic carbenes, as mentioned earlier, has been shown to rival phosphines. The first structurally characterized silver NHC complex was made by using a free carbene and a silver salt.[35] However, generation of the free carbene has been problematic for some NHC systems. This led to the discovery, by several research groups, of silver bases with which silver NHCs could be synthesized from imidazolium salts in-situ. In 1997, Bertrand and colleagues reported the synthesis of a silver NHC from triazolium salts using silver acetate.[36] Lin and Wang, in 1998, reported the syntheses of silver NHCs using Ag_2O.[37]

Danopoulos and colleagues reported the syntheses of silver NHC complexes using Ag_2CO_3 in 2000.[38] These procedures, particularly Lin's, allowed N-heterocyclic carbene complexes of silver to be readily available and have led
to a diverse area of research. Silver N-heterocyclic carbene complexes have played an important role in the development of other metal carbene systems.
Transmetalation reactions using silver carbenes have been reported for a wide variety of transition metals: Au(I), Cu(I), Cu(II), Ni(II), Pd(II), Pt(II), Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III), and Ru(IV). Recent reviews dealing with silver N heterocyclic carbenes have been published by Arnold[39] and Lin and Vasam.[41] There are two types of carbenes: Fischer carbene and Schrock carbenes. Schrock carbenes tend to bind well with early transition metals with high oxidation states. Better π-donation from the filled p orbital to the d_π orbital of the metal can be achieved if the d-orbitals are empty thereby reducing electron repulsion in the overlapping orbitals. The repulsive effects inhibit the strength of the π-donation and overall lead to the destabilization of the metal Schrock carbene bond. Good substituents for Schrock carbenes are groups that are not π-donors, such as alkyl groups. Fischer carbenes σ bond to the metal but have an empty p orbital in which to accept electron density. At least one substituent group for Fischer carbenes is able to act as a good π donor. The empty p orbital of the Fischer carbene is stabilized by significant π contribution from both the substituent-(s) and the metal. The need for good π-back donation from the metal to the empty p orbital of the carbene is critical. Fischer carbene complexes of metals that are poor π -donors, early transition/high oxidation state metals, have been shown to be unstable. On the other hand, complexes of late transition/low oxidation state metals tend to be significantly more stable.

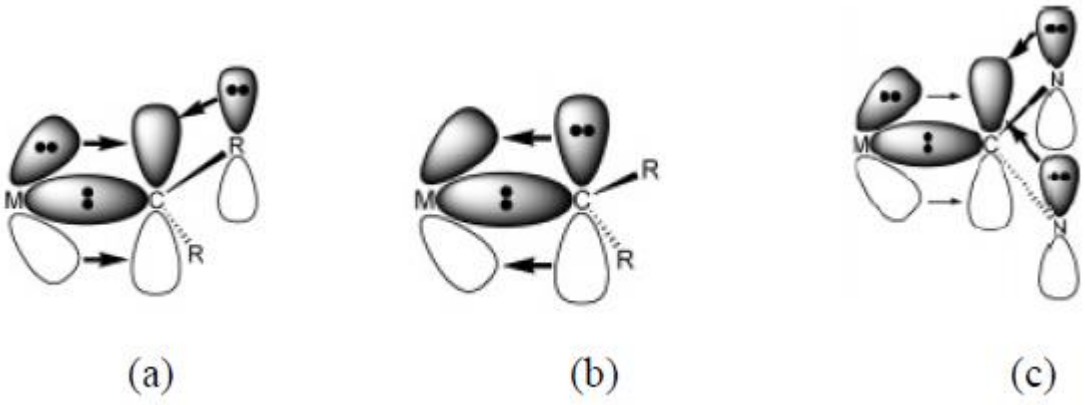


Figure 1.12. *Orbital diagrams of a Fischer carbene (a), Schrock carbene (b) and N-Heterocyclic carbene (c).*

Several theoretical studies have been done involving N-heterocyclic carbene complexes of group 11 metals.[33,34,40] Bond strengths of group 11 NHC complexes follow the pattern Au > Cu > Ag. While the silver NHC bonds were calculated to be relatively the weakest, the overall strength of the gold NHC bond is quite strong. An analysis of the bonding, by Frenking and co-workers, revealed the population of the relevant orbitals in the group 11 NHC complexes. This analysis is consistent with the bonding orbitals of the Ag(I) being a hybridization of the filled d_z^2 orbital and the empty s orbital. This is rationalized as Coulombic repulsion from the lone pair of the NHC forcing the d_z^2 and s orbitals to hybridize.[40] An analysis of similar systems, by Meyer and colleagues, has led to the same conclusion.[33] Frenking also suggested that the M-carbene bonds for M= Cu, Ag, and Au were mostly ionic in nature with covalent interactions being non-negligible. Analyses of NHC carbenes of both silver NHC halide complexes and silver N-heterocyclic biscarbenes by Ziegler and Rauk's energy decomposition schemes suggested that the bonds are mostly electrostatic in nature, with orbital interactions making a smaller contribution.[34] The π-donation of the nitrogen atoms to the empty p orbital increases upon complexation to group 11 metals. This is due to the donation of electron density from the carbene to the metal. The carbene therefore draws more electron density to itself by increasing the amount of electron density withdrawn from the lone pairs of the adjacent nitrogen atoms. Structural evidence also supports this theoretical view by comparison of the carbene-nitrogen bond distances of the complex vs the free carbene.[27,35]

1.5 Homogeneus catalysis.

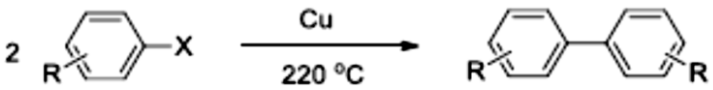
The term catalysis was firs employed by Berzelius in 1836 it identify a new entity capable of promoting the occurrence of a chemical reaction by a "catalytic contact". In his view, the catalyst was seen as something that is added to the reaction to speed up the rate of the reaction (catalytic force) without being consumed or produced in the process. As for the industrial catalytic processes, catalytic production of sulphuric acid. i.e. lead chamber process, where oxidation of sulphur dioxide to sulphur trioxide was performed in the presence of a mixture of nitric oxides (NO/NO_2) as catalyst, dates back to eighteenth century. However, catalyst started to play a major impact on the chemical industry

starting from the beginning of the twentieth century. Currently more than 95% of chemicals being produced via a process that includes at least one catalytic step.[42]

Traditionally catalyst were distinguished into homogeneous and heterogeneous. This distinction is linked to the fact that the catalyst operates respectively in the same phase where the reaction occurs (homogeneous catalysis) or in different phase (heterogeneous catalysis). Most of the processes using homogeneous catalyst occur in liquid phase whereas for the heterogeneous catalysis, the catalyst is usually in a solid form and the reaction occurs either in the liquid or gaseous phase.[43] The fact that the catalyst is in a distinct phase with respect to the reaction medium, accounts for the major advantage of the heterogeneous catalysts over the homogeneous as it makes the separation and reutilization of heterogeneous catalyst simple and cheap compared to the homogeneous catalyst. A great variety of homogeneous catalyst are known, ranging from Bronsted and Lewis acids widely used in organic synthesis, metal complexes, metal ions, organometallic complexes, organic molecule up to biocatalyst (enzyme, artificial enzymes). As a general picture, the main difference is the fact that in the case of homogeneous catalyst, every single catalytic entity can act as a single active site. This make the homogeneous catalysts intrinsically more active and selective than traditional heterogeneous catalysts such as oxides or supports metal particles.

The transition metal-catalysed reaction has become a powerful tool in organic synthesis in the past decades, which has played an important role in developing chemical science and technology by the discovery and development of new types of chemical compounds and powerful new synthetic methodologies.[42] Commonly, transition metal catalysts are based on metals such as Palladium,[43] Nickel,[44] Copper,[45] Cobalt,[46] Iron,[47] Gold,[48] Manganese,[49] Rhodium[50] and Ruthenium.[51]

Since the findings of the Ullmann reaction (Scheme 1.4), copper salts as catalysts have been known for more than one century and served well for C– N, C–S, C–O and other bond formation reactions.[64] In the past years, copper has received increasing attention for the construction of various bonds in organic synthesis. Copper catalysts fascinate chemists for several reasons. First of all, copper is very cheap compared to Palladium and the total amount of copper on earth is vast. Furthermore, copper salts generally present a low toxicity. More importantly, copper can take part in cross-coupling chemistry in a way strikingly similar to Palladium and possesses unique chemoselectivity and reactivity.



Scheme 1.4: *Ullmann reaction.*

Although increasing attention has been paid to the design of Cu complexes with polydentate ligands as model of copper oxidase,[52h,k,m-53] the use of multicopper complexes for such reactions still remain a scarcely explored area of research. Recently, the easy generation and characterization of copper(II)

triethanolamine complexes, adopting di- tri-, tetra-, and polynuclear structures, as well as their catalytic application in alkanes oxidation have been achieved.[53 f,g]

Moreover, have also been reported the easy synthesis of a series of trinuclear triangular Cu(II) clusters, all based on the relatively stable [Cu_3(μ_3-OH)(μ-moiety, through the reaction of copper(II) carboxylates with pyrazole (Hpz).[54] These triangular SBUs (secondary building units) spontaneously self-assemble to give different 1-, 2-, or 3-D MOFs, depending on the carboxylate and ancillary ligands.[54b]

In these nearly planar triangular Cu_3(μ_3-OH) clusters, the tetracoordinated metals show steric accessibility at the axial sites, thus resulting in possible interesting candidates for catalytic processes. The trinuclear Cu(II) clusters (Figure 1.13) act as remarkably active and selective catalysts or catalyst precursors for liquid biphasic (MeCN/H_2O) peroxidative oxidation (by aqueous H_2O_2 in a slightly acidic medium, at room temperature and atmospheric pressure) of cyclohexane and cyclopentane to the corresponding alcohols and ketones.

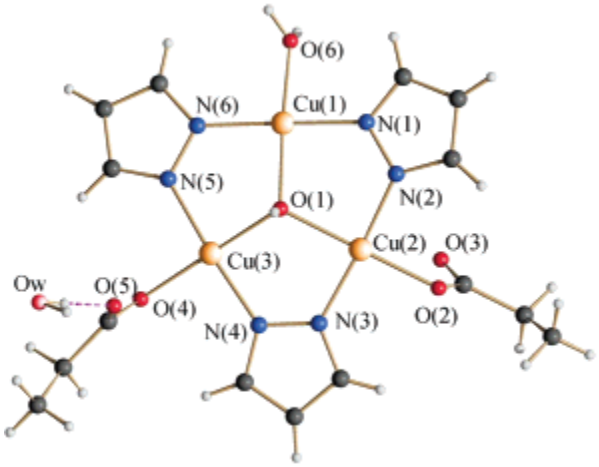


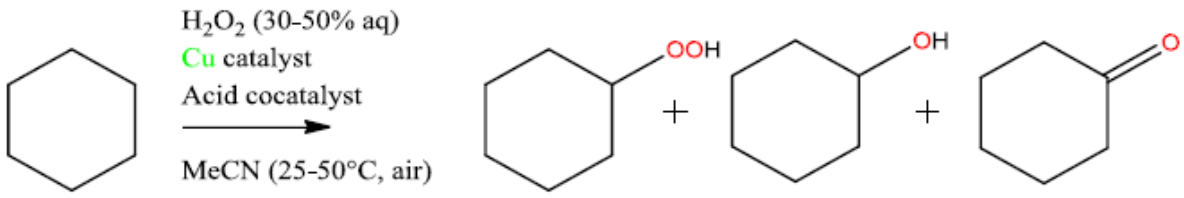
Figure 1.13. *Views of [Cu_3(μ_3-OH)(μ-pz)$_3$]$^{2+}$, with the atom labelling scheme.*

There are some sporadic reports on the application of multicopper complexes in alkane oxidation reported before 2005.[56,57] By this time various multicopper(II) complexes and coordination polymers self-assembled from copper salts and simple aminopolyalcohol and benzenecarboxilates were synthesized. The obtained compound were found to be highly efficient and versatile catalysts or catalyst precursors for the mild oxidation of alkanes (typically cycloalkanes) by the H_2O_2 to the corresponding alkyl hydroperoxides, alcohols and ketones [53f,g, 58-59,61-63] as well as for the hydrocarboxylation of gaseous and liquids C_n (n = 2-9) alkanes, by CO and H_2O and in the presence of a peroxisulphates oxidant, to give C_{n+1} carboxylic acid.[64-72]

Since then, the types of multicopper catalytic systems applied in alkane oxidation have also been extended to new Cu(II) complexes and coordination polymers with azo derivatives of β-diketones [73-75], Schiff bases [76-79], pyrazole and various carboxylate ligands.

Many research studies have been focused on the establishment of more efficient oxidation protocols particularly by employing new transition metal based catalytic systems and performing oxidation with H_2O_2 under mild conditions. In the presence of various multicopper catalyst or catalyst precursor C_6H_{12}

is oxidized by aqueous H_2O_2 to a mixture of cyclohexyl hydroperoxide, (CyOOH) (main primary product), cyclohexanol and cyclohexanone, the alcohol and ketone being the major final products after the autodecomposition of CyOOH or its reduction with PPh_3.[84] This mild oxidation typically precedes in aqueous acetonitrile medium, under atmospheric pressure, at r. t. or with a slight heating (50°C), and in presence (optional) of an acid co-catalyst.(scheme 1.5)



Scheme 1.5

1.6 Biological test on mononuclear Au(I) complexes.

The consolidated and exceptional antitumor activity of Platinum (II) compounds on the clinical treatment of different types of cancers is unfortunately accompanied by serious side effects and by the occurrence of cis-platin resistance.[85] The continuous struggle to overcome these latter drawbacks led to two other platinum based drugs: oxaliplatin and carboplatin.[86] However, chemists are still seeking new and more potent metal based drugs to reach a good compromise between an optimal cytotoxic activity and minor liver and kidney toxicities, typical for these kinds of drugs.[87] Coinage metals have been taken in consideration as alternative metals in the design of metal based drugs; among them, some Gold(I)complexes had success first for their efficacy against inflammatory diseases such as rheumatoid arthritis, and then for their ascertained antineoplastic activity. Simultaneously with the cytotoxicity studies, a great effort has been made to identify the molecular targets for gold(I) based drugs that are comparable to Platinum based drugs, but this topic is still a challenge for researchers.[88,89] Classes of gold(I) compounds containing phosphanes as ligands [90-92] or ancillary ligands [93-97] have been studied, which are similar to the well-studied auranofin, consisting of a sugar frame bound to a gold(I) triethylphosphane ligand. Some examples of phosphane complexes, being the most active in vivo, reached the pre-clinical pharmacological evaluation.[98]

Unfortunately, severe hepatotoxicity was verified and stopped their development. The conclusion of this promising study was that the hydro/lipophilicity balance of the gold complex is the likely key to be focused on in order to achieve the [99-101] goal.

Hence, the design of gold complexes for biological testing should consider the involvement of more hydrophilic phosphane and/or other polar or more bio-compatible co-ligands. Based on these previous studies, a new class of gold(I) complexes with phosphane ligands and biomolecules such as azoles has been designed by Rossana Galassi and co-workers. This choice was particularly important given that pyrazoles and imidazoles play a pivotal role in the coordination chemistry of gold in the +1 oxidation state. Moreover, in pyrazoles, substitution at the 3 and/or 5 position adjacent to the nitrogen

atoms is particularly easy to achieve, and can strongly affect the steric environment around the N-donors and any metal ions coordinated to them.[102]

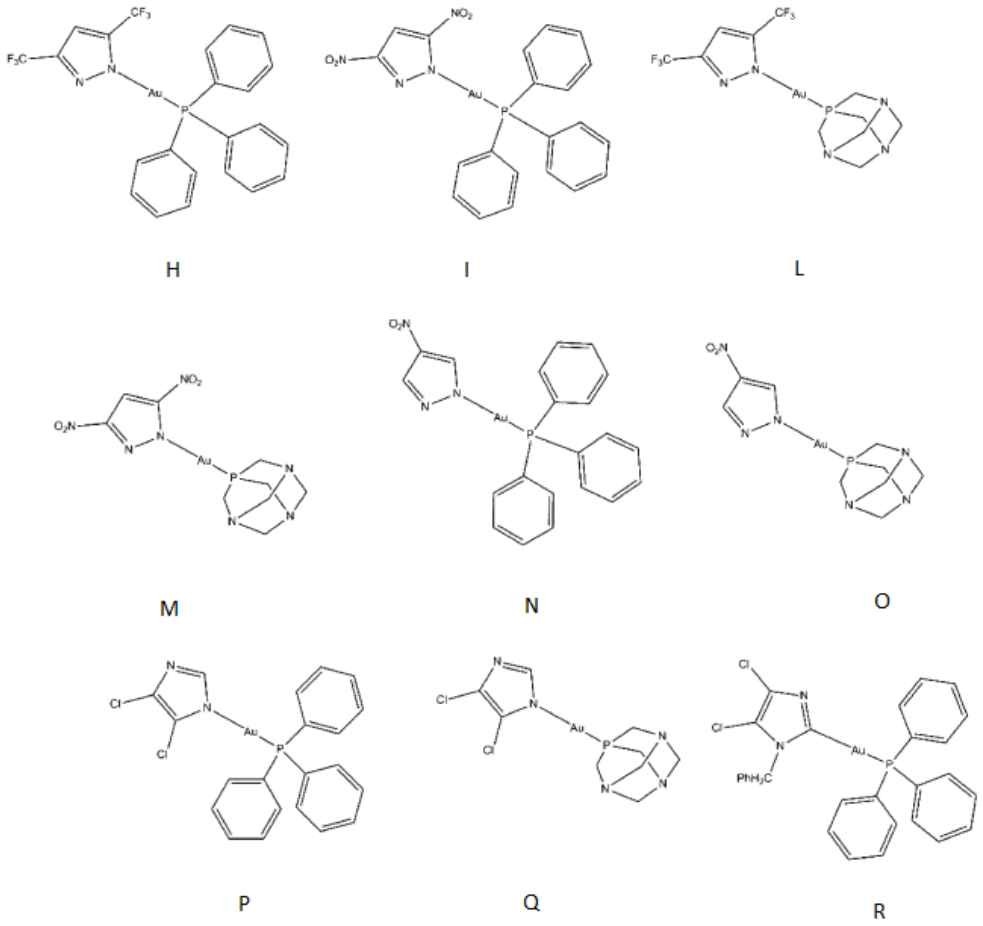


Figure 1.14.

The antiproliferative effects of gold(I) azolate compounds were investigated in a panel of various human cancer cells containing samples of breast (MCF-7), lung (A549), cervical (A431), colon (LoVo and LoVo MDR), and ovarian (2008 and C13*) cancers. Cytotoxicity was evaluated by means of an MTT test after 72 h of treatment with increasing concentrations of the tested compounds. For comparison purposes, the cytotoxicity of cis-platin, the most widely used metallodrug, was evaluated in the same experimental conditions.

Uncoordinated azole ligands proved to be scarcely effective in decreasing cancer cell viability over 7 cell lines. Among the gold(I) coordination compounds, triphenylphosphane derivatives proved to be more effective with respect to the TPA analogues. The TPA derivatives L, O and Q showed mean IC_{50} half maximal inhibitory concentration (μM) values (excluding those calculated for LoVo MDR and C13*cells) of 32.81 (27.11–43.44), 17.92 (10.31–24.35) and 12.15 (6.48–17.45), respectively, which were from 2 to 4 times higher than that of cis-platin (7.63 μM). The triphenylphosphane derivatives N and P showed relevant antiproliferative activity eliciting IC_{50} values (μM) within the same order of magnitude (average IC_{50} of 1.03 and 1.21 μM for N and P, respectively) and about 6 times lower than

cis-platin. Notably, compounds H and I emerged as the most effective in killing cancer cells, with IC_{50} averages roughly 10 times lower than those of cis-platin (average IC_{50} of 0.89 and 0.68 μM for H and I, respectively). Interestingly, these complexes reached antitumor activities in the low micromolar range, which were even lower than those obtained with the phosphine gold(I) drug auranofin.[103,104] With all the azolate gold(I) complexes, very interesting results have been obtained against the ovarian carcinoma cis-platinresistant (C13*) cells. In C13* cells, cis-platin resistance has been correlated with reduced cell drug uptake, high cellular TrxR and glutathione levels, and enhanced repair of DNA damage.[85] Cytotoxicity assays testing all the gold(I) derivatives H-R against the 2008/C13* cell line pair showed a similar pattern of response across the parental and resistant sub-lines and allowed the calculation of RF values (RF = Resistant Factor, which is defined as the ratio between IC_{50} values calculated for the resistant cells and those arising from the sensitive ones) roughly 7.5-fold lower than that obtained with cis-platin (RF = 9.0).

These data clearly reveal no cross-resistance phenomena. Additionally, gold(I) complexes were tested against a multidrug resistant (MDR) colon carcinoma subline, LoVo MDR cells. Tested on a LoVo/LoVo MDR cell line pair, pyrazolategold(I)-triphenylphosphane and -TPA derivatives allow the calculation of an RF value up to 10 times lower than that obtained with doxorubicin, clearly suggesting that pyrazolate gold(I) complexes are not potential MDR substrates. Conversely, 4,5-dichloro-1-imidazolate–gold(I) derivatives P and Q showed a significantly lower cytotoxicity potency against resistant sub-line LoVo MDR, attesting they do not overcome MDR phenomena.

2. AIM OF THE WORK

As a general goal, this work has the finality to refine the understanding of a peculiar aspect of the coordination chemistry of coinage metals with pyrazoles and imidazoles. As already introduced in the first part of this thesis, the chemistry of gold(I) trinuclear cyclic derivatives is well known either for the Lewis pi-base properties affording to supramolecular luminescent species, and on the regard of oxidative reactions leading to mixed-valence cyclic compounds or to mononuclear Au(I) carbene species. When the central metal is silver this last reactivity was not developed. In fact, Ag(I) trinuclear cyclic derivatives can be obtained both with pyrazoles and with imidazoles. These latters are rare and their chemistry is still not very known. Hence, the reactivity of $[Ag_3\text{-}\mu\text{-}C^2,N^3\text{-}(1\text{-benzylimidazolate})_3]$ as potential Lewis acid or base has not been investigated yet. As a consequence an aim of this work will be to evaluate the possibility to obtain silver carbene species by oxidative reactions with alkyl or acyl halides toward Ag(I) trinuclear cycles or by adding of acids.

The synthesis of mononuclear nitrogen bonded or carbene bonded derivatives will be attempted to verify the coordination ability of imidazoles and pyrazoles containing substituents such as chloride, cyanide, trifluoromethyl or nitrogroups. The formation of cyclic derivatives as homologous series is in fact restricted in the cases of 3,5-bis(trifluoromethyl)pyrazole.

Furthermore, since some Cu complexes are known to be active as catalyst or catalyst precursor, another aim of this work will be to test the catalytic activity of Cu complexes towards MW assisted peroxidation of cycloalkane to cyclohexyl alcohol and cyclohexylperoxide.

In the case some products will be obtained they will be tested for the biological activity.

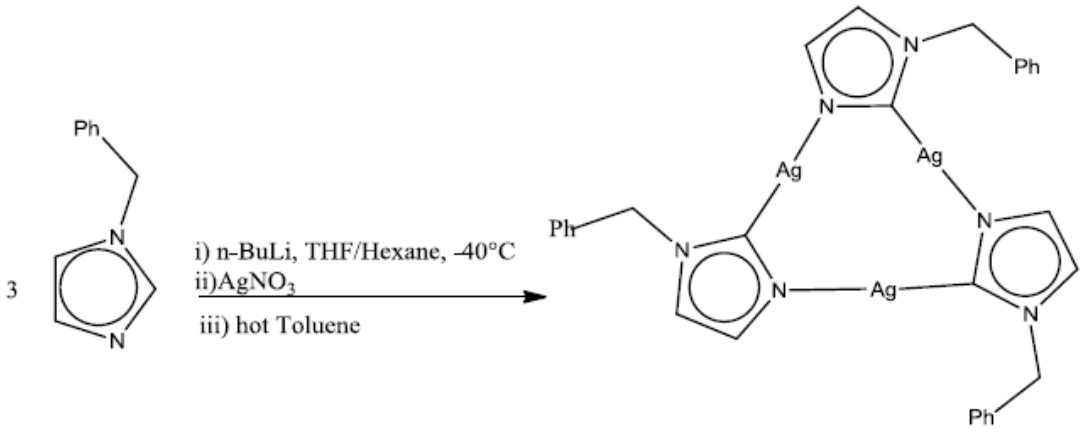
3. RESULTS AND DISCUSSIONS

3.1 Imidazolate Ag, Au derivatives.

The coordination chemistry of the imidazolate ligand discussed in this paragraph is restricted to silver(I) and Au(I) metal ions.

As already introduced in the previous section, a goal of this project is to verify the behaviour of some silver(I) imidazolate complexes to compare with those already known of gold(I).

To study the eventual analogy of silver(I) and gold(I) 1-benzylimidazolate trinuclear cyclic derivatives on the regards of oxidative addition of alkyl- or acyl- chloride, the synthesis of the silver derivative was performed according to the following scheme:



Scheme 3.1. *Synthesis of compound* ***1****.*

The compound **1** was characterized by ^{1}H NMR and IR spectroscopies, elemental analysis etc.(^{1}H-NMR ($CDCl_3$) δ 7.4-7.2(m.5H); 7.02(s, 1H); 6.98(s, 1H); 5.31(s, 2H). IR (cm^{-1}): 3150 (w), 2853 (w) (Car-H; C=O).
Moreover the crystal structure was determined by X-ray Crystal diffraction.

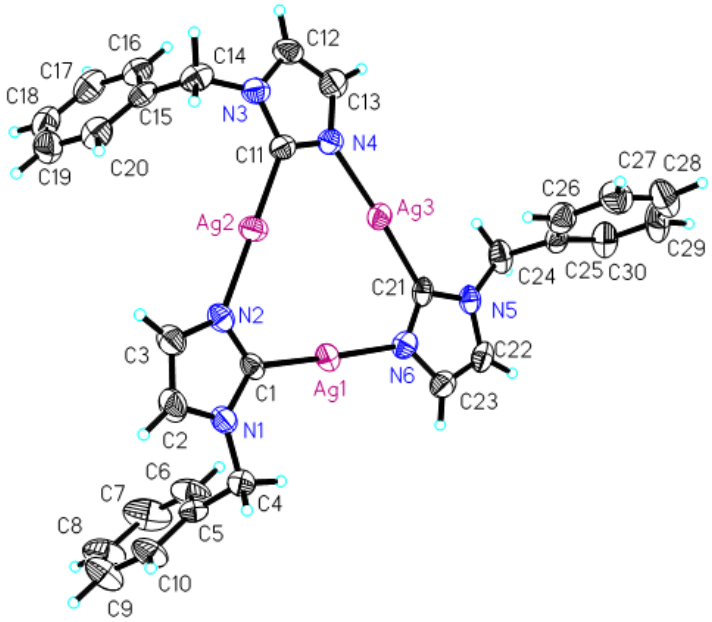


Figure 3.1. *Ortep plot of the crystal structure of compound* ***1***

The compound **1** exists in the packing unit as a columnar sequence of dimer of trimers as it is possible to observe in figure 3.2 where the trinuclear units are joint by argentophilic bondings at 3.168 Å. The two silver trimers adopt a chairlike metal framework structure. The crystal structure of compound **1** and its packing are shown in figures 3.1 and 3.2, respectively. The crystal structure data and structure refinement are listed in table 3.1 (tables in appendix). In table 3.2 the bond lengths and the angles for compound **1** are listed. The compound $[\mu\text{-C,N(1-benzylimidazolate)Ag}]_3$, **1**, crystallizes in the triclinic space with the special group P1 and, so far, it represents the first example of a silver(I) trinuclear cyclic derivative with a C,N bridging ligand. The nine membered $Ag_3N_3C_3$ metallacycle is not perfectly planar and the C-Ag-N environments are not linear. The silver atoms in the nine membered cycle draw an almost regular triangle with an average distance Ag-Ag of 3.514 Å. This distance is longer than that found between the two trimer units which is 3.1683(6) Å for $[\mu\text{-N,N(3,5-diphenylpyrazolate)Ag}]_3$ (average 3.383 Å)[110a], and that found for $[\mu\text{-N,N(pyrazolate)Ag}]_n$ (3.3718 Å)[110b]. The Ag-Ag distances depict a regular metal triangle on the contrary of what revealed in the linked dimers of silver trimers where these distances are pretty different going from 3.387(2) to 3.528(2) Å. The average distance of Ag-N in **1** is 2.089 Å, equal to that reported by Fackler [110] and it is slightly longer than that observed in $[\mu\text{-N,N(pyrazolate)Ag}]_n$ (average, 2.067 Å), and in the middle of those reported for the linked silver trimers reported by Meyer; whilst the Ag-C average distance is 2.057 Å. Strong deviations from linearity have been observed in the N-Ag-C angles with values ranging from 173.51° to 175.73°. Such deviations are not limited to those angles which are interested to the argentophilic bondings, but they occur in all the N-Ag-C angles of the cycle. These angles are close by to those observed for N-Ag-N in $[\mu\text{-N,N(3,5-diphenylpyrazolate)Ag}]_3$ (average 175.73 °)[110] but larger than those recorded for $[\mu\text{-N,N(pyrazolate)Ag}]_3$ where the pyrazole contains in 3,5 position functionalized thioether groups (i. e. 172.25°). In complex **1**, two C-N-Ag angles have close values, 117.9(3)° and 118.9(3)° while the angle

C_{21}-N_6-Ag_1 has a value of 121.5(3)°. Such trend has been observed also in the N-C-Ag angles; in fact the angles N_2-C_1-Ag_1 and N_6-C_{21}-Ag_3 have a very similar values (123.9(3)° and 122.1(3)°) while the angle N_4-C_{11}-Ag_2 is 125.2(3)°. Such distortions are likely due to the intermolecular interactions of two trimers with short Ag---Ag contact yielding a dimer of trimers, as it is shown in figure 3.2. Moreover in the crystal packing a dimer of **1** (A) interacts with another dimer (B) throught Ag2B---Ag3A and Ag2B---Ag2A interactions at 3.496(1) Å and 3.504(1) Å, respectively. Dimers of trimers have been already found in trinuclear silver structures in [μ-N,N(pyrazolate)Ag]$_3$ or in [μ-N,N(3,5-bis-trifluoromethyl-pyrazolate)Ag]$_3$, but also heteronuclear trimers Ag_2Au or Au_2Ag interact each other with short metallophilic contacts yielding dimers of trimers in the solid state.[116]

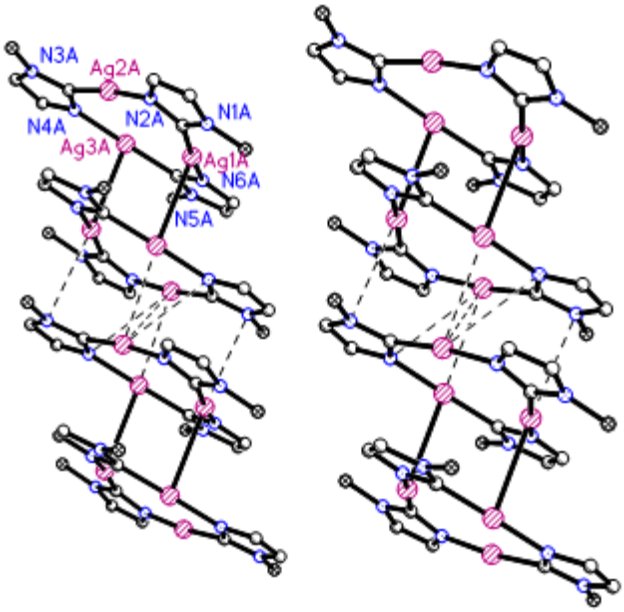


Figure 3.2. *Columnar packing in the molecule of the compound* ***1****.*

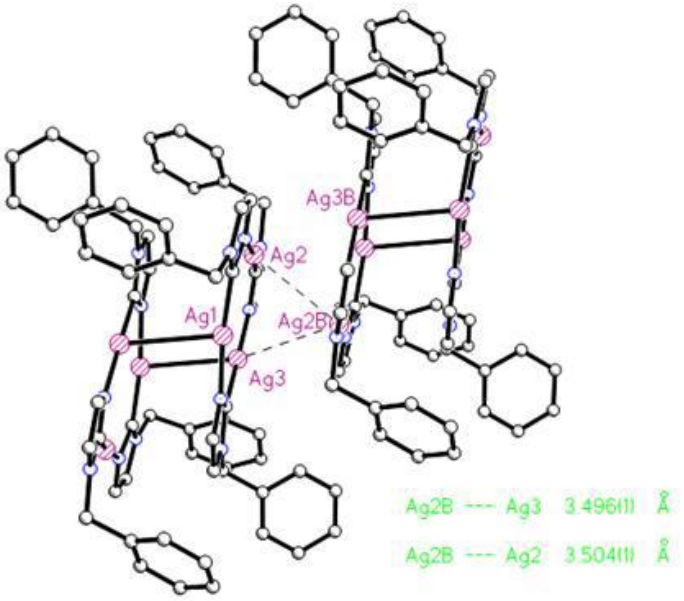
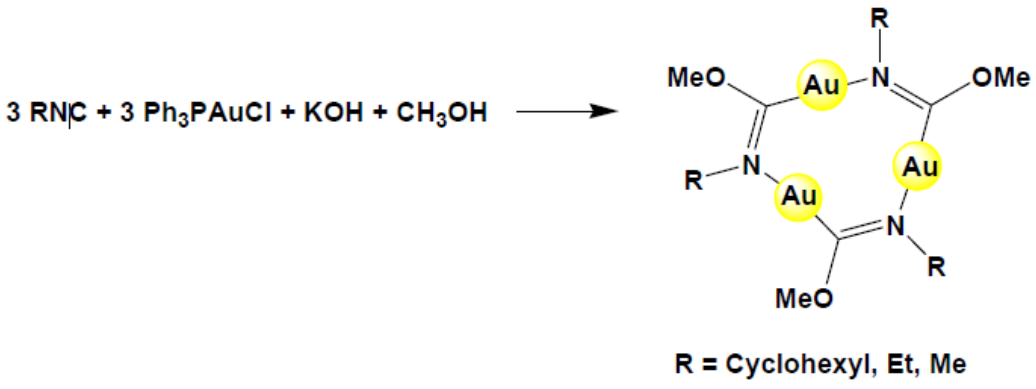


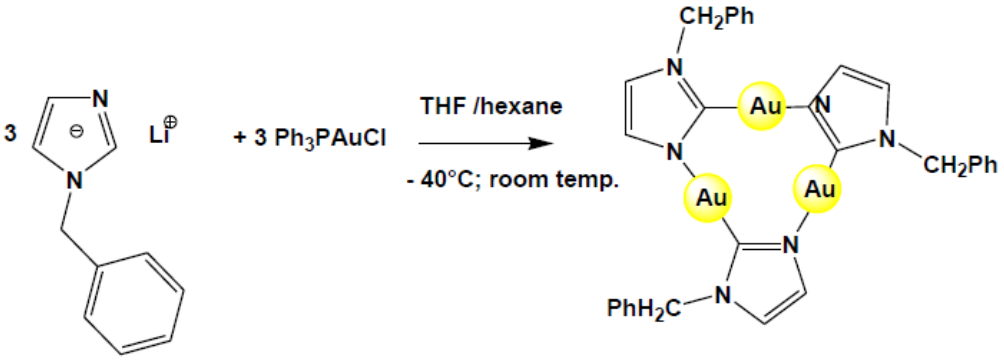
Figure 3.3. *Depiction of the secondary interactions in the dimer of trimers of compound* ***1***

A comparison with the crystal structure of the [Au-C^2N^3-(1-benzylimidazolate)]$_3$ can be discussed.[106] The gold(I) trinuclear compound crystallizes in C2/c monoclinic space group but also in this case the formation of dimer of trimers was observed with aurophilic distance of 3.3465(4) Å. The hexanuclear metal framework adopts a semiprismatic conformation with one long (3.558 Å) and one short (3.346 Å) intertrimer aurophilic distances and a torsion angle of -17°. The metal conformation is the main difference between the gold and silver trimers being the prismatic structure pretty rare in the case of d^{10} complexes and it has been reported for polimorph of [Au(μ-C(OMe)=NMe]$_3$ [107] and for {[3,5-(i-pr)$_2$Tz]Au}$_3$.[108]

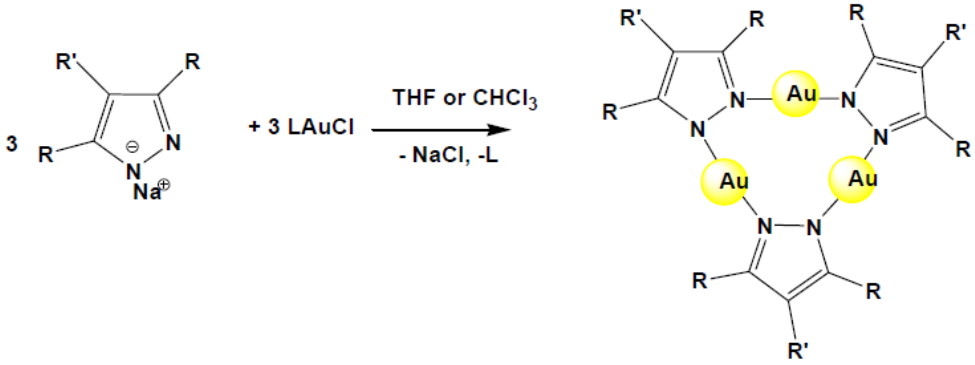
As concerns the synthesis, the methods affording the trinuclear gold(I) complexes can be resumed in the following schemes:



a) Starting from carbeniate ligands



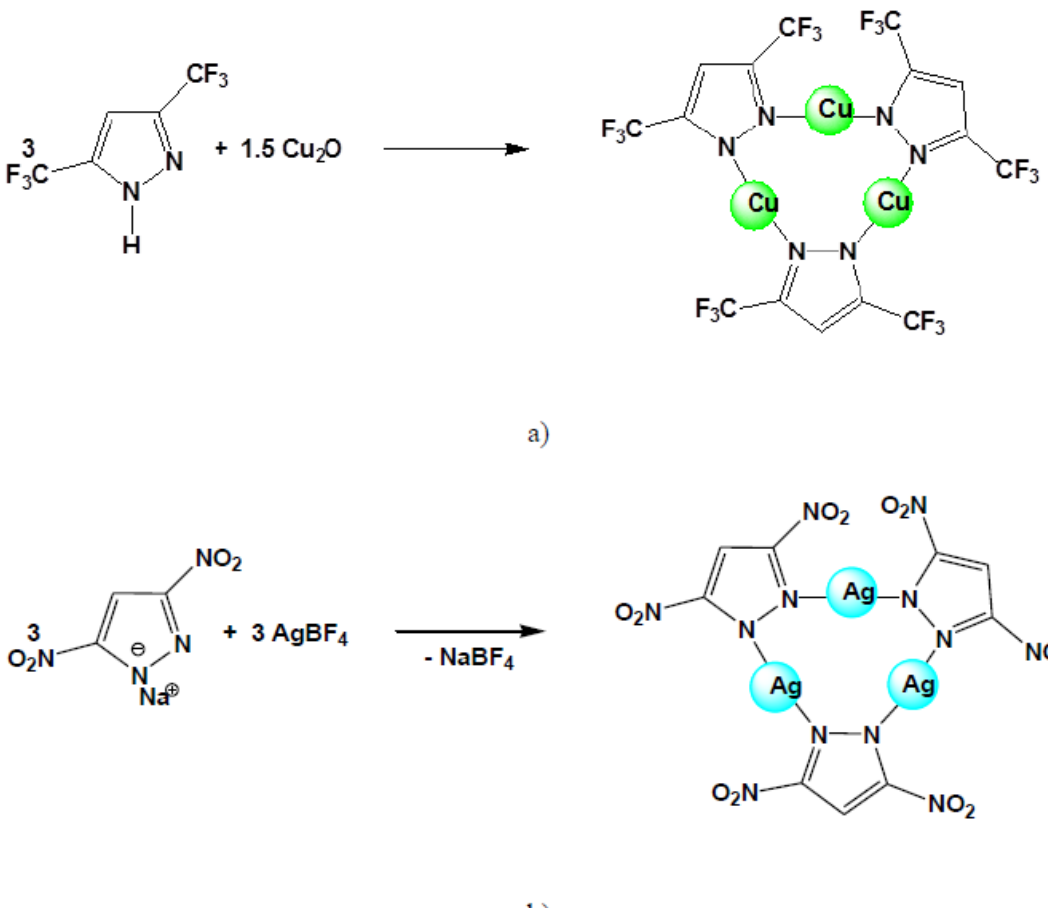
b) Starting from imidazole ligands



c) Starting from pyrazolate ligands

Scheme 3.2. *Examples of synthesis paths to obtain trinuclear cyclic gold(I) compounds from carbeniates, imidazoles and pyrazoles.*

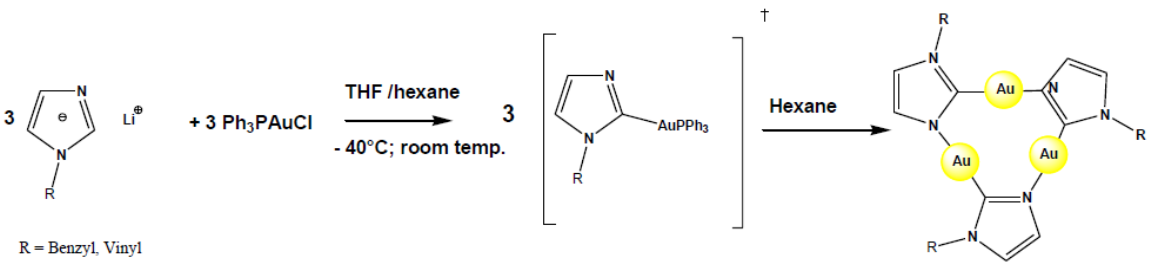
The formation of the silver(I) and copper(I) analogos can be achieved by adding the corresponding silver salts (usually $AgBF_4$, $AgCF_3SO_3$ or $AgNO_3$)[109] or copper salts (CuCl, $[Cu(CH_3CN)_4]BF_4$ etc)[110] to the pyrazolate salt or by adding the corresponding M_2O (where M = Cu, Ag) to the neutral azoles [111]. This latter method avoids the step of the deprotonation of the ligand as the oxide works as base. Scheme 3.3.[111]



Scheme 3.3. *a) Dias method[111] and b) Fackler method.[110]*

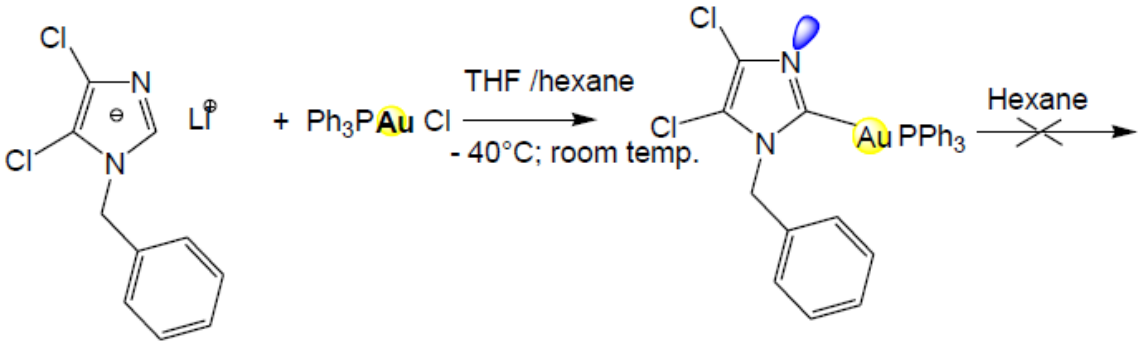
The synthesis of the compound **1** follows scheme 3.1 where $AgNO_3$ is the metal source. The critical aspect of this synthesis is the purification. The extraction with hot toluene allows to obtain crystals by lowering temperature aggiungi T°C (0 - +4°C) even though the yield of pure compound is pretty low.

There is a strong influence of the substituents on the azole on the synthesis of the gold(I) trinuclear derivatives. In fact the formation of the gold(I) compound with 1-benzylimidazole, if compared to the silver analogous, should present the formation of an intermediate where the $AuPPh_3$ is bound to the C_2 of the imidazole, as described in the following scheme:



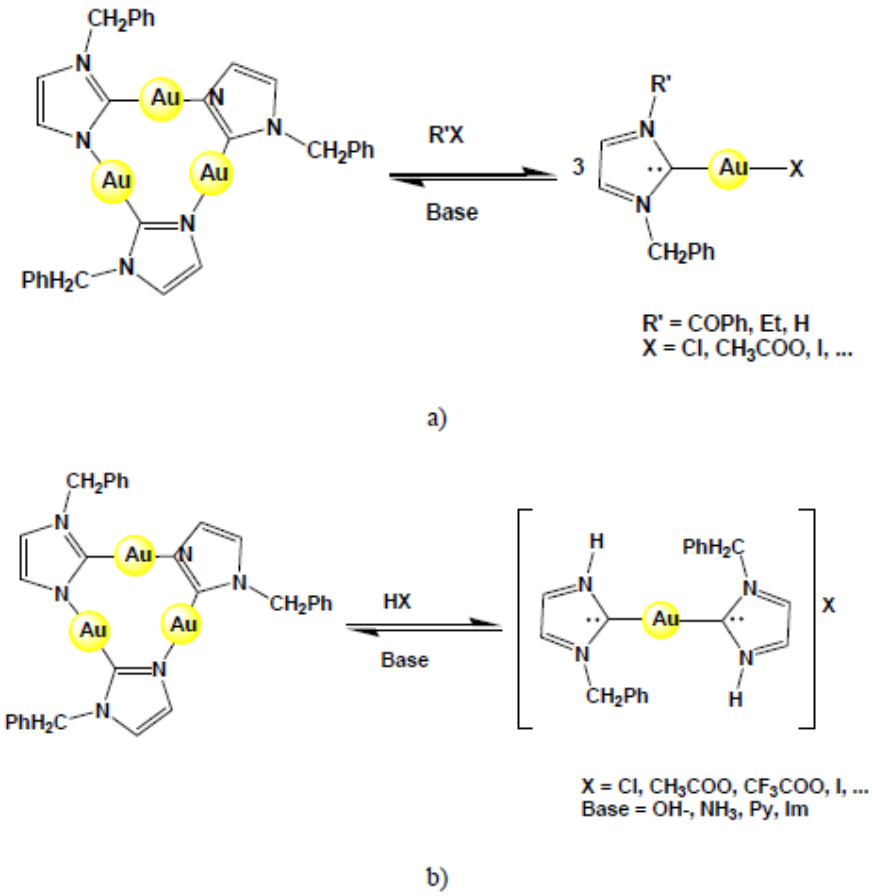
Scheme 3.4. *General scheme for the formation of the gold(I) 1-substituted imidazolate trimer.*

The formation of the cycle can be observed only after stirring with hexane which facilitates the removing of the PPh_3 allowing the cyclization by coordination to the N. The change of the substituent on N, for example with the vinyl group instead of the benzyl, does not affect the formation of the cycle and the corresponding cyclic trinuclear gold(I) compound is observed in high yield by following the reaction path of scheme 3.4. The introduction of withdrawing susbtituents in the azole cycle in position 4 and 5 affords to different results: the unique formation of the stable mononuclear C2 aurated compound, which is the intermediate in scheme 3.4, was observed. Vigorous stirring with hexane or oxidative treatment of the PPh_3 does not lead to the formation of the trimer, while the mononuclear compound seems to be inert to all the above mentioned treatments (scheme 3.5).



***Scheme 3.5**. Formation of the mononuclear compound where the gold(I)PPh_3 is bound to the C2.*

The formation of mononuclear derivatives by starting from the gold(I) trinuclear derivative can also be achieved by adding alkyl or acyl halides or acids (scheme 3.6a). The nature of the corresponding mononuclear derivatives is carbenic. The removal of the substituent on the N_3 by the treatment with weak or strong bases yields the trinuclear species back with a high extent of reversibility (scheme 3.6a and 3.6b).



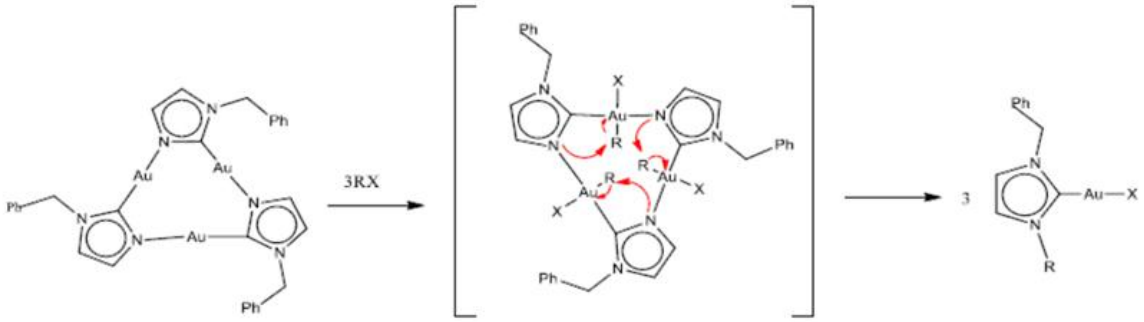
***Scheme 3.6**. Formation of monocarbene from addition of alkyl or acyl halides a) and scheme of the reversible reaction by adding acids or bases b).*

This reactivity was ascertained for the gold(I) trinuclear cyclic compound where the ligand is 1-benzyl imidazole or 1-vinylimidazole but it has never been tested for the silver analogous, compound **1**. As a consequence, to reach the first aim of this work, the reaction of compound **1** with benzyl chloride was performed in CH_2Cl_2 with a mole ratio of 1 : 3.

The solution was stirred for 2 hours and the reaction was monitored by TLC and IR spectroscopy. After two hours the solution became dark without the formation of any precipitate. From the analysis of the IR spectra it was observed the disappearance of the typical bands due to the trimer, at 1265cm^{-1} as in example, and the formation of a new compound, which stability was very poor given the presence of grey silver or silver chloride nanoparticles. The IR spectrum of this last derivative shows bands at 3115 and 3029 cm^{-1} in the aromatic C-H stretchings region. These bands could not be attributed to the imidazolium salt (see in the experimental part, 3156, 3086 and 3028 cm^{-1}) and neither to the corresponding carbene derivative (see in the experimental part, 3162, 3132 and 3100 cm^{-1}). Even the reaction with benzoyl chloride didn't afford to the carbene derivative already observed in the gold(I) trimer reactivity (scheme 3.7). In this case the unreacted benzoyl chloride IR bands remained

unchanged while the bands associated to the silver trimer disappeared, but no compounds was isolated.

The fact we do not observe the formation of the carbene silver derivative can be due to the fact that the silver(I) does not support oxidative addition that it can be the first step of the reaction followed by a reductive elimination with formation of the monocarbene derivative in the case of gold.[17]

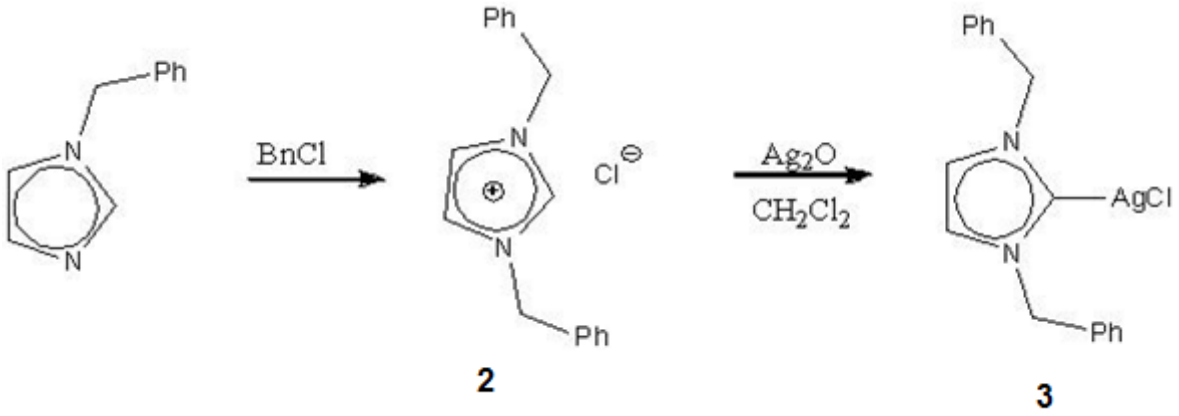


Scheme 3.7. *Depiction of the possible mechanism for the eliminative reduction and consequent formation of the carbene.*

Another explanation on the unreactivity of silver trimer on the regards of acyl or alkyl halides might be the low stability of the corresponding carbene complex. Then the synthesis of the corresponding carbene was attempted by starting from the corresponding imidazolium salt. The synthesis was performed according to literature method [37] and following the reaction scheme **3.8**.

The synthesis proceeds by the formation of the imidazolium salt and further treatment with Ag_2O following a literature method already published.[112] The imidazolium salt, compound **2**, and the corresponding silver carbene, compound **3**, were characterized by ^{1}H and ^{13}C NMR, IR spectroscopies, elemental analysis and ESI mass spectrometry. The hydroscopic salt, **2**, was characterized mainly by the ^{1}H NMR spectrum resonance at 10.86 ppm in $CDCl_3$ corresponding to the hydrogen of the C_2 of the imidazole ring and to a C_2 signal in the ^{13}C NMR spectrum at 144.94 ppm. Upon metallation these signals undergo a disappearance as concerns the ^{1}H signal and a low frequency shift at 180 ppm in the ^{13}C NMR for the C2. In the IR spectrum of the imidazolium salt we observe strong absorptions due to the water and the C-Har stretching at 3442, 3376, 3244 cm^{-1} and 3152, 3126, 3074 and 3032 cm^{-1} respectively; in the corresponding silver derivative these latter undergo some blueshifts with resonances at 3162, 3132 and 3100 cm^{-1}. In the ESI spectra, while the imidazolium cation yield the main peak at 249 m/z in the positive field, the corresponding carbene silver derivative shows the main peak as the [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Ag]at 605 m/z in addition to the low intense imidazolium salt peak at 249 m/z likely formed in the ionization source. These last results highlight the pretty stable nature of this carbene complex and we can state the addition of benzylchloride did not afford the carbene for the inability of silver to achieve higher oxidation state, reinforcing the idea that the oxidative process at the central metal is the first step of this reactivity also in the case of the gold(I) complexes. Both the spectroscopic studies and the elemental analysis do not explain the real nature of this compound, that is if is a monocarbene or a bis carbene species. The

ultimate answer came from the single crystal structure determination which allowed a final attribution of the structure. Crystals of compound **3** were allowed to grow from a CH_2Cl_2 solution where hexane was layered. The crystal structure showed the presence of a dimer of carbene through silver–chloride interaction at 3.071 Å and the angle at C-Ag-Cl at 163.38 °. In figure 3.4 is reported the crystal structure while in the table 3.3 some preliminary results as concerns the crystal data.



Scheme 3.8. Synthesis of compounds **2** and **3**.[37]

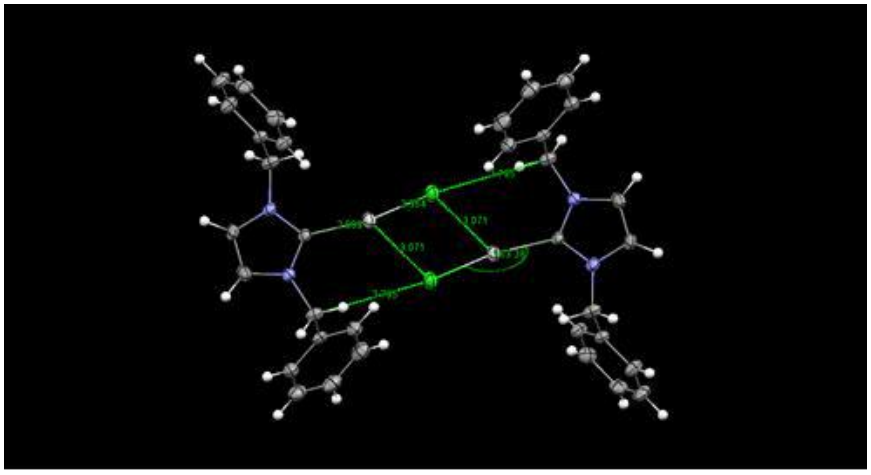
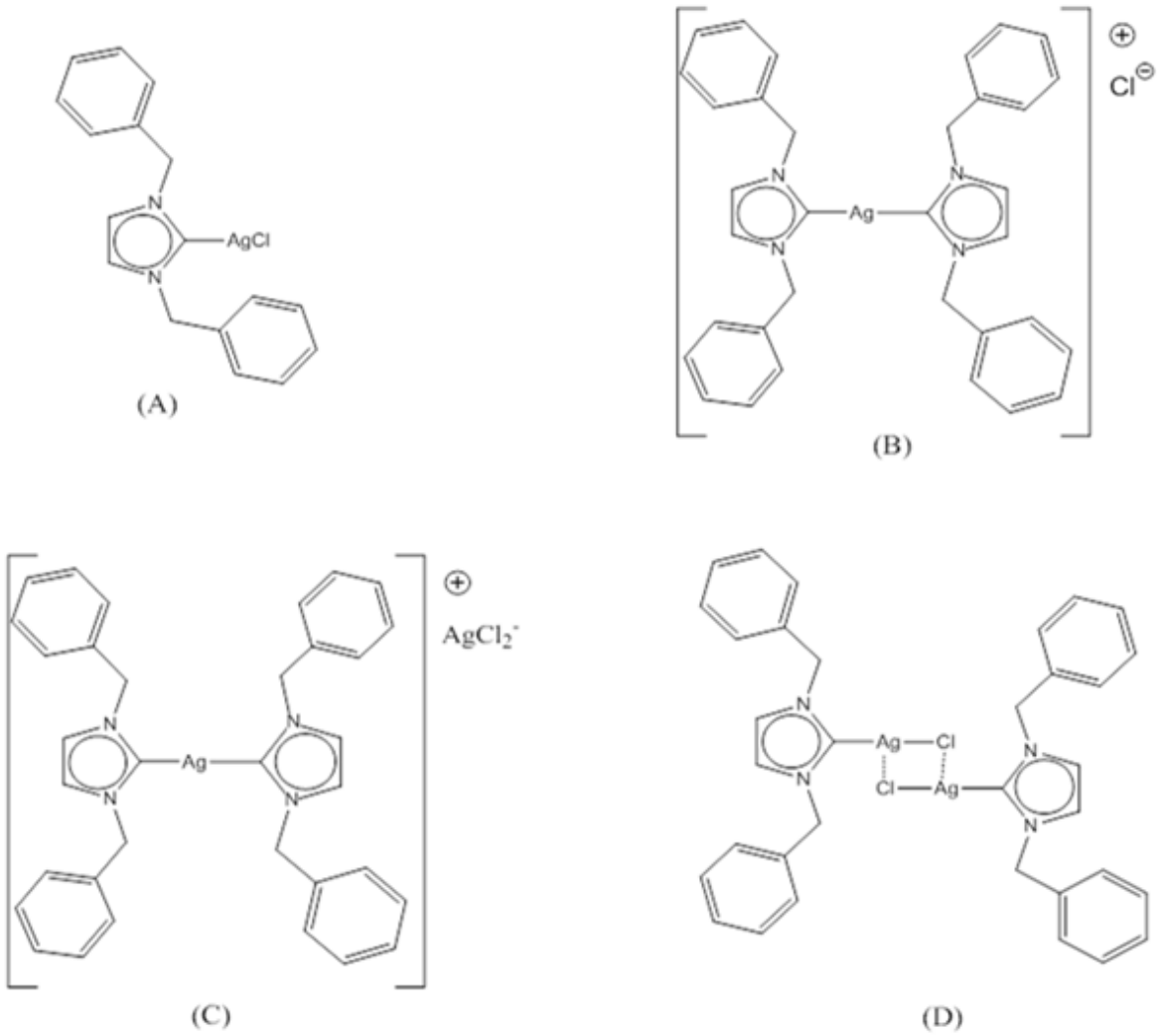


Figure 3.4. ORTEP plot of the silver carbene of 1,3-dibenzyl-imidazolyl-2-yliden ligand, compound3.

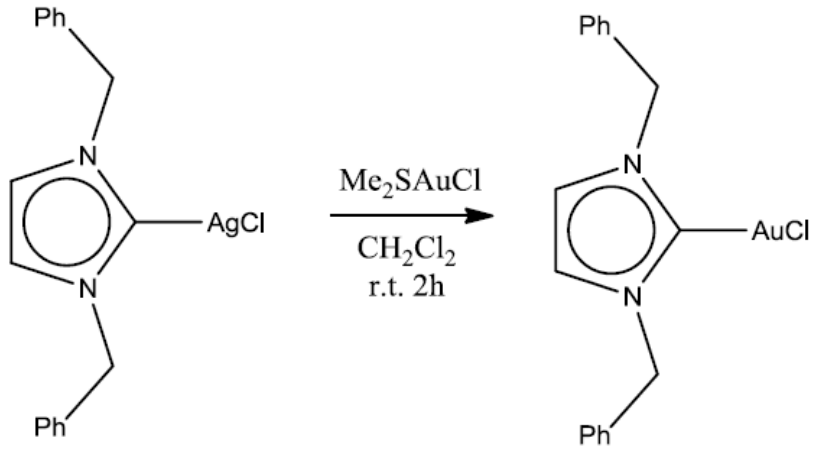
The structure of compound 3 mostly overlaps to that already published by Rourke in 2007.[38] The interpretation of the experimental data and the crystal structure is pretty crucial as the possible structures for the silver carbene can be resumed as monocarbene (A) [NHC-AgCl],[38] (B) biscarbene $[(NHC)_2Ag]^+$ $[Cl]^-$ [125]or (C) $[(NHC)_2Ag]^+$ $[AgCl_2]^-$ and also as monocarbene dimer through Ag-Ag contacts (D) $[NHC\text{-}AgCl]_2$ [38] (scheme 3.9).[113]



Scheme 3.9. *Possible nature of the carbene complexes with silver chloride.*

The structures A, C and D corresponds the same elemental analysis, different melting points (not often reported in literature), and similar IR absorptions. They could change in the ^{1}H and ^{13}C NMR chemical shifts. From literature many experimental data are available regarding symmetric or non symmetric carbene ^{13}C chemical shifts. By analysing the data already reported [112] for structure A the signal falls around 150-160 ppm ($CDCl_3$) [37], structure C at 180-189 ppm (Br, DMSO)[111] while structure D falls at 175-185 ppm (Br, $CDCl_3$) [37] depending the nature of the carbene and of the counterion (Cl, Br or other). In compound **3** the ^{13}C NMR signal falls at 180 ppm in $CDCl_3$, quite different from that reported in literature (151 ppm in the same solvent)[37] This diversity in the chemical shift might be explained by considering that in the ESI-MS spectrum, in the positive field, the peak at 605 m/z can be attributed to the bis carbene species (structure B in scheme 3.9) likely formed during a solution rearrangment. In fact these fluxional behaviours have been already detected for structure A, C and D in the ESI-MS spectrometry.[38] As concerns compound **3**, it is likely that as soon as it is dissolved in CH_3OH it rearranges to the bis-carbene species.

A general reaction scheme refers that by treating the silver carbene , compound **3**, with a gold(I) precursor such as Me_2SAuCl or with copper(I) salt the metal exchange occurs. (scheme 3.10)



***Scheme 3.10**. Transmetallation reaction affording to compound **4**.*

The transmetallation reaction with gold(I) have exceptional yield and the gold(I) carbene was obtained as the only product, compound **4.**

The gold(I) compound is stable in solution and at ^{13}C-NMR the C_2 signal falls at 172 ppm in $CDCl_3$. This result agrees with the data of ^{13}C-NMR reported in literature[114-116] but a definitive attribution of a structure cannot be chosen, because also in this case we find in the ESI-MS spectrum the signal due to the biscarbene species of type B, scheme3.9, and the actual nature of the carbene could be attribute only when the single crystal structural determination will be ultimate.

On the contrary of what observed in the case of the silver carbene, by treatment of the gold(I) carbene in CH_3OH with a solution of sodium hydroxide, the quantitative formation of the cyclotrimer is observed by monitoring the reaction by TLC, as already observed.

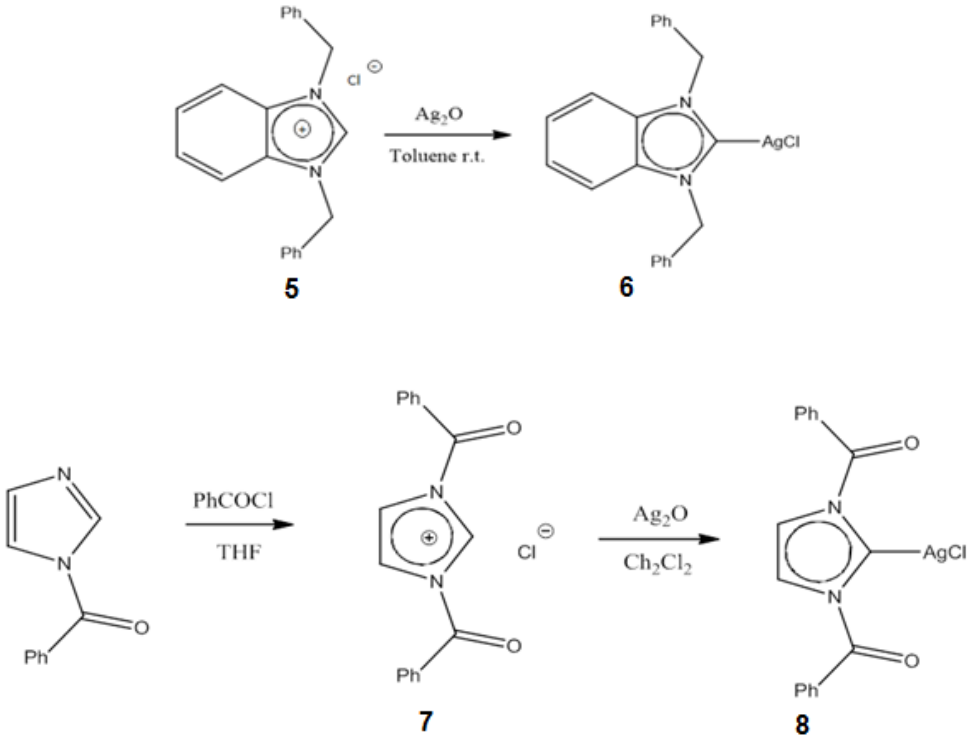
In the FIR, for compound **4,** it is possible to observe the Au-Cl stretching absorption at 331 cm^{-1},[115] while for the C_2--Au vibrational mode absorption a band at 573 cm^{-1} was observed and attribute to this bond stretching, while in compound **3** the attribution of the corresponding Ag-C stretching falls at 471 cm^{-1}, almost 98 cm^{-1} redshifted.

The transmetallation reaction of scheme 3.10 was successful in the case of gold(I) but failed when the exchanging metal was copper(I). In fact the reaction with CuCl and $[Cu(CH_3CN)_4]BF_4$ did not afford to the corresponding copper(I)carbene. The direct reaction between the imidazolium salt and $CuCF_3SO_3$, upon previous treatment with potassium tert-buthyloxide, was performed according to a procedure reported in literature [118] or by adding the Cu_2O to the imidazolium salt.[119] In both cases it was not possible to isolate the Cu(I) carbene species and a blue and pasty suspension was obtained.

The syntheses of the 4,5-Dichloro-, 4,5-Dicyano imidazolium chloride were attempted according to the method previously adopted.[37] In both cases the imidazolium salt was not obtained and the unreacted starting materials were recovered from the reaction mixture. The presence of withdrawing groups does

not allow the alkylation of the N3. As a consequence an electron rich substituted imidazole, the Benzimidazole, was successfully used.

According to scheme 3.8 also the 1,3-dibenzyl-benzoimidazolium, compound **5**, and the 1,3-dibenzoyl-imidazolium salts, compound **7,** were used to obtain the corresponding silver carbene compounds (compounds **6** and **8**, respectively). Both substituents confer planarity to the system and the presence of additional carbonyl groups in compound **6**, furnishes also additional donor atoms for binding to the silver ions.



Scheme 3.11. *reaction scheme for the formation of compound **6**, **7** and **8***

Compound **6** presents a ^{13}C NMR signal which is at higher frequencies (163.96 ppm) compare to compound **4** (171 ppm) and in compound **8** (172 ppm). In this latter case the formation of a silver derivative can be debated also by considering the band attributed to the CO stretchings in the IR spectrum. These bands are displaced if compared to starting imidazolium salt, compound **7**, from 1774 and 1728 cm^{-1} to an unique absorption at 1677 cm^{-1}. This redshift can be explain as the likely formation of the carbene silver species where the donor atoms are in some way involved for additional interactions with the central metal. In the ESI MS several bands were detected in the positive field, some of them attributable to mono-silver species not well recognized, while in negative field only the benzoate ion was detected. However the formation of the silver derivative, compound **8**, is still under debate.

3.2 Pyrazolate Au, Ag and Cu derivatives.

The chemistry of imidazolate and coinage metals in the (+1) is pretty articulate taking into consideration the wider coordination modes can be adopted. In the case of pyrazolate the coordination chemistry affording to trinuclear derivatives is simpler and the formation of the homologous series of cyclic trinuclear compounds can be achieved with classic synthesis strategies such as those described in scheme 3.2c or scheme 3.6a and 3.6b. The introduction of withdrawing groups in 3,5- or 4- position in the pyrazole ring such as CF_3 does not hamper the formation of the cyclic compounds for all the coinage metals. All the three cycles have been structurally studied and they also show thermochromic behaviour.[118]

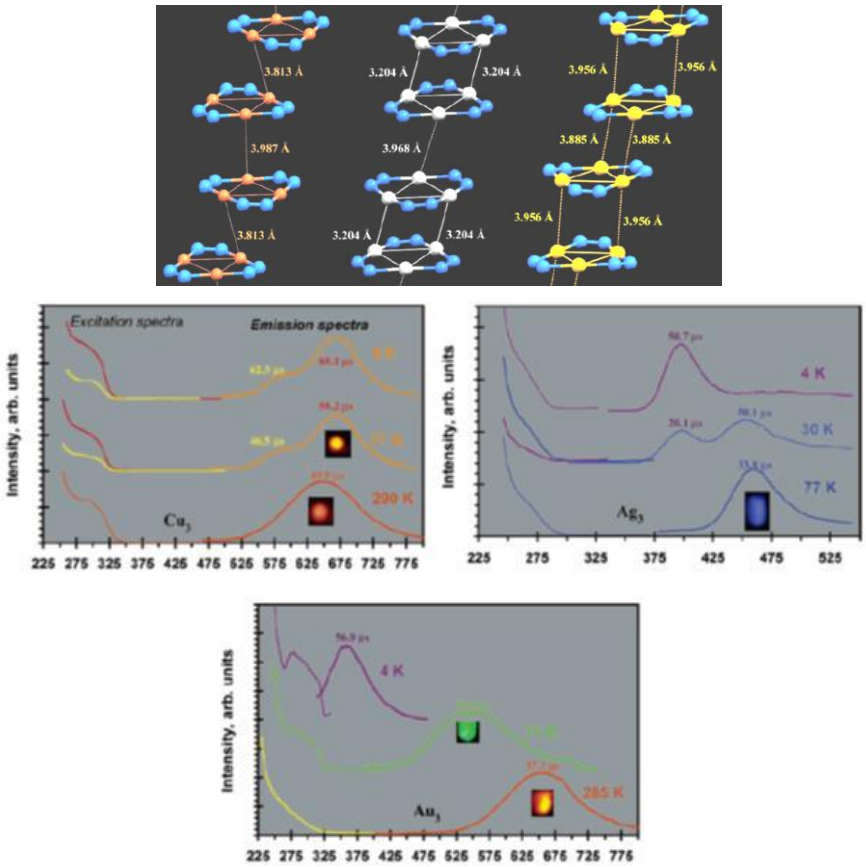
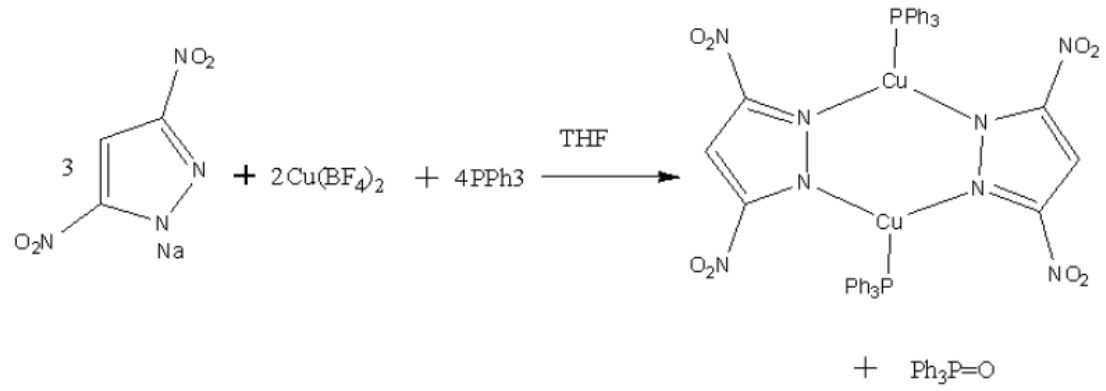


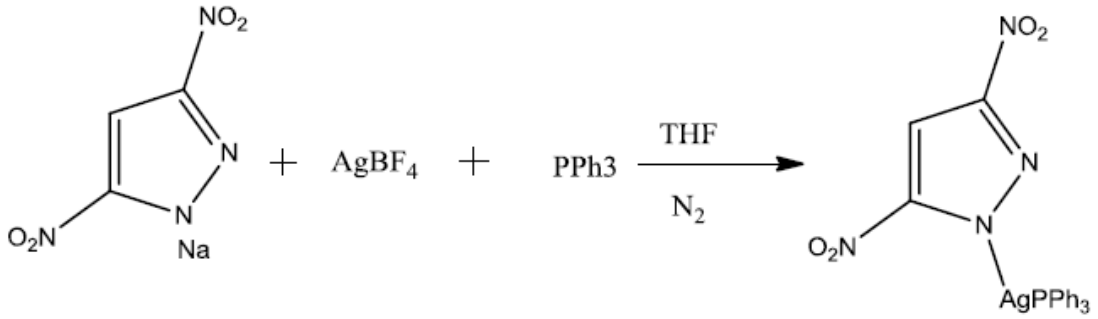
Figure 3.5. *a) Columnar packings and intermolecular metallophilic interactions for compounds [Cu-3,5-pz$(CF_3)_2]_3$ (left), [Ag-3,5-pz$(CF_3)_2]_3$ (central), [Au-3,5-pz$(CF_3)_2]_3$ (right). b) Thermochoromic emission spectra for Cu_3, Ag_3 and Au_3 solid state at different temperatures.*

The employment of a pyrazole having in 3,5 positions the NO_2 groups should afford to a very similar coordination chemistry. Actually the formation of the silver trinuclear compound was performed according to the scheme 3.3b.[109,110] However when the synthesis of Au(I) or Cu(I) was approached according to the classic methods, no cycles were obtained and the kinetically and thermodynamically stable mononuclear derivatives were obtained. The gold(I) compounds [(3,5-pz$(NO_2)_2$-AuPPh_3] as well as the congener [(3,5-pz$(CF_3)_2$-AuPPh_3] have been already reported.[120] The conversion of [(3,5-

$pz(NO_2)_2$-$AuPPh_3$] to the cycle by treating with hexane, oxidative stressing of the phosphane ligand or by treating with coordinating base, was not successful and it did not afford to any cyclization. Also by using more labile gold(I) precursors such as $Ph_3AsAuCl$ or Me_2SAuCl the cycle was never obtained. The substitution of CF_3 with NO_2 introduces a higher stability of the mononuclear derivative and the lack of cyclization is likely due to a poorer donor ability of the N^2 of the pyrazole ring or to resonance structures of the pyrazolate which are not favourable for the cyclization. This last aspect is underlined also by the fact that the formation of the cyclic trinuclear copper(I) derivative has never obtained following all the synthetic strategies above mentioned (scheme 3.5 and 3.6). Only by reacting the 3,5-dinitropyrazolate salt with $Cu(BF_4)_2$ in the presence of a co-ligand such as a phosphane (acting also as reducing agent) compound **9** was isolated in good yield (Scheme 3.12)



a)



b)

Scheme 3.12. *Reaction scheme for compound* ***9*** *(a) and* ***10*** *(b).*

The characterization of compound **9** was performed by elemental analysis, ^1H and ^{31}P NMR, ESI MS and IR. From these data the formation of a compound where the phosphane is coordinated to a metal cation is clear as in the ^{31}P NMR a signal at 3.76 ppm is present as well as in the IR spectrum the peak at 1097 cm^{-1} is typical for P-quaternary carbon stretching. Moreover the C_4-H stretching band in compound **9** falls at 3154 cm^{-1}, 14 cm^{-1} blushifted if compared to the cyclic silver derivative [μ-N,N-3,5-$pz(NO_2)_2$-Ag]$_3$ (3140 cm^{-1}) and 14 cm^{-1} redshifted if compared to the [(3,5-$pz(NO_2)_2$-$AuPPh_3$] at 3168

cm^{-1}. In the ESI MS peaks due to the $[Cu(PPh_3)_2]^+$ were detected in positive field. The final evidence of the nature of this compound came out from the X-ray Crystal structure determination. The ortep plot of the structure of compound **9** is reported in figure 3.6 and the crystal data in table 3.4.

Representative bond distances and angle in Table 3.5. The dinuclear nature of compound $[Cu\text{-}(3,5\text{-}(NO_2)_2pz)(PPh_3)]_2$ has been evidenced by single crystal X Ray diffraction analysis. Each copper atom is trigonally coordinated considering the two nitrogen atoms of the bridging ligands and the phosphorous atom of the phosphane molecule. The coordination around the copper atoms deviates significantly from the planarity being Cu1 and Cu2 out of the pertinent coordination plane of 0.1924(4) and 0.2674(4) Å respectively. The six member Cu-[N-N]2-Cu ring presents a boat conformation, but considering that the copper atoms lie out of the pyrazolate average planes with deviations spanning from a minimum of 0.0231(4) Å for Cu1 with respect to $N_5N_6C_4C_5C_6$ ring up to 0.3376(4) for Cu2 with respect to $N_1N_2C_1C_2C_3$ ring, the boat conformation results slightly twisted. The crystal packing of the compound is built up by a strong network of Van der Waals interactions between the nitro groups and between the nitro groups and the nitrogen atoms of the pyrazolate ring of adjacent molecules.

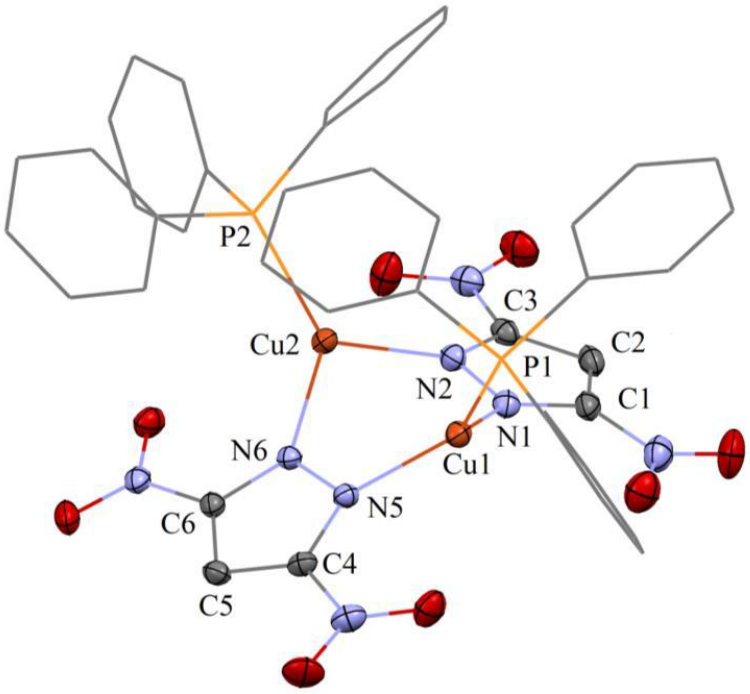
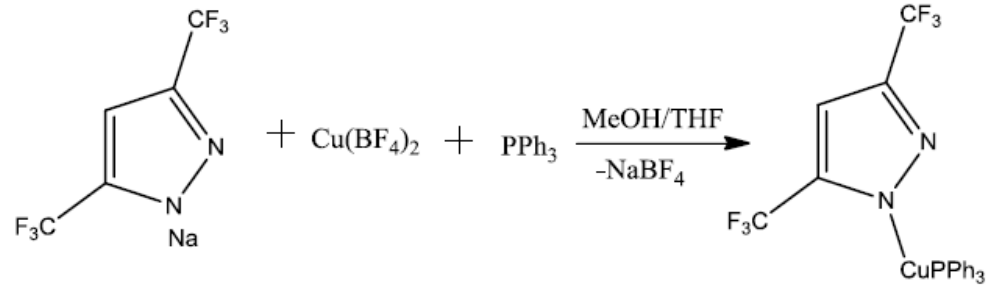


Figure 3.6. *Ortep view of $[Cu\text{-}(3,5\text{-}(NO_2)2pz)(PPh_3)]_2$, compound **9**, phosphine ligands have been drawn in wireframe model. Ellipsoids when shown, are at their 30% level.*

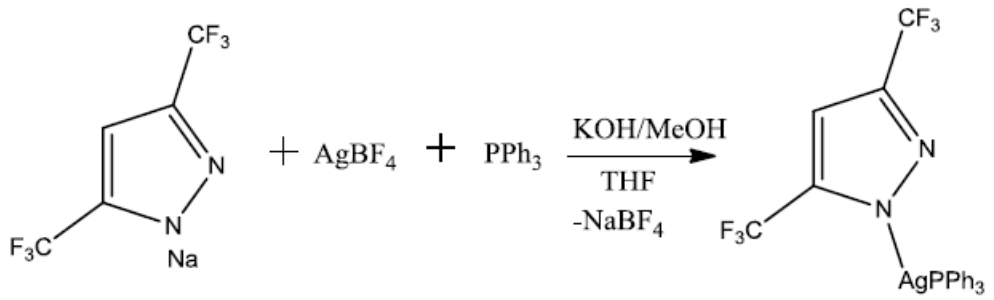
The reaction of the 3,5-$(NO_2)_2$pz sodium salt with silver tetrafluoborate affords to the trinuclear cycle, but in the presence of a coordinating ligand such as the PPh_3, the mononuclear compound **10** can be obtained.(Scheme 3.12b) The mononuclear nature of this compound can be attributed by the analysis of the VT ^{31}P NMR spectra. At room temperature in CD_2Cl_2 two broad signals appear, by lowering the temperature at 233°K a sharp double doublets appear due to the one bond coupling of ^{31}P-^{109}Ag and ^{31}P-^{107}Ag with a ratio of the coupling constant equal to 1.15 and values typical for mononuclear of

structure. The IR C_4-H stretching band falls at 3155 cm^{-1} very close by to the one already mentioned above for compound **9** (3154 cm^{-1}). We can't discuss these absorptions merely according to the Pauling electronegativity values (Au 2.54, Ag 1.93 and Cu 1.9) of the central metal, as the silver and copper derivatives show similar absorptions but in the case of gold we should observe a redshift instead of a blueshift. If we compare the values of the IR absorption due to the P-C quaternary bond we can observe that none large shift is present. It is clear that upon coordination we have some other electronic delocalization effects to take place.

The substitution of the NO_2 groups in positions 3 and 5 with CF_3 in the pyrazole and the further treatment with the corresponding metal salts, leads to the formation of the copper and silver compounds **11** and **12.** (scheme 3.13a and 3.12b respectively) By comparing the ^{31}P NMR spectra for **9** and **11**, having both as central metal copper(I), we observe a high frequencies shift in the last case (3.76 ppm for **9** and -2.29 ppm for **11**). The C_4-H band falls at 3141 cm^{-1} if compared with compound 9 (3154 cm^{-1}) with a redshift of 13 cm^{-1}. In compound **12** we observe the same trend of the redshift by comparing compound **10** and **12**, with a shift of 25 cm^{-1} (3155 cm^{-1} compound **10** and 3130 cm^{-1} in compound **12**). In the ESI MS for compound **11**, in addition to the $[Cu(PPh_3)_2]^+$ already observed for compound **9**, also the semi oxidized product was obtained such as $[Cu(PPh_3)(PPh_3{=}O]^+$ at 587 and 605 m/z, respectively.



a)



b)

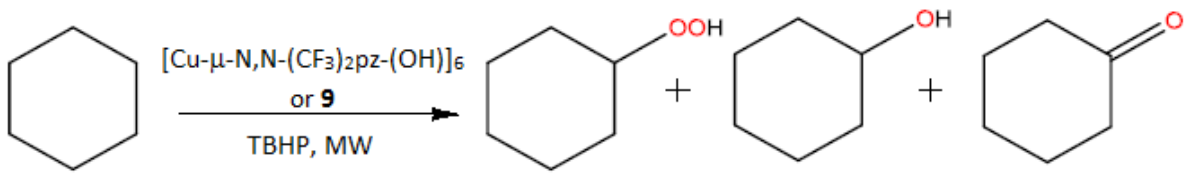
Scheme 3.13 *.reaction scheme of the formation of compound* ***11*** *(a) and* ***12*** *(b).*

3.3 Catalytic studies.

Compound **9** was tested also as catalyst for the peroxidation of alkane, according to a fertile collaboration with Profssa Martins and professor
Pombeiro of Istituto Superior Tecnico at Lisbon in Portugal to whom I am very grateful for the preliminary data I could insert in this thesis.
Compound **9** was studied comparatively with an hexanuclear cyclic copper(I) compound having as bridging ligand the 3,5-$(CF_3)_2$pyrazolate and hydroxyl groups. The molecular structure of this latter compound resembles those already published by Mohamed et al.[121] In this [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$ compound a highly hydrated cavity is present on the contrary of what already observed in the previous compounds were Cl^-, Br^-, I^- and NO_2^- were found as encapsulated anions.

3.3.1 Catalytic studies on compound 9 and [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$.

Compounds [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$ and **9** act as very effective homogeneous catalysts towards the neat microwave (MW) assisted peroxidative (with aq. *tert*-butyl hydroperoxide, TBHP) oxidation of cyclohexane to cyclohexanol and cyclohexanone via formation of cyclohexyl hydroperoxide (CyOOH) as primary product. This further evolves in a mixture of cyclohexanol and cyclohexanone (final products, Scheme 3.14). The formation of CyOOH was proved by using the method purposed by Shul'pin.[122] The addition of PPh_3 prior to the GC analysis of the products resulted in a marked increase of the amount of cyclohexanol (due to the reduction of CyOOH by PPh_3, with the formation of phosphane oxide) and in a corresponding decrease of cyclohexanone (Scheme 3.14).



Scheme 3.14. *Microwave-assisted neat oxidation of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone with tert-butyl hydroperoxide catalysed by the Cu complexes this [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$ or **9**.*

A very high yield, up to 58% (**9**) or 51% ([Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$) of oxygenated products, is obtained at optimized conditions: 0.5 h (**9**) or 1.5 h ([Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$) of MW irradiation at 100°C (see Figure 3.7 and Table 3.6 in the appendix), using 0.2% molar ratio of copper catalyst relatively to the substrate, in the presence of 2,2,6,6-tetramethyl-piperidinyloxyl radical (TEMPO, 2.5% molar ratio *vs*. substrate).

For the Cu(II) catalytic system, the amount of catalyst plays a significant role as depicted in Figures 3.7 and 3.8. The increase from 1 to 5 µmol of **9** on the reaction medium leads to a yield increment from 22 to 37%, whereas 10 µmol of **9** allow to reach the maximum yield faster (in 1 hour, instead of the 2 hours of MW irradiation needed for 5 µmol of **9**). The effect of the quantity of catalyst on the yield of products is not so evident for the Cu(I) system ([Cu-µ-N,N-$(CF_3)_2$pz-$(OH)]_6$). Moreover, addition of TEMPO to the reaction mixture allows the maximum yield of cyclohexanol and cyclohexanone to be achieved after the very short MW irradiation time of 0.5 or 1 h, for 10 or 5 µmol of **9**, respectively (Figure 3.7). The same behaviour is observed for the Cu(I) catalytic system.

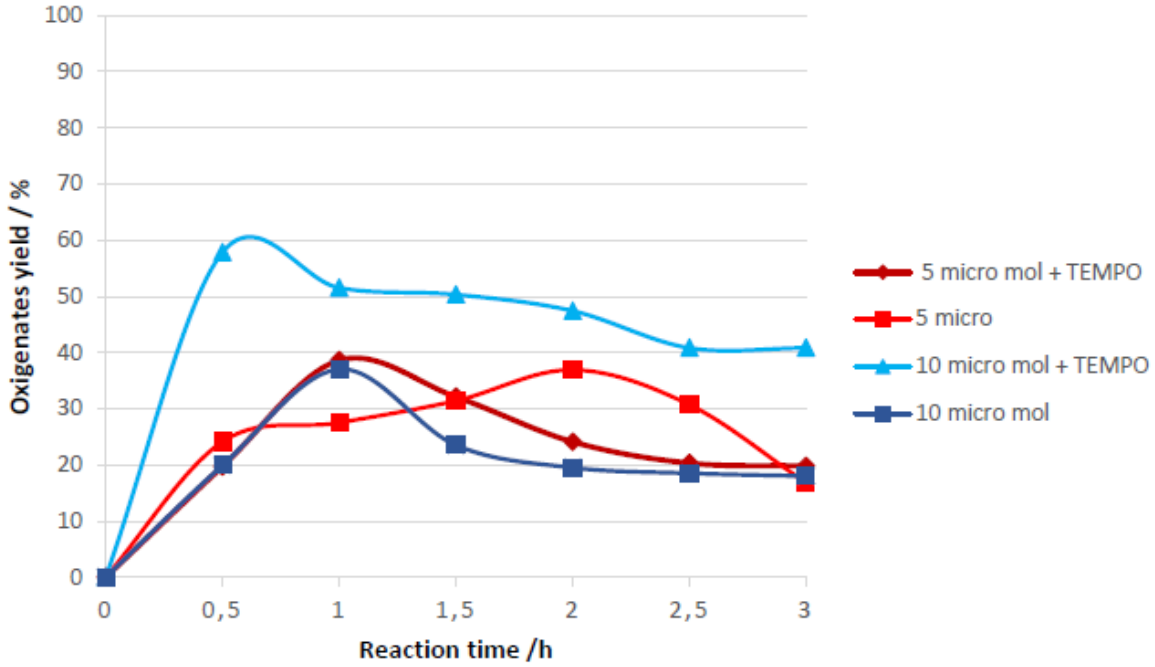


***Figure 3.7**. Effect of the reaction time, catalyst (**9**) amount and TEMPO additive on the yield of cyclohexanol and cyclohexanone obtained by microwave-assisted neat oxidation of cyclohexane with THBP.*

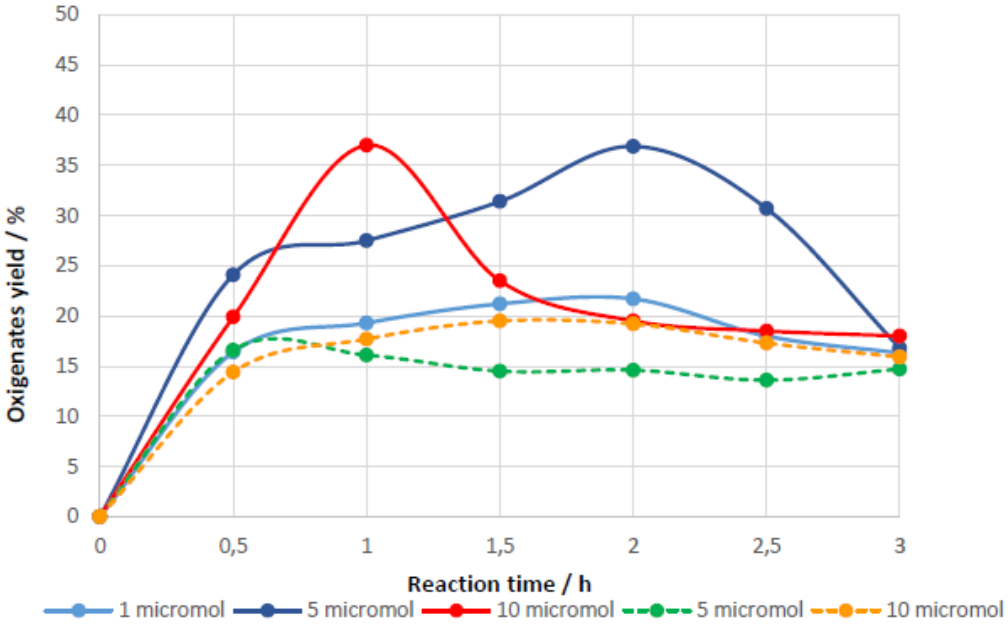


Figure 3.8. *Effect of the reaction time and catalyst (**9** or [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$) amount on the yield of cyclohexanol and cyclohexanone obtained by additive-free microwave-assisted neat oxidation of cyclohexane with THBP.*

The catalytic activity of [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$ and **9** is also sensitive to the temperature as depicted in figure 3.9 for **9**.

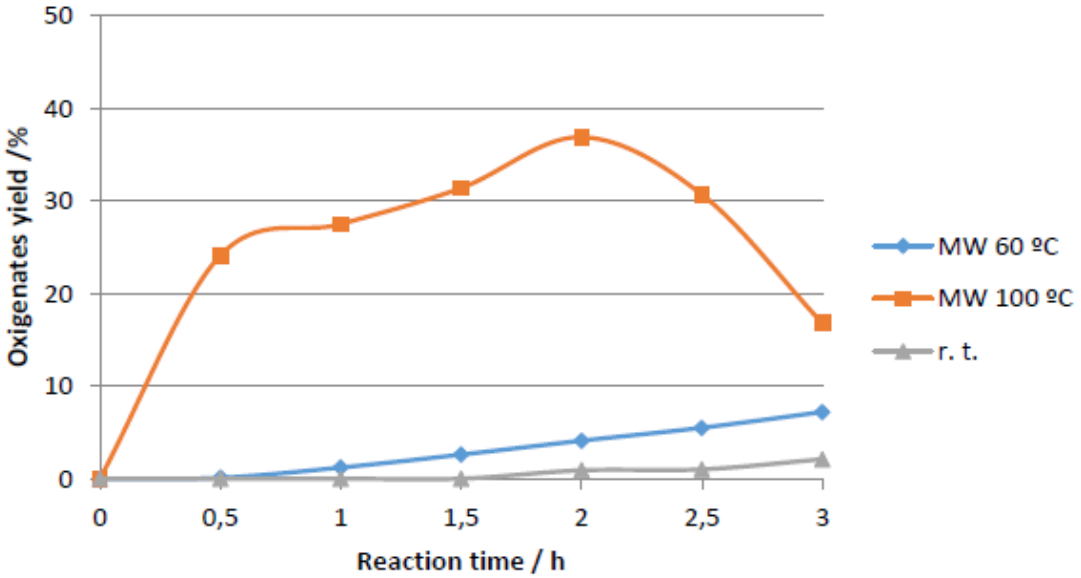


Figure 3.9. *Effect of the reaction temperature on the yield of cyclohexanol and cyclohexanone obtained by additive-free neat oxidation of cyclohexane with THBP, catalyzed by **9** (0.1% molar vs. substrate).*

The promoting role of certain acids, in particular pyrazine carboxylic acid (Hpca), on the catalytic oxidation of various cycloalkanes catalyzed by metal complexes is well known.[123] In our catalytic systems, the presence of Hpca has a strong inhibiting effect on the catalytic activity of both this [Cu-μ-N,N-$(CF_3)_2$pz-(OH)]$_6$ and **9** (Figure 3.10). A similiar behavior was previously found.[124]

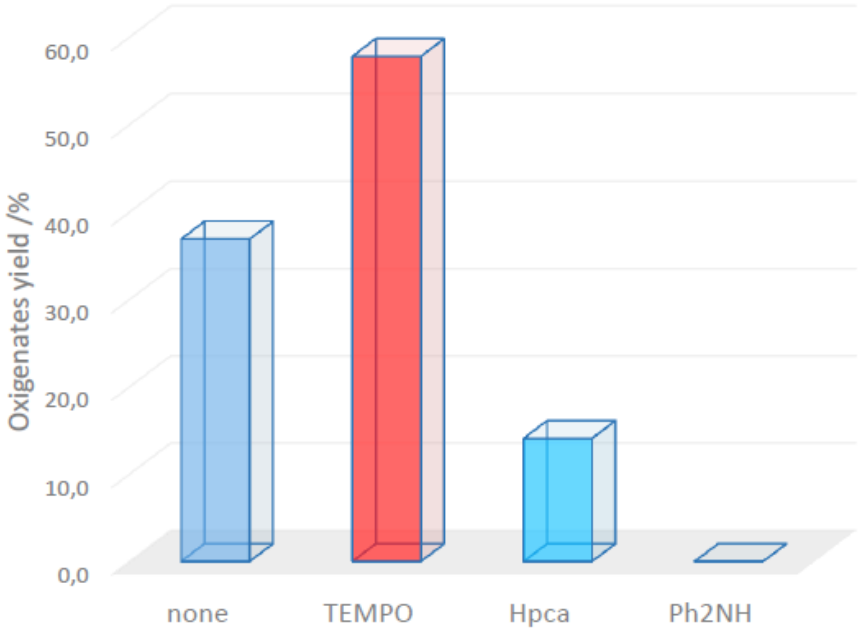


Figure 3.10. *Effect of different additives on the the yield of cyclohexanol and cyclohexanone obtained by microwave-assisted neat oxidation of cyclohexane with THBP, catalyzed by* ***9*** *(0.1% molar vs. substrate).*

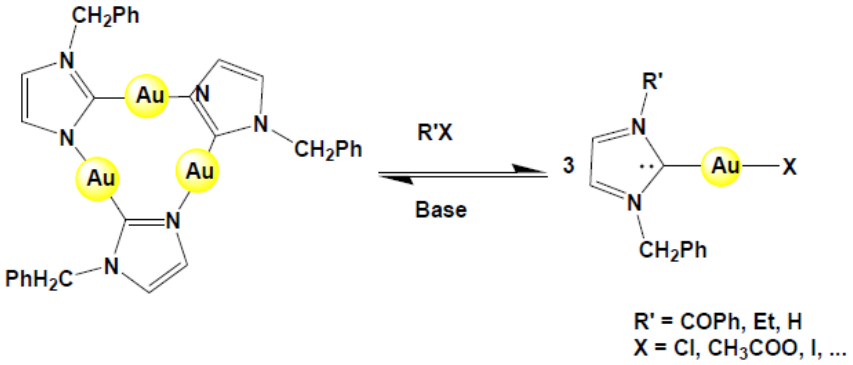
Addition of a radical trap (*e.g.*, Ph_2NH, Figure 3.10) to the reaction mixture results in the suppression of the catalytic activity. This behaviour, along with the formation of cyclohexyl hydroperoxide (typical intermediate product in radical-type reactions) and the promotion detected by addition of TEMPO, supports the hypothesis of a free-radical mechanism for the cyclohexane oxidation carried out in this study. All the data are collected in table 3.6.

4. CONCLUSIONS

In this chemistry project the following aims have been achieved:

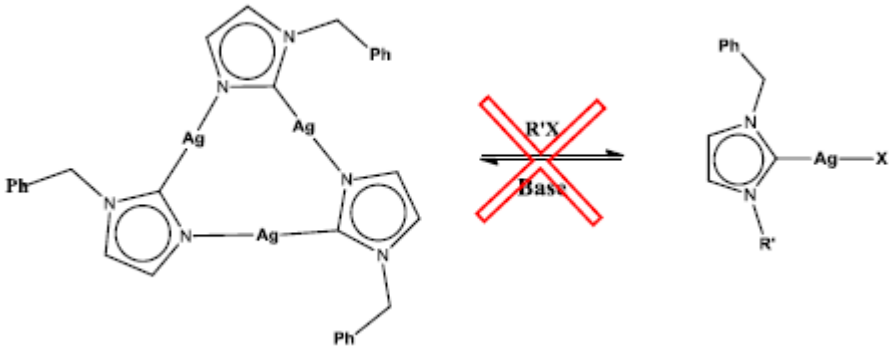
1. The synthesis and the structural characterization of a new trinuclear cyclic silver(I) derivative having as bridging ligand the 1-benzylimidazole has been performed.

2. This new compound has been treated with alkyl or acyl chlorides to see if it resembles the reactivity of the gold(I) analogous.



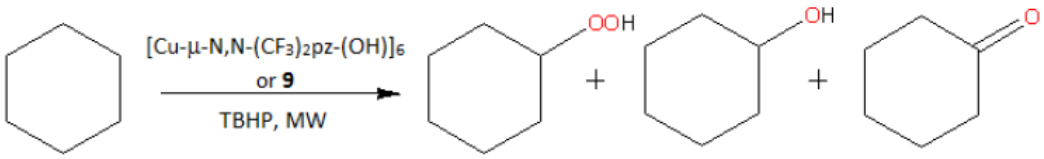
3. For a better understanding of this reactivity also the silver and gold(I) carbene derivatives have been synthesized with 1,3-dibenzylimidazolium and 1,3-dibenzyl-benzoimidazolium salts. The carbene derivatives were obtained in good yield and crystals for the X-ray crystal structure determination were obtained. In addition, the synthesis of a new carbene species was attempted with imidazoles containing withdrawing groups without success as expected.

4. As a conclusion of this first part we can assess that the chemistry of trinuclear cyclotrimer of silver(I) does not resemble the one of the gold(I). The fact that silver cannot achieve higher oxidation states limits the oxidation of the cyclotrimer metal centres by addition of alkyl or acyl halides to afford the consequent carbene species by the reductive elimination. On the other hand, by treating the carbene silver(I) derivatives obtained by alternative routes, the reaction with weak or strong base does not give back the cyclotrimer. So as final assessment we can conclude that even though silver and gold cyclotrimers possess very similar molecular structure, the chemistry of these trinuclear derivatives on the regards of reversible oxidation/reduction is strongly affected by the nature of the central metal. Moreover, in this work it has been proved that the oxidation to the central metal is the key step to obtain carbene derivatives from cyclotrimers.



5. The chemistry of pyrazoles having withdrawing groups such as NO2 and CF3, on the regards of copper centres is unsuccessful if the target is to obtain cyclotrimers and, in a special way, if the ligand is 3,5-dinitropyrazole. Extending the synthesis study to the synthesis of intermediate species containing phosphane as co-ligand, new monomeric Ag(I) and Cu(I) compounds have been isolated in optimal yield and characterized by analytical and spectroscopic techniques.

6. The copper compound with 3,5-(dinitro)pyrazole and PPh3 as coligand, [Cu-N,N-(3,5(NO2)2pz)-PPh3]2, has been used for catalytic studies on the regard of the MW assisted peroxidation of cycloalkane to cyclohexyl alcohol and cyclohexanone via cyclohexylperoxide. The use of this catalyst in this reaction affords to better yields (up to 58%) and shorter reaction time (6h for the processes reported in literature and a maximum of 2h for our test) depending on the catalyst amount and on the use of TEMPO.



The catalytic activity of [Cu-N,N-(3,5(NO2)2pz)-PPh3]2 was compared to that of an hexanuclear Cu(II) derivative having as bridging ligand the 3,5-(CF3)2pyrazole. Between them the [Cu-N,N-(3,5(NO2)2pz)-PPh3]2 shows better activity both in terms of yield of conversion as well as in time of conversion.

5. EXPERIMENTAL PART

The analytical samples were stored at room temperature, the Cu(I) derivatives under nitrogen atmosphere. Samples for microanalysis were dried under vacuum (20°C, 0.1 torr) till constant weight. C, H and N elemental analyses were performed by the CARLO-ERBA ELEMENTAL ANALYSIS mod. 1106 mycroanalyser at University of Camerino. Infrared spectra (4000 □ 100 cm^{-1}) were recorded with PERKIN-ELMER SYSTEM 2000 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on an Oxford-400 Varian spectrometer. Chemical shifts, in ppm, for ^{1}H NMR spectra are relative to internal Me_4Si. Melting points were determined with an instrument ELECTROTHERMAL ENGINEERING LTD Mod.9100. Mass spectra (ESI-MS) were obtained for negative ions through HP Series 1100 MSD spectrometer. Solutions (ca. 0.1 mM) were prepared using MeOH as solvent. The experimental conditions were as following: the organic phase flow was 300 µL/min, the drying gas flow (N_2) was 10 L/min, the nebulization pressure was 30 psig, the temperature of the drying gas was 350°C, the value for the fragmentor was fixed to 30, the acquisition of the data was performed by scanning in ranges from 500 to 2000 amu.

5.1 Crystal structure of compound 1.

Data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[126] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[127] which corrects for Lp and decay. Absorption corrections were applied using SADABS[131] supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[128] program and refined by least squares method on F^2, SHELXL-97,[129] incorporated in SHELXTL-PC V 5.10.[130]
The structure was solved in the space group P1 (# 2) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsoids.

Synthesis of [Ag-C^2,N^3-(1-benzyl-imidazole)]$_3$, compound 1.

To a solution of 1-benzylimidazole (0.528 g, 3.3 x10^{-3} mol) in 15 ml of THF, 1.3 ml (3.3x10^{-3}) of BuLi were added (2.5 ml in hexane) under nitrogen atmosphere. The solution was stirred for 30 minutes at -40°C. After the temperature was warmed up at -10°C and was stirrer for other 30 minutes. After that 169.87 g, of $AgNO_3$ (3.3x10^{-3}). The reaction was stirred for 30 minutes at room temperature in the darkness. The solution was evaporated to dryness and the extractions with hot toluene (6 x 20 ml) were performed. To the toluene solution 4 ml of hexane were added and a white solid was obtained with a yield of 58%. The sample was further purified with crystallization in DCM/Hexane.

^{1}H-NMR ($CDCl_3$) δ 7.4-7.2(m.5H); 7.02(s, 1H); 6.98(s, 1H); 5.31(s, 2H)
Elemental analysis for$C_{30}H_{27}N_6Ag_3$ calcd %: C 45.31, N 10.57, H 3.42. found %: C 45.05, N 10.39, H 3.61
IR (cm^{-1}): 3150 (w), 2853 (w), 1480(w),1405(w), 1344(m), 1307(m), 1266(s), 1168(ms), 1154(ms), 1125(m), 1099(m), 1074(m), 1028(m), 965(w), 895(wm), 846(w), 823(wm), 767(m), 695(m), 668(m), 630(m), 575(m), 459(w), 400(m) cm^{-1}

Synthesis of 1,3-dibenzyl-imidazolium chloride, Compound 2.

1.6 g of 1-benzylimidazole (10.1 mmol) were dissolved in 10 mL of toluene and the solution was added dropwise at 0°C to liquid 1-benzyl chloride (1.06 g: 8.37 mmol) dissolved in 40 mL of toluene. The reaction mixture was stirred for 35 minutes. The solution was evaporated to dryness to obtain an oily product. After washing with cyclohexane and further with ethyl acetate, 1.877 g of an ivory product was obtained. Yield 80 %.
^{1}H NMR ($CDCl_3$, r. t., □) : 10.86 (s, 1H), 7.42 (m, 4H), 7.29 (m, 8H), 5.5 (s, 4H).
^{13}C NMR ($CDCl_3$, r. t., □) : 144.94, 137.66, 129.37, 128.4, 128.07, 123,07, 122.26, 120,19, 111.39, 48.29.
MIR (cm^{-1}):3442 (m), 3376 (m), 3244 (w-m), 3152 (w-m), 3133 (m-w), 3075 (m), 2999 (m),2111.2 (w), 1973 (w), 1832 (w), 1749 (w), 1623 (m), 1586 (w), 1566 (m), 1553 (s), 1496 (m), 1459 (m-s), 1444(s), 1426 (w), 1407 (w), 1374 (m), 1352 (m), 1301 (w), 1278 (m), 1234 (m), 1148 (vs), 1109 (m), 1073 (m), 1026 (m), 951 (w), 929 (w), 907 (w), 877 (w), 806 (s), 779 (s), 751 (m), 733 (m), 712 (vs).
FIR (cm^{-1}) : 664 (m), 633 (s), 615.6 (m), 588 (m), 573 (s), 523.6 (s. br), 476 (m), 464.7 (m), 347 (m), 310 (w). 172 (w), 119 (vs).
ESI(-) (CH_3OH) m/z, %: 605.2 (100), 319 (100), 248 (22). ESI(+) (CH_3OH) m/z %: 533 (24) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Cl]$^+$, 249 (100) [(1,3-dibenzyl-imidazolium)]$^+$.
Elemental analysis for $C_{17}H_{17}ClN_2$, calcd %: C 71.70; N 9.84, H 6.02. Found %: C 70.43; N 10.20, H 6.32.

Synthesis of [1,3-dibenzyl-imidazolyl-2-yl-silver chloride]$_2$, compound 3.

250 mg of the 1,3-dibenzyl-imidazolium chloride salt (0.88 mmol) were dissolved in 21.6 mL of CH_2Cl_2. To this solution solid Ag_2O (102 mg; 0.44 mmol) was added. The grey suspension was stirred for two

hours at room temperature then CH_2Cl_2 was added till most of the precipitate dissolved. After filtration over a celite bed 20 mL of hexane were added. The solution was let to crystallize. 190 mg of a white microcrystalline product was obtained. Yield 51 %.

^{1}H NMR ($CDCl_3$, r. t., □) : 7.38 (m, 6H), 7.24 (4H), 6.92 (m, 2H), 5.21 (s, 4H).

^{13}C NMR ($CDCl_3$, r. t., □) :180.64 (carbene C2), 135.5, 128.9, 128, 121.7, 55.9 (s).

MIR (cm^{-1}): 3162 (w-m), 3132 (m-w), 3100 (m), 2948 (m), 1963 (w), 1887 (w), 1817 (w), 1671(m), 1602 (w), 1584 (w), 1562 (m), 1494 (m), 1450.5 (s), 1413 (m), 1413(m), 1358 (m), 1335 (w), 1309.6 (w), 1228 (s), 1204 (w), 1181 (w), 1159.6 (m), 1152 (m), 1102 (m), 1076 (m), 1029 (m), 992 (vw), 960 (vw), 907 (w), 936 (w), 852 (w), 821 (s), 792 (m), 770 (m), 724 (vs), 705 (s), 697 (vs), 662 (s).

FIR (cm^{-1}): 662 (m), 613 (w), 584.6 (m), 471 (w), 459 (m), 436(m), 358 (w), 342 (w), 312 (w), 290 (m), 275 (w), 243 (m), 213 (m), 192 (w), 162 (w), 130 (w), 116.6 (w), 102 (m), 81.5 (vs), 72 (s), 53 (vs), 37 (s).

ESI(-) (CH_3OH) m/z, %: 201.1 (100). ESI(+) (CH_3OH) m/z %: 605.3 (100) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Ag]$^+$, 249 (35) [(1,3-dibenzyl-imidazolium)]$^+$.

Elemental analysis for $C_{17}H_{17}AgClN_2$, calcd %: C 52.00; N 7.13, H 4.36. Found %: 51.50; N 6.87, H 4.06.

Synthesis of [1,3-dibenzyl-imidazolyl-2-yl-gold chloride], compound 4.

50 mg of the 1,3-dibenzyl-imidazolyl-2-yl-silver chloride (0.1278 mmol) were dissolved in 3 mL of CH_2Cl_2. To this solution, a solution of Me_2SAuCl (37 mg; 0.1278 mmol) in 3 mL of CH_2Cl_2 was added. The white suspension was stirred for three hours at room temperature. The suspension was centrifuged. The solution was concentrated to half volume and 10 mL of hexane were added. The solution was let to crystallize. 62 mg of a white microcrystalline product was obtained. Yield 99%.

^{1}H NMR ($CDCl_3$, r. t., □) : 7.34 (m, 10H), 6.86 (m, 2H), 5.38 (s, 4H).

^{13}C NMR ($CDCl_3$, r. t., □) : 171.39 (s, C2), 135.15 (s), 129 (m), 121.17 (s), 55.4(s).

MIR (cm^{-1}): 3158 (w-m), 3128 (m-w), 3103 (m), 3032 (w), 2996 (m),2921 (w-m) 1977 (w), 1954 (w), 1887 (w), 1826 (w), 1804 (w), 1685 (m), 1603 (w), 1584 (w), 1576 (m), 1563 (m),1496 (m), 1450.6 (s), 1419 (m), 1357 (m), 1330 (w), 1311 (w), 1235 (s), 1218 (w), 1205 (w), 1185 (w), 1162 (m), 1075 (m), 1033 (m), 995 (vw), 971 (vw), 950.5(w), 906 (w), 936 (w), 855 (w), 844 (s), 823 (w), 791 (m), 766 (m), 722 (vs), 709 (s), 693 (vs), 677 (s).

FIR (cm^{-1}): 593.6 (m), 572.9 (m), 511.5 (w), 456.7 (m, br), 406 (w), 390 (vw), 380 (w), 362 (w), 340 (s), 319 (s), 293 (m), 285 (w), 271.7 (m), 262 (m), 240 (m), 218 (m), 198 (vw), 191 (w), 163.7 (w), 143.7 (vw), 137 (vw), 129 (w), 108 (s), 92.6 (m), 84.8 (m), 66 (m), 58 (m), 52 (m), 46 (m-s), 33 (m).

ESI(-) (CH_3OH) m/z, %: 515 (100) [1,3-dibenzyl-2yl-Au + 2 Cl]$^-$, 393 (62), 365 (51), 235 (42), 117 (48).

ESI(+) (CH_3OH) m/z %: 693.3 (100) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Au]$^+$, 763 (35). 249 (18) [(1,3-dibenzyl-imidazolium)]$^+$.

Elemental analysis for $C_{17}H_{16}AuClN_2$, calcd %: C 42.37; H 3.35, N 5.83. Found %: C 43.01; H 4.02, N 6.32.

Synthesis of 1,3-dibenzyl-benzoimidazolium chloride, compound 5.

3.0 g of benzoimidazole (2.5 x 10^{-2} mol) were dissolved in 20 mL of acetonitrile. To this solution solid K_2CO_3 (5.26 g, 3.8 10^{-2} mol) was added and the suspension was let stir for half hour at 80°C. To the warm solution, 1-benzyl chloride (3.21 g; 2.5 x 10^{-2} mol) was added. The reaction mixture was let to react at 80°C for 24 hours. The reaction mixture was stirred for evaporated to dryness. The crude product were treated with 40 mL of CH_2Cl_2. The methylenic solution was extracted with water (20 mL x 1 time). The organic phase was treated with Na_2SO_4 and after filtration 3.28 g of the product was obtained by removing the solvent. Yield 63 %.The 1-benzyl-benzoimidazole (2.09 g, 1.0 x 10^{-2} mol) was dissolved in toluene and 1.15 mL of benzylchloride (1.265 g; 1.0 x 10^{-2} mol) were added dropwise at room temperature. The solution was warmed at 80°C for 24 hours. The solution was evaporated to dryness and the solid product was washed with ethyl acetate (20 mL x 3 times) yielding the pure 1,3-dibenzyl-benzoimidazolium chloride. Yield 68 %.

^{1}H NMR (DMSO, r. t., □) : 10.23 (s, 1H), 7.97 (m, 2H), 7.61 (m, 2H), 7.61 (m, 4H), 7.38 (m, 6H), 5.79 (s, 4H).

^{13}C NMR (DMSO, r. t., □) : 163.55 (w), 144.55 (s), 137.3, 129, 128, 127.7, 122.7, 122 (s), 119.87, 111, 48.

MIR (cm^{-1}): 3359 (m), 3126 (m-w), 3066 (m), 3034 (w), 2947 (w), 1973 (w), 1832 (w), 1768 (w), 1613 (m), 1586 (w), 1558 (m), 1494 (m), 1452 (m-s), 1442 (s), 1427 (w), 1368 (m), 1333 (m), 1286 (m), 1264 (m), 1241 (m), 1203 (w),1188 (s), 1149 (w), 1072 (m), 1029 (m), 974 (w), 934 (w), 910 (w), 887 (w), 853 (w), 834 (m), 776 (s), 766 (m), 729 (m), 695 (vs).

FIR (cm^{-1}): 675 (w), 664 (w), 566 (m), 477 (w), 449 (m), 424 (m), 403 (w), 390 (w), 371 (w), 332 (w), 295 (vw), 236(w), 218 (w), 186 (w), 164 (w), 148(w), 114 (w), 1008 (m), 90 (vs), 80 (vs).

ESI(-) (CH_3OH) m/z, %: 369 (21), 153 (100). ESI(+) (CH_3OH) m/z %: 633 (26) $[(1,3\text{-dibenzyl-benzoimidazolyl-2yl})_2\text{-Cl}]^+$, 299 (100) $[(1,3\text{-dibenzyl-benzoimidazolium})]^+$, 209 (29) $[(1\text{-benzyl-benzoimidazolyl-2yl})]^+$.

Elemental analysis for $C_{21}H_{19}ClN_2$, calcd % C 75.33; N 8.37, H 5.72. Found %: C 76.30; N 9.98, H 5.78.

Synthesis of [1,3-dibenzyl-benzoimidazolyl-2-yl-silver chloride]$_2$, compound 6.

100 mg of the 1,3-dibenzyl-benzoimidazolium chloride salt (0.298 mmol) were dissolved in 10 mL of CH_2Cl_2. To this solution solid Ag_2O (34 mg; 0.149 mmol) was added. The white-grey suspension was stirred for two hours at room temperature. To this suspension 20 mL of hexane were added. After centrifugation the solution was evaporated to dryness. The solid was dried, dissolved in CH_3OH filtered over a celite bed and dried obtaining 71 mg of an oily product. Yield 64%.

^{1}H NMR (DMSO, r. t., □) : 7.72 (m, 2H), 7.36 (12H), 5.75 (s, 4H).

^{13}C NMR ($CDCl_3$, r. t., □) : 163.96 (s), 137 (s), 134 (s), 129 (m), 128 (s), 124 (s), 113 (s), 52.6 (s).

MIR (cm^{-1}): 3062 (w), 3032 (w), 2975 (w), 2947 (w), 2918 (w), 1957 (w), 1887 (w), 1869 (w), 1818 (w), 1658 (w), 1602 (w), 1587 (w), 1557 (w), 1494 (m), 1477 (m), 1453 (s), 1442 (s), 1359 (m), 1343 (m),

1332 (m), 1278 (m), 1205 (w), 1185 (m), 1123 (m), 1079 (m), 1025 (m), 933 (vw), 902 (m), 848 (w), 852 (m), 821 (w), 785 (m), 770 (vs), 746 (vs), 727 (m), 698 (vs).

FIR (cm^{-1}): 625 (m), 578.7 (m), 451.7 (m), 408 (w), 391.8 (vw), 344.7 (w), 310 (w), 295 (m), 271 (w), 238 (m), 212 (m), 199 (vw), 184 (w), 160 (w), 147 (vw), 135 (vw), 125 (w), 102 (s), 81 (m), 66.5 (m), 48 (m-s).

ESI(-) (CH_3OH) m/z, %: 201.1 (100). ESI(+) (CH_3OH) m/z %: 605.3 (100) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Ag]$^+$, 249 (35) [(1,3-dibenzyl-imidazolium)]$^+$.

Elemental analysis for $C_{21}H_{18}AgClN_2$ +CH_2Cl_2, calcd %: C 50.17; N 5.32, H 3.83. Found %: 51.50; N 6.87, H 4.06.

Synthesis of 1,3-dibenzoyl-imidazolium chloride and 1,3-dibenzoyl-imidazolium-silver chloride, compound 7 and compound 8.

4.54 g of imidazole (6.7 x 10^{-2} mol) were dissolved in 200 mL of toluene. To this solution a solution containing 20 mL of toluene and benzoyl chloride (4.69 g, 3.87 mL; 3.3 x 10^{-2} mol) was added at 8°C. The solution was let to stir for 16 hours at room temperature. A white precipitate of imidazolium salt was obtained. The suspension was filtered over a gooch and the solution was
evaporated to dryness. An oil was obtained (compound **7**). The oil was dissolved in THF and 2.48 g of benzoyl chloride were added (2.74 mL; 1.8 x 10^{-2} mol). The solution was stirred overnight and evaporated to dryness. A green oil was obtained. 630 mg (0.23 x 10^{-2} mol) of this oil were treated with 20 mL of CH_2Cl_2 and 263 mg of Ag_2O (0.1137 x 10^{-2} mol). The suspension was stirred for two hours. The suspension was filtered over a celite bed. The solution was concentrated to dryness. A waxy solid was obtained. After treatment with diethyl ether a white crystalline solid was obtained. Yield 83 %.

Compound **7**: MIR (cm^{-1}): sp28 3148.7 (w), 3061.9 (w), 3038.5 (w), 2915.8(w), 2553 (w), 1774.7 (s), 1728.5 (s), 1667 (w), 1597.8 (m-w), 1579.8(m-w), 15156 (w), 1490 (w), 1449.5 (s), 1388 (w), 1370 (w), 1343 (w), 1309 (m-s), 1279 (s), 1208 (vs), 1173 (s), 1097 (m-w), 1072 (s), 1038 (s), 1016(s), 996.5 (s), 938 (w), 892.9 (s), 871.7 (s), 777 (m-s), 708 (s), 688.9 (s), 673.5 (s).

Compound **8**: ^{1}H NMR (CD_2Cl_2, r. t., □) : 10.08 (s, broad), 8.6 (s, 1H), 8.13 (m, 4H), 7.61 (m, 2H), 7.51 (m, 4H), 7.32 (m, 1H)

^{13}C NMR (CD_2Cl_2, r. t., □): 172 (s), 134 (s), 130 (s), 128(m).

MIR (cm^{-1}): 3072 (m), 3034 (w), 2881 (w), 2827 (m), 2667 (m), 2606 (w), 2555 (m), 1916 (w), 1793 (w), 1677 (vs), 1602 (s), 1582 (s), 1497 (m), 1454 (s), 1420 (s), 1323 (s), 1310 (vs), 1186 (s), 1128 (m), 1101 (m), 1073 (m), 1027 (m), 933 (w), 805 (s), 704 (s), 683 (vs), 666 (vs).

FIR (cm^{-1}): 675 (w), 664 (w), 566 (m), 477 (w), 449 (m), 424 (m), 403 (w), 390 (w), 371 (w), 332 (w), 295 (vw), 236(w), 218 (w), 186 (w), 164 (w), 148(w), 114 (w), 1008 (m), 90 (vs), 80 (vs).

ESI(-) (CH_3OH) m/z, %: 121 (100) [PhCOO]$^-$. ESI(+) (CH_3OH) m/z %: 615 (15), 571 (32) 525 (58), 481 (80), 437 (84), 393 (83), 349 (64), 282 (71), 267 (100), 203 (57), 193 (79), 161 (71), 105 (82).

Elemental analysis for$C_{17}H_{12}AgClN_2O_2$, compound **8**, Calcd %: C 48.88, N 6.68, H 2.88. Found %: C 51.36; N 5.89, H 3.51.

Synthesis of $[Cu_2(\mu\text{-}N,N\text{-}3,5\text{-}(NO_2)_2pz)_2(PPh_3)_2]$, compound 9.

To a mixture of Ph_3P (0.174 g; 0.66 mmol) and $Cu(BF_4)_2$ (0.104 g; 0.44 mmol) in dry THF, the sodium pyrazole salt (0.08 g; 0.44 mmol) was added and the suspension was stirred over night at room temperature. The orange suspension was evaporated under vacuum to give an orange solid. The solid was dissolved in dichloromethane and extracted 3 times with 10 ml water. The organic phase was dried with Na_2SO_4, filtered over a paper filter and concentrated. The solution was layered with hexane and orange crystals of **9** were recovered. Yield 78 %. M. p: 121-123°C

IR(cm^{-1}): 3154 (w), 3051.5, (w) 1586 (w), 1539.7 (s), 1492 (s), 1479 (s,sh), 1455 (m), 1436 (m), 1368 (s), 1329 (s), 1296 (m), 1222 (w), 1182 (s), 1161 (m), 1097 (s), 1076 (m), 1047 (m), 1025 (m), 1010 (w), 997 (w), 967 (m), 925 (w), 915 (w), 833 (s), 812 (s), 741 (s), 706 (vs), 691.05 (vs).
^{1}H NMR (acetone-d^6, δ): 7.58 (s, 1H), 7.39 (m, 3H), 7.32 (m, 12H).
^{31}P NMR (acetone-d^6, δ): 3.76 (s).
ESI (-) MS (CH_3CN; m/z) : 377 (100) $[(3,5(NO_2)_2pz)_2 + Cu]^-$, 157 (63) $[3,5(NO_2)_2pz]^-$; ESI (+) MS (CH_3CN; m/z) : 603 (24), 587 (100) $[PPh_3)_2 + Cu]^+$; 366 (61).
Elemental analysis for $C_{42}H_{42}Cu_2N_8O_8P_2$, calcd %: C52.33; H3.34; N11.60; found %: C52.29, H3.38, N 11.58 (%)

Synthesis of $[Ag(\mu\text{-}N,N\text{-}3,5\text{-}(NO_2)_2pz)(PPh_3)]$, compound 10.

Ph_3P (0.067 g; 0.25 mmol) dissolved in 10 mL of dry THF, solid $AgBF_4$ was added (0.05 g; 0.25 mmol). The solution was stirred for one hour and the sodium pyrazole salt (0.05 g; 0.25 mmol) was added. The suspension was stirred over night at room temperature. The ivory suspension was evaporated under vacuum to give an ivory solid. The solid was dissolved in dichloromethane and extracted 3 times with 10 ml water. The organic phase was dried with Na_2SO_4, filtered over a paper filter and concentrated. The solution was layered with hexane and white crystals were recovered. Yield 68 %.

IR(cm^{-1}): 3155 (w), 3050, (w), 3007 (vw), 1539 (s), 1486 (s), 1449 (s,sh), 1435 (m), 1361 (s), 1328 (s), 1291 (m), 1187 (s), 1097 (s), 1074 (m), 1028 (m), 997 (w), 918 (w), 833 (s), 742 (s), 706 (vs), 691 (vs).
^{1}H NMR (acetone-d^6, δ): 7.48-7.35 (m, br, 16H).
^{31}P NMR (acetone-d^6, δ, 258K): 14.83 (dd, $^1J_{31P\text{-}107Ag}$ = 636 Hz, $^1J_{31P\text{-}109Ag}$ = 733 Hz).
ESI (-) MS (CH_3CN; m/z) : 156.9 (100) $[(3,5(NO_2)_2pz)]^-$, 376.6 (30) ; ESI (+) MS (CH_3CN; m/z) : 500.3 (37) $[AuPPh_3 + CH_3CN]$, 721 (100) $[PPh_3)_2 + Au]^+$; 935 (10) 1075 (30) $[Au(PPh_3)_2 + 3,5(NO_2)_2pz]+$.
Elemental analysis for $C_{21}H_{16}AgN_4O_4P$, calcd %: C 47.84; H 3.06; N 10.63; found: C 47.19, H 3.48, N 10.58 (%)

Synthesis of $[Cu(\mu\text{-}N,N\text{-}3,5\text{-}(CF_3)_2pz)_2(PPh_3)]$, compound 11.

To a mixture of Ph_3P (0.155 g; 0.58 mmol) and $Cu(BF_4)_2$ (0.136 g; 0.39 mmol) in dry THF, the sodium pyrazole salt (0.08 g; 0.39 mmol) was added and the suspension was stirred over night at room

temperature. The suspension was evaporated under vacuum to give an orange solid. The solid was dissolved in dichloromethane and extracted 3 times with 10 ml water. The organic phase was dried with Na_2SO_4, filtered over a paper filter and concentrated. The solution was layered with hexane and light yellow crystals were recovered. Yield 69 %.

IR(cm^{-1}): 3141 (w), 3050.5, (w) 1585 (w), 1573 (s), 1480 (s,sh), 1434 (m), 1385 (w), 1329 (s), 1309 (m), 1260 (m), 1184 (s), 1158 (m), 1120 (m), 1095 (s), 1070 (m), 1027 (m), 1016 (m), 998 (w), 971 (m), 917 (w), 851 (s), 807 (s), 741 (s), 723 (m), 706 (vs), 691.05 (vs).
^{1}H NMR (CD_2Cl_2, δ): 7.7 (m, 1H), 7.21-7.37 (m, 15H).
^{31}P NMR (CD_2Cl_2, δ): - 2.29 (s, br).
SI (-) MS (CH_3CN; m/z) : 203 (56) $[(3,5(CF_3)_2pz)]^-$, 469 (100)) $[(3,5(CF_3)_2pz)_2 + Cu]^-$, 1003 (38). ESI (+) MS (CH_3CN; m/z) : 587 (100) $[PPh_3)_2 + Cu]^+$, 605 (22) $[PPh_3)(O{=}PPh_3) + Cu]^+$., 721 (19).
Elemental analysis for $C_{23}H_{16}CuF_6N_2P$, calcd %: C 52.23; H 3.05; N 5.30; found: C52.29, H3.38, N 11.58 (%)

Synthesis of [Ag(μ-N,N-3,5-$(CF_3)_2$pz)(PPh_3)], compound 12.

Ph_3P (0.067 g; 0.25 mmol) dissolved in 10 mL of dry THF, solid $AgBF_4$ was added (0.05 g; 0.25 mmol). The solution was stirred for one hour and a methanolic solution of the sodium pyrazole salt (0.051 g; 0.25 mmol) was added. The suspension was stirred over night at room temperature. The whitesuspension was evaporated under vacuum to give a white solid. The solid was dissolved in dichloromethane and extracted 3 times with 10 ml water. The organic phase was dried with Na_2SO_4, filtered over a paper filter and concentrated. The solution was layered with hexane and white-yellow crystals were recovered. Yield 71 %.
IR(cm^{-1}): 3130 (w), 3081 (w), 3059, (w), 3007 (vw), 1587 (s), 1516 (m), 1501 (m), 1480 (s), 1435 (s), 1361 (s), 1348 (s), 1337 (m), 1309 (w), 1252 (s), 1226 (m,sh), 1147 (s), 1096 (s), 1027 (m), 997 (w), 972 (m), 853 (m), 808 (m), 744 (vs), 706 (s), 691 (vs).

^{1}H NMR (acetone-d^6, δ): 7.51-7.21 (m, br, 16H).
^{31}P NMR (acetone-d^6, δ, 258K): 15.28 (dd, broad).
ESI (-) MS (CH_3CN; m/z) : 203 (78) $[(3,5(CF_3)_2pz)]^-$, 336 (18), 513 (100) $[(3,5(CF_3)_2pz)_2 + Ag]^-$,648 (17), 1135 (41); ESI (+) MS (CH_3CN; m/z) : 410 (15) 633 (100), 943 (24) $[[(3,5(CF_3)_2pz) + (PPh_3Ag)_2]^+$.
Elemental analysis for C21H16AgN4O4P, calcd %: C 47.84; H 3.06; N 10.63; found: C 47.19, H 3.48, N 10.58 (%)

Synthesis of [Au(μ-N,N-3,5-$(NO_2)_2$pz)(PPh_3)].[120]

60 mg of the sodium pyrazole salt (0.33 mmol) were dissolved in 5 mL of THF. To this solution 3 mL of a THF solution of Ph_3PAuBF_4 (0.180 g; 0.33 mmol) was added. The suspension was stirred for three hours at room temperature and filtered over a celite bed. The colorless solution was evaporated under vacuum to give white solid which was washed with diethyl ether and then dissolve d in CH_2Cl_2 and layered with hexane. Yield 88 %. M. p: 162.4 - 163.5°C

IR(cm^{-1}): 3168 (w), 3054, (w), 3030 (vw), 1586 (w), 1543(s), 1489 (s), 1449 (s,sh), 1435 (m), 1361 (s), 1325 (s), 1294 (m), 1222 (w), 1181 (s), 1098 (s), 1067 (m), 1046 (m), 1025 (m), 995 (w), 923 (w), 831 (s), 812 (s), 740 (s), 711 (vs), 679 (vs).

^{1}H NMR (acetone-d^{6}, δ): 7.83-7.60 (m, 16H).

^{31}P NMR (acetone-d^{6}, δ): 31.06 (s).

ESI (-) MS (CH_3CN; m/z) : 156.9 (100) $[(3,5(NO_2)_2pz)]^-$, 376.6 (30) ; ESI (+) MS (CH_3CN; m/z) : 500.3 (37) $[AuPPh_3 + CH_3CN]^+$, 721 (100) $[(PPh_3)_2 + Au]^+$; 935 (10) 1075 (30) $[Au(PPh_3)_2 + 3,5(NO_2)_2pzAu]^+$.

Elemental analysis for $C_{21}H_{16}AuN_4O_4P$ + 0.5 THF calcd %: C 42.35; H 3.09; N 8.59; found: C 42.50, H 3.09, N 8.40 (%)

Synthesis of [Au(μ-N,N-3,5-(CF_3)2pz)(PPh_3)].[120]

To a solution of CH_3OH (6 mL) and 3,5-bis(trifluoromethyl)pyrazole (0.1 g; 0.49 mmol) 2.75 mL of 1 % methanolic solution of KOH (0.49 mmol) was added. After few minutes, 5 mL of a solution of Ph3PAuBF4 in THF (0.49 mmol) was added. After a magnetic stirring of an hour the suspension was filtered. The colourless solution was then concentrated to dryness and an oily product was obtained. The crude product was washed with hexane and crystallized by a mixture of CH_2Cl_2/hexane. Yield 75 %. M. p. 124.2-125.8 °C.

^{1}H NMR (CD_2Cl_2, 293K): 7.62-7.56 (m, 15H, PPh3), 6.96 (s, 1H, pz).

^{31}P NMR (CD_2Cl_2, 293K): 31.79 (s).

IR (cm^{-1}): 3144vw, C-Hpz, 3059vw, 3048vw, 1621vw, 1589w, 1546m, 1530m, 1497m, 1482m, 1436s, 1352m, 1332w, 1310w, 1253vs, 1220s, 1157s, sh, 1139vs, 1101vs, 1075s, 1010vs, 974s, 925m, 849m, 816m, 745s, 712s, 689vs.

ESI(-) (CH3CN) m/z, %: 202.9 (70) $[3,5-(CF_3)_2pz)]$, 468.5 (55), 602.3 (100) $[3,5(CF_3)_2pz)_2Au]$; ESI(+)(CH_3CN) m/z %: 242.3 (18) $[3,5(CF_3)_2pz + K]^+$, 500.1 (30) $[Au(PPh_3) + CH_3CN]^+$, 721.3 (25) $[Au(PPh_3)_2]^+$, 1121 (100) $[Au(PPh_3)_2$+ $3,5(CF_3)_2pzAu]^+$.

Elemental analysis for $C_{23}F_6H_{16}N_2P$, calcd %: C 41.71; H 2.43; N 4.23, found %: C 41.82; H 2.17; N 4.54.

Table 5.1 *Compound list and their experimental data.*

Compound	**Name**	**13C NMR**	**31P NMR**	**IR cm-1 (Car-H; C=O stretching)**	**η (%)**	**ESI-MS (+) *m/z (%)***
Compound 1	**[Ag-C_2,N_3-(1-benzyl-imidazole)]$_3$**	Not observed	Not observed	3150, 2853,	58	
Compound 2	**1,3-dibenzyl-imidazolium chloride**	144.94 C2	Not observed	3442 , 3376, 3244, 3152, 3133, 3075, 2999, 2111, 1973, 1832, 1749,	80	**533** (24) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Cl]$^+$, **249** (100) [(1,3-dibenzyl-imidazolium)]$^+$
Compound 3	**[1,3-dibenzyl-imidazolyl-2-yl-silver chloride]$_2$**	180.64 C2	Not observed	3162, 3132, 3100, 2948, 1963, 1887, 1817, 1671	51	**605.3** (100) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Ag]$^+$, **249** (35) [(1,3-dibenzyl-imidazolium)]$^+$.
Compound 4	**[1,3-dibenzyl-imidazolyl-2-yl-gold chloride]**	171.39 C2	Not observed	3158, 3128, 3103, 3032, 2996 2921,	99	**693.3** (100) [(1,3-dibenzyl-imidazolyl-2yl)$_2$-Au]$^+$, **763 (35).**

6. APPENDIX

H-NMR compound 3

Table 3.1. Crystal data and structure refinement for compound **1**.

Identification code	compound 1
Empirical formula	C30 H27 Ag3 N6
Formula weight	795.19
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.3430(10) Å b = 12.486(1) Å-→b= 96.123(2)° c = 14.254(1) Å-→g = 91.965(2)°
Volume	1409.2(3) Å3
Z	2
Density (calculated)	1.874 Mg/m3
Absorption coefficient	2.095 mm-1
F(000)	780
Crystal size	0.20 x 0.05 x 0.05 mm3
Theta range for data collection	1.71 to 27.81°

Table 3.2. Selected bond lengths [Å] and angles [°]* for compound **1**.

Ag(1)-C(1)	2.051(5)
Ag(1)-N(6)	2.080(4)
Ag(1)-Ag(3)#1	3.1683(6)
Ag(2)-C(11)	2.062(4)
Ag(2)-N(2)	2.100(4)
Ag(3)-C(21)	2.059(4)
Ag(3)-N(4)	2.089(4)

C(1)-Ag(1)-N(6)	173.50(17)
C(1)-Ag(1)-Ag(3)#1	104.85(12)
N(6)-Ag(1)-Ag(3)#1	81.43(11)
C(11)-Ag(2)-N(2)	173.52(16)
C(21)-Ag(3)-N(4)	175.75(17)
C(21)-Ag(3)-Ag(1)#1	81.16(12)
N(4)-Ag(3)-Ag(1)#1	99.67(10)
N(6)-C(21)-Ag(3)	122.1(3)
N(5)-C(21)-Ag(3)	131.1(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,- z+1

Table 3.3. Preliminary data on the crystal structure of compound **3**

Bond precision : C-C	= 0.0038 A
Wavelength	=0.71073
Cell:	a=8.131(2) b=10.005(3) c=10.501(3)
Temperature:	293 K
Angles	α=88.228(4) β=68.172(4) γ=85.028(4)
Volume	790.0(4)
Space group	P -1
Hall group	-P 1
Moiety formula	C17H16AgClN2
Sum formula	$C_{17}H_{16}AgClN_2C_{17}H_{16}AgClN_2$
Mr	391.64
Dx,g cm-3	1.646
Z	2
Mu (mm-1)	1.439
F000	392.0
F000'	390.60
h,k,l max	11,14,15

Nref	4842 4808
Data completeness=	0.993 Theta(max)= 30.550
R(reflections)=	0.0318(3998)
wR2(reflections)=	0.0826(4808)
S	1.052
Npar	190

.

Table 3.4. Details for the X-ray data collection for complound **9**.

Formula	C42H32Cu2N8O8P2
Molecular weight	965.77
Crystal system	Triclinic
Space group	*P-1*
***a*/Å**	10.093(2)
***b*/Å**	12.325(2)
***c*/Å**	19.251(3)
α/°	72.496(3)
β/°	87.743(3)
γ/°	66.218(3)
Volume, Å3	2080.9(6)
Z	2
D_{calc}/g cm^{-3}	1.541
F(000)	984
μ(Mo-K*α*)/mm^{-1}	1.163
Reflections collected	28774
Unique reflections	10015
Observed reflections [I>2□(*I*)]	7113 [R_{int} = 0.0486]
***R*, *wR* [*I* > 2*σ*(*I*)]**	*R* = 0.0400; *wR* = 0.0860
***R*, *wR* [all data]**	*R* = 0.0673; *wR* = 0.0969

$R = \Sigma|Fo - Fc|/\Sigma|Fo|$; $wR = [\Sigma [w(Fo^2 - Fc^2)^2]/ \Sigma [w(Fo^2)^2]]^{1/2}$

Table 3.5. Selected bond distances (Å) and angles (°) for compound **9**:

N1-Cu1	2.0217(19),
N5-Cu1	1.998(2),
P1-Cu1	2.1981(7),
N2-Cu2	1.974(2),
N6-Cu2	2.004(2),
P2-Cu2	2.1812(8);
N5-Cu1-N1	104.09(8),
N5-Cu1-P1	126.42(6),
N1-Cu1-P1	126.87(6),
N2-Cu2-N6	102.17(8),
N2-Cu2-P2	132.41(6),
N6-Cu2-P2	120.20(6).

Table 3.6. Selected data for the MW-assisted oxidation of cyclohexane by t-BuOOH (aq. 70%) catalysed by 9 or $[Cu\text{-}\mu\text{-}N,N\text{-}(CF_3)_2pz\text{-}(OH)]_6$.

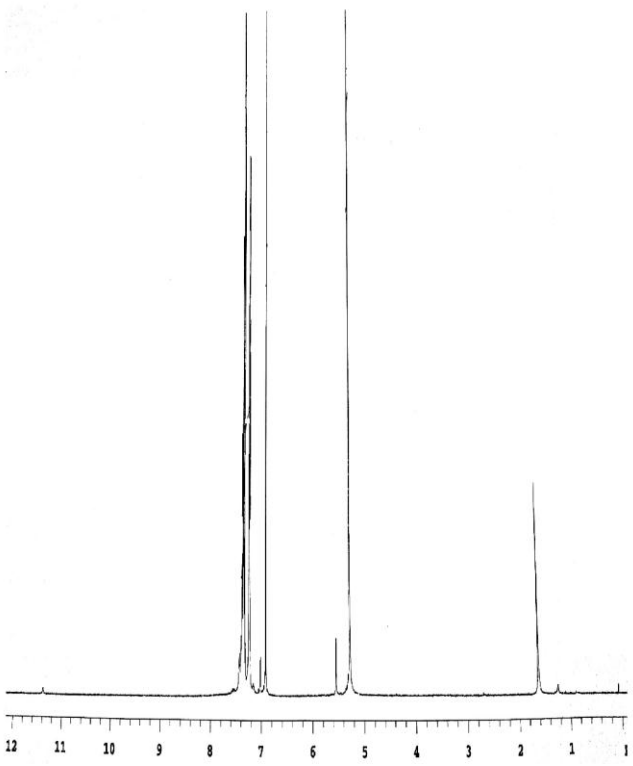
Entry	Catalyst	Catalyst/ substrate (%)	Co-catalyst	Temp (ºC)	Reaction time (h)	Yield (%) [b]			CyOH / CyO
						CyO	CyOH	Total	
1	**5**	0.1	-	100	0.5	4.4	12.2	16.6	2.8
2			-		1.0	4.4	11.7	16.1	2.7
3			-		1.5	3.9	10.6	14.5	2.7
5			-		2.0	3.9	10.7	14.6	2.7
6			-		2.5	3.7	9.9	13.6	2.7
7			-		3.0	4.0	10.7	14.7	2.7
8		0.2	-		0.5	3.9	10.5	14.4	2.7
9			-		1.0	5.5	12.2	17.7	3.1
10			-		1.5	5.1	14.4	19.5	2.8
11			-		2.0	5.1	14.1	19.2	2.8
12			-		2.5	4.5	12.8	17.3	2.8
13			-		3.0	4.1	11.8	15.9	2.9
14		0.1	TEMPO		0.5	7.7	12.4	20.1	1.6
15					1.0	8.1	13.2	21.3	1.6
16					1.5	9.5	15.0	24.5	1.6
17					2.0	10.3	17.6	27.9	1.7
18					2.5	9.6	16.0	25.6	1.7
19					3.0	9.2	15.7	24.9	1.7
20		0.2			0.5	8.4	13.2	21.6	1.6
21					1.0	9.2	13.3	22.5	1.4

22					1.5	8.7	14.9	23.6	1.7
23					2.0	8.3	14.2	22.5	1.7
24					2.5	7.1	12.3	19.6	1.7
25					3.0	6.8	11.9	18.7	1.8
26		0.1	-	60	0.5	0.1	0.0	0.1	0
27			-		1.0	0.4	0.8	1.2	2.0
28			-		1.5	0.8	1.8	2.6	2.2
29			-		2.0	1.2	2.9	4.1	2.4
30			-		2.5	1.8	3.7	5.5	2.0
31			-		3.0	2.4	4.8	7.2	2.0
32		0.02	-	100	0.5	7.7	8.7	16.4	1.1
33			-		1.0	8.6	10.7	19.3	1.2
34			-		1.5	10.2	11.0	21.2	1.1
35			-		2.0	11.2	10.5	21.7	0.9
36			-		2.5	10.2	7.8	18.0	0.8
37			-		3.0	9.0	7.3	16.3	0.8
38		0.1	-		0.5	10.6	13.5	24.1	1.3
39			-		1.0	12.0	15.5	27.5	1.3
40			-		1.5	12.9	18.5	31.4	1.4
41			-		2.0	15.4	21.5	36.9	1.4
42			-		2.5	12.8	17.9	30.7	1.4
43			-		3.0	7.0	9.8	16.8	1.4
44		0.2	-		0.5	8.0	11.9	19.9	1.5
45			-		1.0	16.1	20.9	37.0	1.3
46	**6**		-		1.5	9.6	13.9	23.5	1.4
47			-		2.0	7.9	11.6	19.5	1.5
48			-		2.5	7.5	11.0	18.5	1.5
49			-		3.0	7.2	10.8	18.0	1.5
50		0.1	TEMPO		0.5	8.2	11.5	19.7	1.4
51					1.0	16.2	22.4	38.6	1.4
52					1.5	13.4	18.7	32.1	1.4
53					2.0	10.3	13.8	24.1	1.3
54					2.5	8.8	11.5	20.3	1.3
55					3.0	8.2	11.6	19.8	1.4
56		0.2			0.5	18.7	39.1	57.8	2.1
57					1.0	15.9	35.6	51.5	2.2
58					1.5	16.6	33.7	50.3	2.0
59					2.0	14.8	32.6	47.4	2.2
60					2.5	12.2	28.6	40.8	2.3
61					3.0	11.6	29.2	40.8	2.5
62		0.1	Hpca		0.5	0.1	0.2	0.3	2.0
63					1.0	4.5	7.4	11.9	1.6
64					1.5	4.9	7.1	12.0	1.4

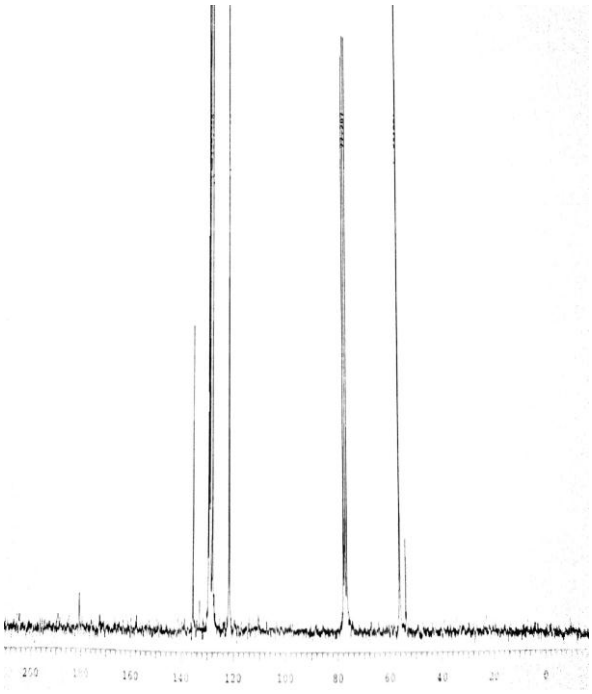
65					2.0	6.4	7.7	14.1	1.2
66					2.5	6.0	5.9	11.9	1.0
67					3.0	9.1	7.8	16.9	0.9
68	-	-	-	100	1.5	0.0	0.0	0.0	-
69	-	-	TEMPO		1.5	0.0	0.0	0.0	-
70	**6**	0.2	Ph_2NH	100	0.5	0.0	0.0	0.0	-

[a] Reaction conditions: cyclohexane (5 mmol), catalyst (1-10 µmol), *t*-BuOOH (70% in H_2O, 10 mmol), 60 - 100 ºC, TEMPO (when used, 2.5 mol% *vs*. substrate), Hpca (when used, 20 mol% *vs*. substrate), Ph_2NH (when used, 10 mmol). [b] Moles of products [cyclohexanol (CyOH) + cyclohexanone (CyO)] *per* 100 mol of cyclohexane, as determined by GC after treatment with PPh_3.

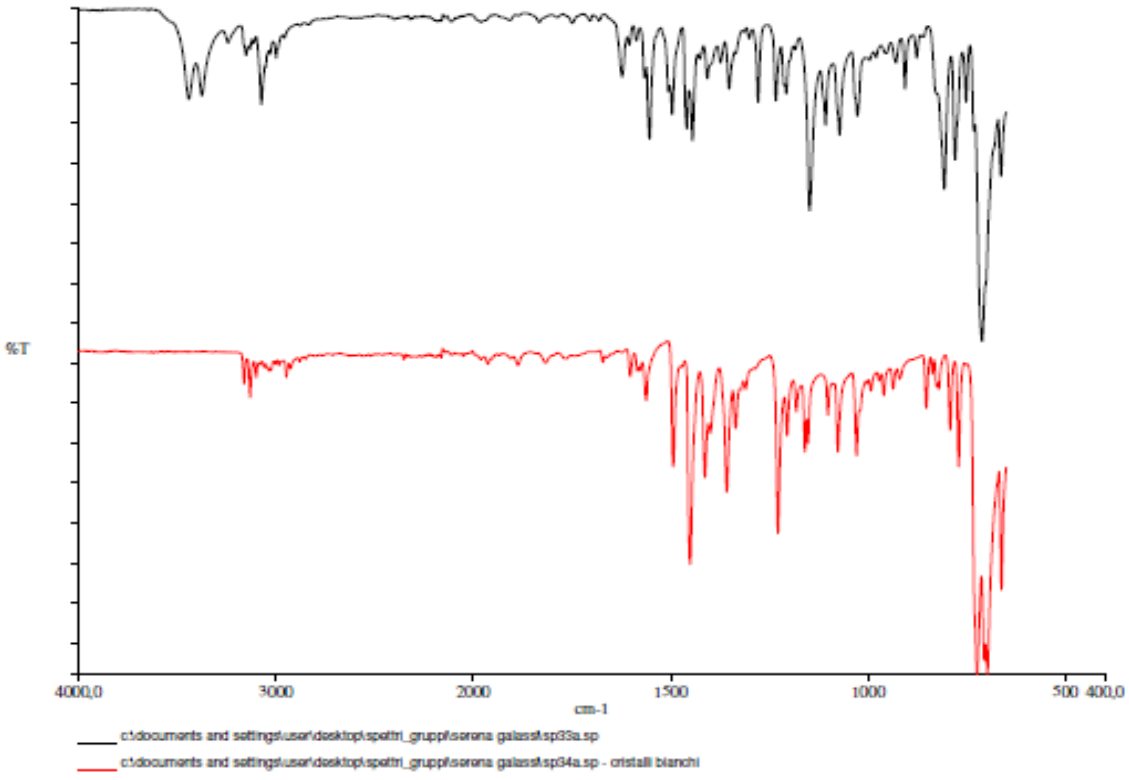
6.1 Characterization of the compounds



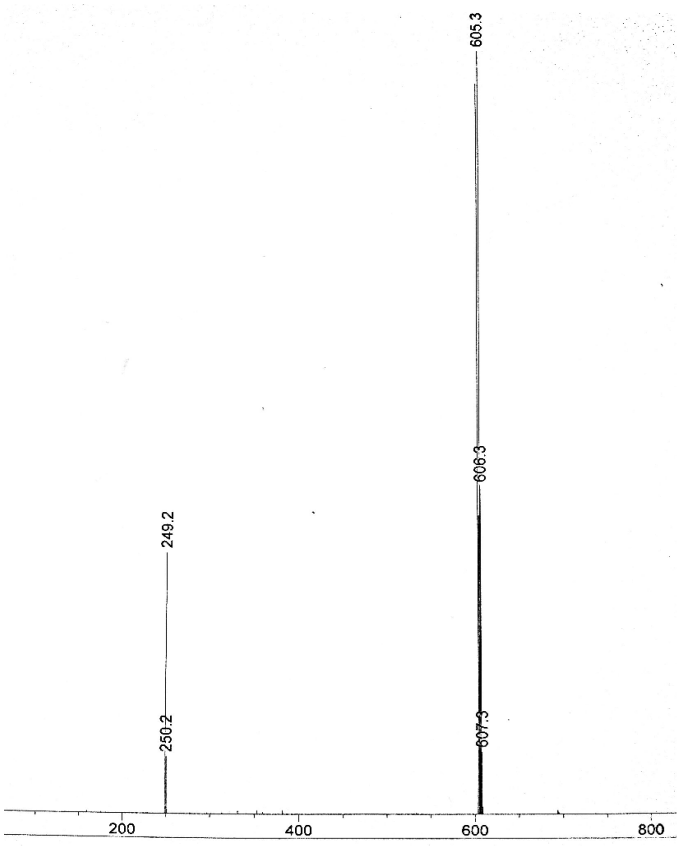
H-NMR spectrum of compound 3



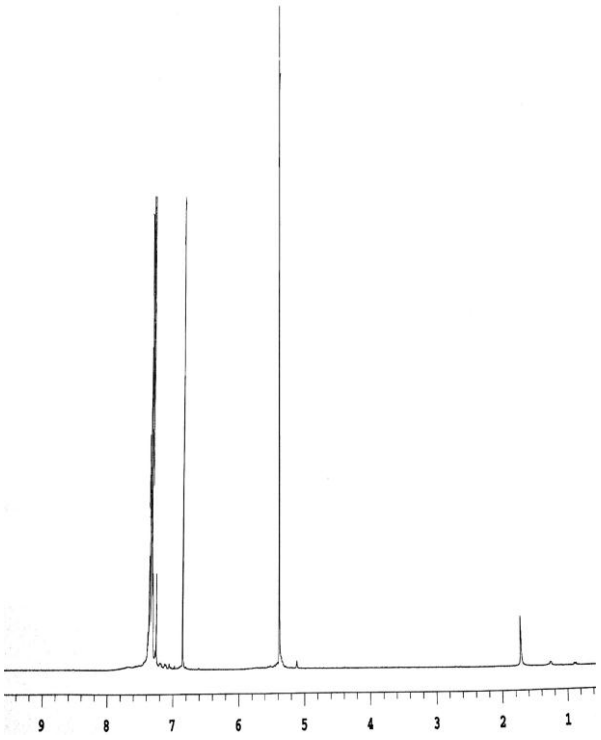
13C-NMR spectrum of compound 3



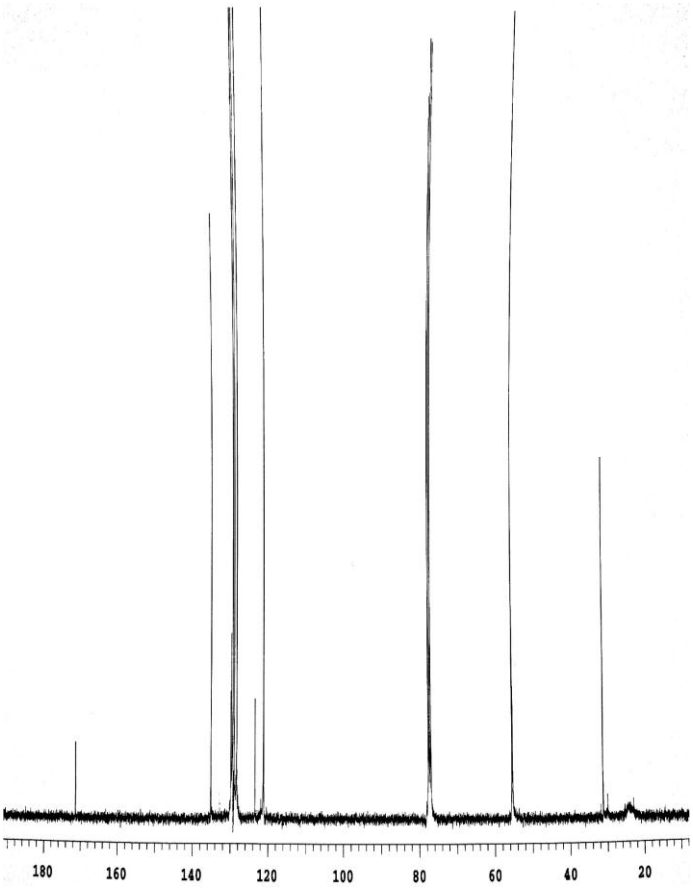
IR spectrum of compound 2 (black) and 3 (red)



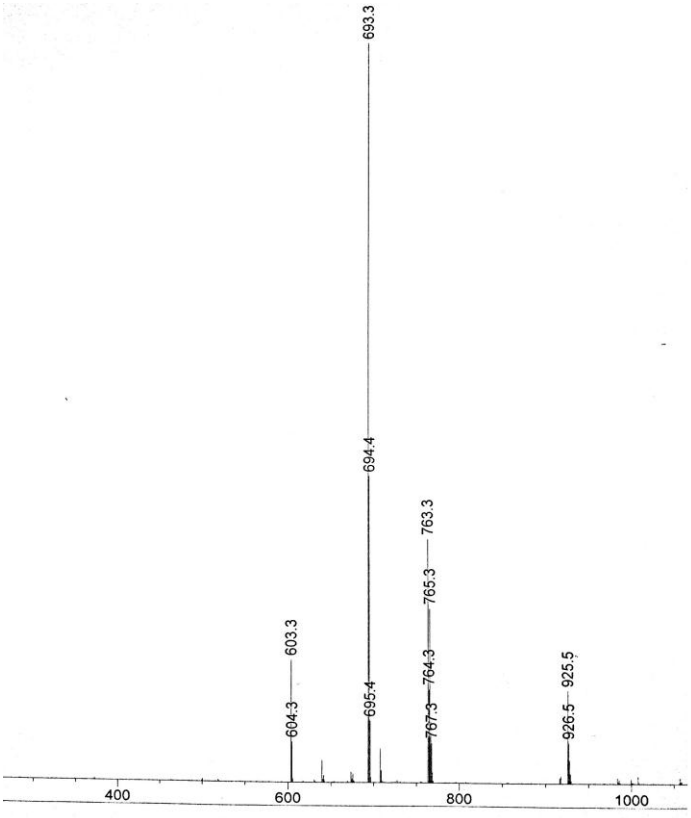
ESI-MS spectrum of compound 3



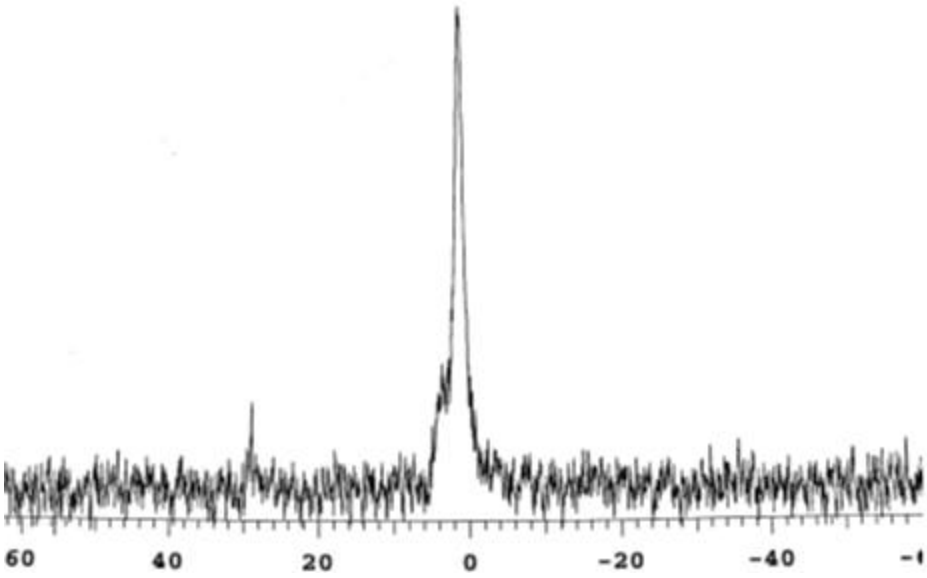
H-NMR SPECTRUM OF COMPOUND 4



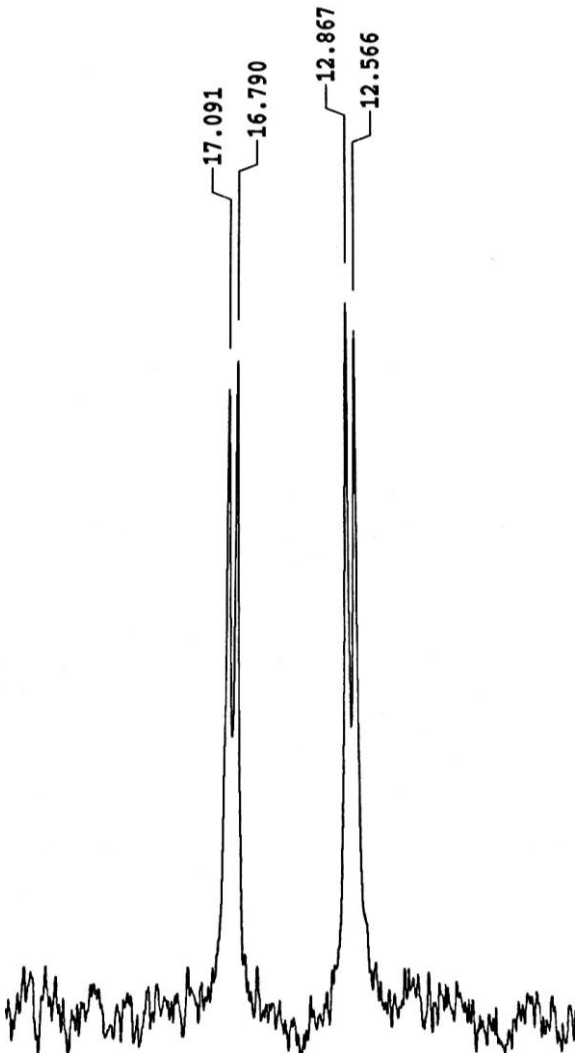
13C-NMR SPECTRUM OF COMPOUND 4



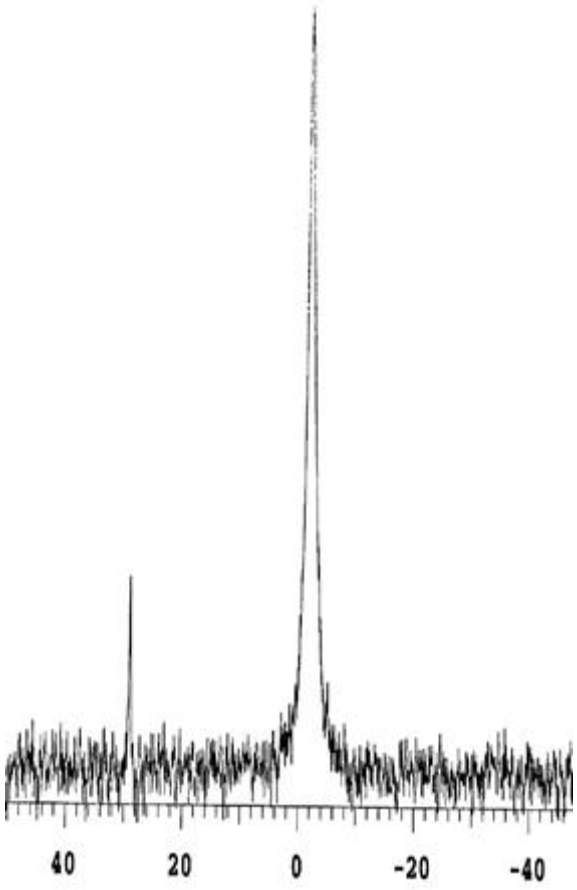
ESI-MS spectrum of compound 4



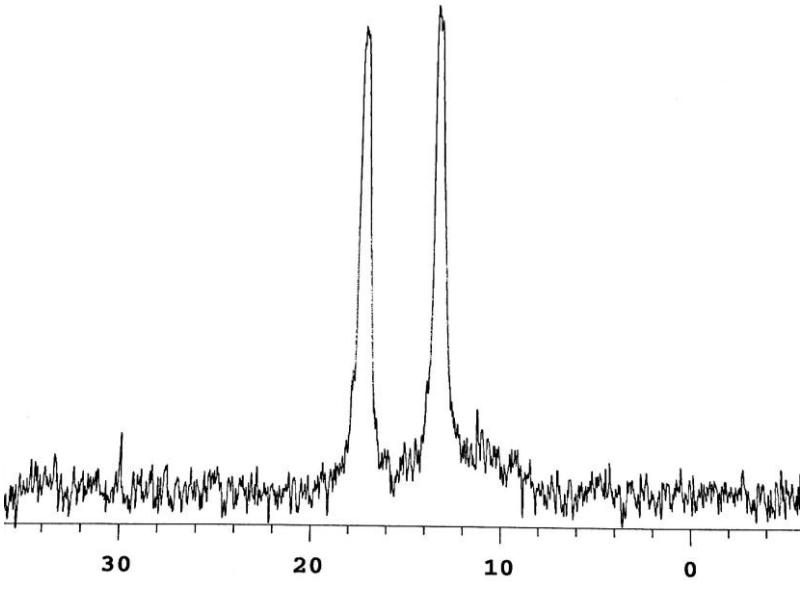
31P-NMR spectrum of compound 9



31P-NMR spectrum of compound 10



31P-NMR spectrum of compound 11



31P-NMR spectrum of compound 12

7.REFERENCES

1. (a) Braunstein, P., *J. Organomet. Chem.* **2004,** 3953; (b) Gavrilova, A. L.; Bosnich, B., *Chem. Rev.* **2004,** 349; (b) Grushin, V.V., *Chem. Rev*. **2004**, 1629; (c) Morise, X.; Braunstein, P.; Welter, R., *Inorg. Chem*. **2003**, *42*, 7752; (d) Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D., *Dalton Trans*. **2003**, 1869; (e) Date, R. W.; Iglesias, E. F.; Rowe, K.E.; Elliott, J.M.; Bruce, D.W., *Dalton Trans*. **2003**, 1914; (f) Robertson, N.; Cronin, L., *Coord. Chem. Rev*. **2002,** 93; (g) Lindler, E.; Schneller, T.; Auer, F.; Mayer, H. A., *Angew. Chem. Int. Ed*. **1999,** *38*, 2155.

2. (a) La Monica, G.; Ardizzoia, G. A, *Prog. Inorg. Chem.* (Ed. K. D. Kenneth) WILEY & Sons, Weinheim. **1997**, *46* 152; (b) Viciano-Chumillas, M.; Tanase, S.; Jos de Jongh, L.; Reedijk, J., *Eur. J. Inorg. Chem.* **2010**, 3403; (c) Klingelea, J.; Decherta,S.; Meyer, F.,

Coord. Chem. Rev., **2009**, *253*, 2698; (d) Halcrow, M. A., *Dalton Trans.* **2009**, 2059; (e) Miras, H. N.; Chakraborty, I.; Raptis, R. G.,

Chem. Commun., **2010**, *46* 2569.

3. (a) Mohamed, A. A., *Coord. Chem. Rev*. **2010**, 254, 1918; (b) Burini, A.; Mohamed, A. A.; Fackler, J. P., *Jr. Comments on Inorg Chem*., **2003**, *24, 253*; (c) Abdou, H. E.; .; Mohamed, A. A.; Fackler, J. P., *Jr. Gold chemistry "Applications and Future Directions in the Life Sciences",* Ed.;: F. Mohr), Wiley-VCH. Weinheim, **2009**, p.1.

4. Malcolm A. Halcrow. *Dalton Trans.,* **2009**, 2059.

5. (a) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; . La Monica G., *J. Am. Chem. Soc.* **1994**, *116*, 7668; (b) Büchner, E., *Chem. Ber.*, **1889**, *22,* 842; (c) Barberà, J.; Lantero, I.; Moyano S.; Luis Serrano, J.; Elduque, A.; Giménez, R., *Chem. Eur. J*. **2010**, *16* 14545.

6. (a) Nomiya, K.; Tsuda, K.; Tanabe, Y.; Nagano, H., *J. Inorg. Biochem.* **1998**, *69* 9; (b) Bonati, F.; Burini, A.; Pietroni, B. R.; Giorgini, E., *Inorg. Chim. Acta*., **1987**, *137*, 81; (c) Bovio, B.; Bonati, F.; Burini, A.; Pietroni, B. R., *Zeitschrift. Naturforschung, teil B*: *Anorganische Chemie.,* **1984**, *39B,* 1747.

7. (a) Ardizzoia, G. A.; Brenna, S.; Castelli, F.; Galli, S.; La Monica, G.; Masciocchi, N.; Maspero, A., *Polyhedron*, **2004**, *23,* 3063; (b) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G., *J. Chem. Soc., Dalton Trans*., **1995**, 1671.

8. (a) Kolks, G.; Lippard, S. J.; Waszczak, J. V.; Lilienthal. H. R., *J. Am. Chem. Soc.,* **1982**, *104* 717; (b) Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B., *J. Organomet. Chem*., **1989**, *375,* 147; (c) Elbierami, O.; Rashdan, M. D.; Nesterov, V.; Rawashdeh-Omary, M. A., *Dalton Trans.,* **2010**, *39,* 9465.

9. Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem*., **1988**, *27,* 4179.

10. (a) Boca, R.; Dlháň, L.; Mezei, G.; Ortiz-Pérez, T.; Raptis, R. G.; Telser, J., *Inorg. Chem*., **2003**, *42,* 5801-5803; (b) Mezei, G.; Rivera-Carrillo, M.; Raptis., R. G., *Inorg. Chim Acta*., **2004**, *357*, 3721.

11. Casarin, M.; Corvaja, C.; di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F.; Tagliatesta, P.,

Inorg. Chem., **2004**, *43,* 5865.

12. Bovio, B.; Bonati, F.; Banditelli, G., *Inorg. Chim. Acta*., **1984**, *87,*

25.

13. Murray, H. H.; Raptis, R .G.; Fackler, J. P., Jr. *Inorg. Chem*., **1988**,

27, 26.

14. Yang, G.; Raptis. R. G., *Inorg. Chem*., **2003**, *42,* 261.

15. Barbera, J.; Elduque, A.; Gimenez, R.; Lahoz, F. J.; Oro, L. A.; Serrano, J. L., *Inorg. Chem*., **1998**, *37,* 2960.

16. Vaughan. L. G., *J. Am. Chem. Soc*., **1970**, *11*, 730.

17. Burini, A.; Pietroni, B. R.; Bovio, B.; Calogero, S.; Wagner, F. E., *J. Organomet. Chem*., **1994**, *470*, 275.

18. (a) Balch, A. L.; Doonan, D. J., *J. Organomet. Chem*. **1977**, *131*,

137. (b) Minghetti, G.; Banditelli, G.; Bonati, F., *Inorg. Chem*. **1979**,

18, 658. (c) Raptis, R.; G.; Fackler, J. P., Jr., *Inorg. Chem*., **1990**, *29*, 5003. (d) Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B., *J. Organomet. Chem*., **1991**, *408*, 271. (e) Raptis, R. G.; Murray, H. H.; Fackler, J. P., Jr. *Acta Cristallogr. C*., **1988**, *44*, 970. (f) Bovio, B.; Burini, A.; Pietroni, B. R., *J. Organomet. Chem*., **1993**, *452*, 287. (g) Vickery, J. C.; Balch, A. L., *Inorg. Chem*., **1997**, *36*, 5978.

19. Shmidbaur, H. and Franke, R., *Inorg. Chim, Acta*, **1975** 85.

20. Bonati F.; Minghetti G.; Banditelli G., J. *Chem. Soc. Chem Commun*., **1974** 88

21. Katad, M.; Sako, K.; Uchida, Y.; Iijima, S.; Sano, H.; Wei H.H.; Sakai H.; Maeda Y., *Bull. Chem. Soc. Jpn.,* **1983**, 945.

22. a) Minghetti, G.; Bandini, A.L.; Banditelli, G.; Bonati, F., *Inorg. Chem*. *Acta,* **1985**, 165;

23. Öfele, K. *J., Organomet. Chem.* **1968**, *12*, 42.

24. Wanzlick, H.-W.; Schonherr, H.-J., *Angew. Chem., Int. Ed. Engl.,***1968**, *7*, 141.

25. Lappert, M. F., *J. Organomet. Chem.,* **1975**, *100*, 139.

26. Lappert, M. F., *J. Organomet. Chem.,* **1988**, *358*, 185.

27. Arduengo, A. J., III; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.,* **1991**, *113*, 361.

28. Bourissou, D.; Guerret, O.; Francüois, P.; Gabbaı, F. P.; Bertrand,G.,

Chem. Rev., **2000**, *100*, 39.

29. Herrmann, W. A.; Kocher, C., *Angew. Chem., Int. Ed. Engl.,* **1997**, *36*, 2162.

30. Herrmann, W. A., *Angew. Chem. Int. Ed.,* **2002**, *41*, 1290.

31. Korotkikh, N. I.; Shvaika, O. P.; Rayenko, G. F.; Kiselyov, A.V.; Knishevitsky, A. V.; Cowley, A. H.; Jones, J. N.; Macdonald,C. L. B. *ARKIVOC* **2005**, *8*, 10.

32. Arduengo, A. J. III; Tapu, D., In *Comprehensive Organic Functional Transformations II*; Katritzky, A. R.; Taylar, R. J. K., Eds.;Elsevier: Oxford, U.K., **2005**, 1103.

33. Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K.

*Organometallics***2004**, *23*, 755.

34. Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**,*23*, 3640.

35. Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C., Davidson,F.

Organometallics **1993**, *12*, 3405.

36. Guerret, O.; Sole´, S.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G., *J. Am. Chem. Soc.* **1997**, *119*, 6668.

37. Wang, H. M. J.; Lin, I., J. B*,. Organometallics* **1998**, *17*, 972.

38. Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. J*., Chem. Soc., Dalton Trans.* **2000**, 4499.

39. Arnold, P. L., *Heteroat. Chem.* **2002**, *13*, 534.

40. Boehme, C.; Frenking, G., *Organometallics* **1998**, *17*, 5801.

41. Lin, I. J. B.; Vasam, C. S., *Comments Inorg. Chem.* **2004**, *25*, 75.

42. (a) Shi, Z.; Zhang, C.; Tang, C.; Jiao, N., *Chem. Soc. Rev.,* **2012**, *41*, 3381; b) Ackermann, L.; Vicente, R.; Kapdi A. R., *Angew. Chem. Int. Ed.,* **2009**, *48*, 9792; c) Ashenhurst, J. A., *Chem. Soc. Rev.,* **2010**, *39*, 540; d) Chinchilla R.; Najera, C., *Chem. Rev.* **2007**, *107*, 874; e) Gligorich, K. M.; Sigman, M. S., *Chem. Commun.,* **2009**, 3854; f) Liu, C.; Zhang, H.; Shi, W.; Lei, A., *Chem. Rev.,* **2011**, *111*, 1780; g) Schultz, M. J.; Sigman, M. S., *Tetrahedron,* **2006**, *62*, 8227; h) Yoshikai, N.; Nakamura, E., *Chem. Rev,.* **2012**, *112*, 2339. h) Casarin, M.; Corvaja, C.; Di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F.; Tagliatesta, P.,

Inorg. Chem., **2004**, *43*, 5865. (i) Casarin, M.; Corvaja, C.; Di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F., *Inorg. Chem.,* **2005**, *44*, 6265.

43. (a) Horn, K. A., *Chem. Rev,.* **1995**, *95*, 1317; b) Miyaura, N.; Suzuki, A., *Chem. Rev.,* **1995**, 95, 2457; c) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A., *Chem. Rev.,* **2000**, *100*, 3067; d) Negishi,

E.; Anastasia, L., *Chem. Rev.,* **2003**, *103*, 1979; e) Zeni, G.; Larock, R. C., *Chem. Rev.,* **2006**, *106*, 4644; f) Lyons, T. W.; Sanford, M. S.,

Chem. Rev., **2010**, *110*, 1147; g) McDonald, R. I.; Liu, G. S.; Stahl, S. S., *Chem. Rev.,* **2011**, *111*, 2981; h) Wu, X.-F.; Neumann, H.; Beller, M. , *Chem. Rev.,* **2013**, *113*, 1; i) Sore, H. F.; Galloway, W. R. J. D.; Spring, D. R., *Chem. Soc. Rev.,* **2012**, *41*, 1845; j) Chen, Q.-A.; Ye, Z.-S.; Duan, Y.; Zhou, Y.-G., *Chem. Soc. Rev.,* **2013**, *42*, 497.

44. (a) Phapale, V. B.; Cardenas, D. J., *Chem. Soc. Rev.,* **2009**, *38*, 1598; b) Yamaguchi, J.; Muto, K.; Itami, K., *Eur. J. Org. Chem.,* **2013**, 19.

45. (a) Stanley, L. M.; Sibi, M. P., *Chem. Rev.,* **2008**, *108*, 2887; b) Alexakis, A.; Backvall, J. E.; Krause, N.; Pamies, O.; Dieguez, M., *Chem. Rev.,* **2008**, *108*, 2796; c) Yamada, K. ; Tomioka, K., *Chem. Rev.,* **2008**, *108*, 2874; d) Reymond, S.; Cossy, J., *Chem. Rev.,* **2008**, *108*, 5359; e) Jerphagnon, T.; Pizzuti, M. G.; Minnaard, A. J.; Feringa, B. L., *Chem. Soc. Rev.,* **2009**, *38*, 1039; f) Hein, J. E.; Fokin, V. V., *Chem. Soc. Rev.,* **2010**, *39*, 1302; g) Zhang, C.; Tang, C.; Jiao, N., *Chem. Soc. Rev.,* **2012**, *41*, 3464; h) Beletskaya, I. P.; Cheprakov, A. V., *Coord. Chem. Rev,.* **2004**, *248*, 2337; i) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R. ; Kozlowski, M. C., *Chem. Rev.,* **2013**, *113*, 6234.

46. (a) Hebrard, F.; Kalck, P., *Chem. Rev.,* **2009**, *109*, 4272; b) Cahiez, G.; Moyeux, A., *Chem. Rev,.* **2010**, *110*, 1435; c) Pattenden, G., *Chem. Soc. Rev.,* **1988**, *17*, 361; d) Lu, X.-B.; Darensbourg, D. J., *Chem. Soc. Rev.,* **2012**, *41*, 1462; e) Gosmini, C. ; Begouin, J. M.; Moncomble, A., *Chem. Commun.,* **2008**, 3221.

47. (a) Correa, A.; Mancheno, O. G.; Bolm, C., *Chem. Soc. Rev.,* **2008**, *37*, 1108; b) Sarhan, A. A. O.; Bolm, C.,*Chem. Soc. Rev.,* **2009**, *38*, 2730; c) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L., *Chem. Rev.,* **2004**, *104*, 6217; d) Sun, C.-L.; Li, B.-J.; Shi, Z.-J., *Chem. Rev.,* **2011**, *111*, 1293.

48. (a) Hashmi, A. S. K., *Chem. Rev.,* **2007**, *107*, 3180; b) Min, B. K.; Friend, C. M., *Chem. Rev.,* **2007**, *107*, 2709; c) Li, Z.; Brouwer, C. ; He, C., *Chem. Rev.,* **2008**, *108*, 3239; d) Krause, N.M; Winter, C., *Chem. Rev.* **2011**, *111*, 1994; e) Corma, A.; Leyva-Perez, A.; Sabater, M. J., *Chem. Rev.,* **2011**, *111*, 1657; f) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y., *Chem. Rev.,* **2012**, *112*, 2467; g) Stratakis, M.; Garcia, H., *Chem. Rev.,* **2012**, *112*, 4469; h) Bandini, M., *Chem. Soc. Rev.,* **2011**, *40*, 1358; i) Lu, B.-L.; Dai, L.; Shi, M., *Chem. Soc. Rev.,* **2012**, *41*, 3318; j) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A.,

Science, **2012**, *337*, 1644.

49. (a) Saisaha, P.; de Boer, J. W.; Browne, W. R., *Chem. Soc. Rev.,* **2013**, *42*, 2059; b) Zhou, B.; Chen, H.; Wang, C., *J. Am. Chem. Soc.,* **2013**, *135*, 1264.

50. (a) Fagnou, K.; Lautens, M., *Chem. Rev.,* **2003**, *103*, 169; b) Hayashi, T.; Yamasaki, K., *Chem. Rev.,* **2003**, *103*, 2829; c) Colby, D. A.; Bergman, R. G.; Ellman, J. A., *Chem. Rev.,* **2010**, *110*, 624; d) Song, G.; Wang, F.; Li, X., *Chem. Soc. Rev.* **2012**, *41*, 3651; e) Etayo, P.; Vidal-Ferran, A., *Chem. Soc. Rev.,* **2013**, *42*, 728.

51. (a) Maas, G., *Chem. Soc. Rev.,* **2004**, *33*, 183; b) Murahashi, S. I.; Zhang, D., *Chem. Soc. Rev,.* **2008**, *37*, 1490; c) Naota, T.; Takaya, H.; Murahashi, S. I., *Chem. Rev.,* **1998**, *98*, 2599; d) Trost, B. M.; Toste, F. D. ; Pinkerton, A. B., *Chem. Rev.,* **2001**, *101*, 2067; e) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H., *Chem. Rev.,* **2012**, *112*, 5879; f) Zhao, P.; Wang, F.; Han, K. L.; Li, X., *Org. Lett.,* **2012**, *14*, 5506.

52. (a) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E., *Chem. ReV*., **1996**, *96*, 2563. (b) Kaim, W.; Rall, J., *Angew. Chem.,* Int. Ed. **1996**, *35*, 43. (c) Holm, R. H.; Kennepohl, P.; Solomon, E. I., *Chem. ReV.* **1996**, *96*, 2239. (d) Klinman, J. P., *Chem. ReV.*, **1996**, *96*, 2541. (e) Cole, A. P.; Root, D. E.; Mukherjiee, P.; Solomon, E. I.; Stack, T. D. P., *Science* **1996**, *273*, 1848. (f) Elliot, S. J.; Zhu, M.; Tso, L.; Nguyen, H.-H. T.; Yip, J. H.-K.; Chan, S. I., *J. Am. Chem. Soc*., **1997**, *119*, 9949. (g) Frausto da Silva, J. J. R.; Williams, R. J. P*., The Biological Chemistry of the Elements*; Oxford University Press: Oxford, **2001**. (h) Itoh, S., *In Comprehensive Coordination Chemistry*, 2nd ed.; McCleverty, J. A., Meyer, T. J., Que, L., Tolman, W. B., Eds.; Elsevier: Dordrecht, **2003**; Vol. 8, Chapt. 8.15, pp 369-

393. (i) Lee D. H*., In Comprehensive Coordination Chemistry*, 2nd ed.; McCleverty, J. A., Meyer, T. J., Que, L., Tolman, W. B., Eds.; Elsevier: Dordrecht, **2003**; Vol. 8, Chapt. 8.17, pp 437-457. (j) Ayala, M.; Torres, E., *Appl. Catal.,* **2004**, *272*, 1. (k) Lieberman, R. L.; Rosenzweig, A. C., *Crit. ReV. Biochem. Mol. Biol.*, **2004**, *39*, 147. (l) Lieberman, R. L.; Rosenzweig, A. C., *Nature,* **2005**, *434*,

177. (m) Yoon, J.; Solomon, E. I., *Inorg. Chem.,* **2005**, *44*, 8076.

53. (a) Karlin, K. D.; Zuberbu¨hler, A. D*.. In Bioinorganic Catalysis,* 2nd ed.; Reedijk, J., Bouwman, E., Eds.; Dekker, New York, **1999**; pp. 469-534. (b) Gamez, P.; Aubel, P. G.; Driessen, W. L.; Reedijk, J.,

Chem. Soc. ReV., **2001**, *30*, 376. (c) Mimmi, M. C.; Gullotti, M.; Santagostini, L.; Battaini, G.; Monzani, E.; Pagliarin, R.; Zoppellaro, G.; Casella, L., *Dalton Trans.,* **2004**, 2192. (d) Mirica, L. M; Ottenwaelder, X.; Stack, T. D. P., *Chem. ReV*., **2004**, *104*, 1013. (e) Lewis, E. A.; Tolman, W. B., *Chem. ReV.*, **2004**, *104*, 1047. (f) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Haukka, M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L., *Angew. Chem., Int. Ed.,* **2005**, *44*, 4345. (g) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Karabach, E. Yu.; Haukka, M.; Guedes da Silva,

M. F. C.; Pombeiro, A. J. L. *Ad*V*. Synth. Catal.,* **2006**, *348*, 159.

54. (a) Casarin, M.; Corvaja, C.; Di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F.; Tagliatesta, P. *Inorg. Chem.* **2004**, *43*, 5865. (b) Casarin, M.; Corvaja, C.; Di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F. *Inorg. Chem.* **2005**, *44*, 6265.

55. Murahashi, S.; Komiya, N.; Hayashi, Y.; Kumano, T., *Pure Appl. Chem.,***2001**, *73*, 311.

56. Otha, T.; Tachiyama, T.; Yoshizawa, K.; Yamabe, T.; Uchida, T; Kitagawa, T., *Inorg. Chem.,* **2000**,*39,* 4358;.

57. Karabach, Y.Y.; Kirillov, A.M.; da Silva, M.F.C.G.; Kopylovich, M.N.; Pombeiro, A.J.L., *Cryst. Growth Des.,* **2006**, *6,* 2200.

58. Kabrach, Y.Y.; Kirillov, A.M.; Haukka, M.; Kopylovich, M.N.; Pombeiro, A.J.L., *J. Inorg. Biochem.,* **2008**, *102,* 1190.

59. Kirillov, A.M.; Kabrach, Y.Y.; Haukka, M.; de Silva, M.F.C.G.; Sanchiz, J.; Kopylovich, M.N.; Pombeiro, A.J.L., *Inorg Chem.,* **2008**, *47*, 162;

60. Gruenwald, K.R.; Kirillov, A.M; Haukka, M.; Sanchiz, J.; Pombeiro, A.J.L., *Dalton Trans.,* **2009**, *2010,* 2109.

61. Kirillova, M.V.; Kozlov, Y.N.; Shul'pina, L.S.; Lyakin, O.Y.; Kirillov, A.M.; Talsi, E.P.; Pombeiro, A.J.L.; Shul'pina, G.B., *j. Catal.,* **2009**, *268,* 26

62. Kirillova, M.V.; Kirillov, A.M.; Mandelli, D.; Cavalho, W.A.;

Pombeiro, A.J.L.; Shul'pina, G.B., *J. Catal.,* **2010**, *272,* 9.

63. Kirillova, M.V.; Kirillov, A.M.; Kuznetsov, M.L.; Silva, J.A.L.; Fraùsto da Silva, J.J.R.; Pombeiro, A.J.L., *Chem. Commun.,* **2009**, 2353;

64. Kirillova, M.V.; Kirillov, A.M.; Pombeiro, A.J.L., *Chem. Eur. J.,* **2010**, *16,* 9485.

65. Kirillova, M.V.; Kirillov, A.M.; Pombeiro, A.J.L., *Adv. Sinth.,* **2009**, *351,* 2936.

66. Kirillova, M.V.; Kirillov, A.M.; Coelho, J.A.S.; da Silva, M.F.C.G.; Nesterov, D.S.; Gruenwald, K.R.; Haukka, M.; Pombeiro, A.J.L.,

Inorg. Chem., **2010**, *49*, 6390.

67. Kirillova, M.V.; Kirillov, A.M.; Pombeiro, A.J.L., *Appl. Catal. A:* Gen **2011**, *401,* 106.

68. Kirillova, M.V.; Kirillov, A.M.; Pombeiro, A.J.L.; Karabach, Y.Y.; Haukka, M., *Dalton Trans.,* **2011**, *40,* 6378.

69. Kirillova, M.V.; Kirillov, A.M.; Shul'pina L.S.; Figiel, P.J.;

Gruenwald, K.R.; da Silva, M.F.C.G.; Haukka, M.; Pombeiro,

A.J.L.; Shul'pina, G.B., *J. Mol. Catal. A. Chem.,* **2011**, *350,* 26.

70. Kirillova, M.V.; Kirillov, A.M.; Martins, A.N.C.; Graiff, C.; Tiripicchio, A.; Pombeiro, A.J.L., norg. Hem., **2012**, *51,* 5224.

71. Kirillova, M.V.; Kirillov, A.M.; Karabach, Y.Y.; Haukka, M., Pombeiro, A.J.L., *Cryst. Growth Des.,* **2012**, *12,* 1069.

72. Mahmudov, K.T.; Kopylovich, M.N.; da Silva, M.F.C.G.; Figiel, P.J.; Karabach, Y.Y.; Pombeiro, A.J.L., *Mol. Catal. A: Chem.,* **2010**,

318, 44.

73. Kopylovich, M.N.; Mahmudov, K.T.; da Silva, M.F.C.G.; Fiegel, P.J.; Karabach, Y.Y.; Kuznetsov, M.L.; Luzyanin, K.V.; Pombeiro, A.J.L., *Inorg. Chem.,* **2011**, *50,* 918.

74. Kopylovich, M.N.; Nunes A.C.C.; Mahmudov, K.T.; Haukka, M.; MacLeod, T.C.O.; Martins, L.M.D.R.S.; Kuznetsov, M.L.; Pombeiro, A.J.L:, *Dalton Trans.,***2011**, *40,* 2822.

75. Salavati-Niasari, M.; Salimi, Z.; Bazarganipour, M.; Davar, F.,

Inorg. Chem. Acta, **2009**, *362,* 3715.

76. Ceyhana, G.; Celik, C.; Urus, S.; Demitras, I.; Elmasta, M.; Tumer, M., *Spectrochim. Acta A,* **2011**, *81,* 184.

77. Basak, S.; Sen, S.; Roy, P.; Gomez-Garcia, C.J.; Hughes, D.L.; Butcher, R.J.; Garribba, E.; Mitra, S., *Aust. J. Chem.,* **2010**, *63,* 479.

78. Roy, P.; Manassero, M., *Dalton Trans.,* **2010**, *39,* 1539.

79. Di Nicola, C.; Karabach, Y.Y.; Kirillov, A.M.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A.J.L., *Inorg. Chem.,* **2007**, *46,* 221.

80. Di Nicola, C.; Garau, F.; Karabach, Y.Y.; Martins, L.M.D.R.S.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A.J.L., *Eur. J. Inorg. Chem.,* **2009**, 666;

81. Contaldi, S.; Di Nicola, C.; Garau, F.; Karabach, Y.Y.; Martins, L.M.D.R.S.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A.J.L., *Dalton Trans.,* **2009**, 4928.

82. Kirillova, M.V.; Kirillov, A.M.; da Silva, M.F.C.G.; Pombeiro, A.J.L., *Eur. J. Inorg. Chem.,* **2008**, 3423.

83. Shul'pina, G.B., *J. Mol. Catal. A: Chem.,***2002**, *189,* 39.

84. Shul'pina, G.B., *C. R. Chim.,* **2003**, *6,* 163.

85. Trimmer E. E.; Essigmann, J. M., *Essays Biochem.*, **1999**, *34*, 191– 211.

86. Paschke, R.; Kalbitz, J.; Paetz, C.; Luckner, M.; Mueller, T.; Schmoll, H.-J.; Mueller, H.; Sorkau, E.; Sinn, E.; *J. Inorg. Biochem.,* **2003**, *94,* 335– 342.

87. Ott, I.; Gust, R., *Arch. Pharm.,* **2007**, *340*, 117–126.

88. Barnard, P. J.; Berners-Price, S. J., *Coord. Chem. Rev.,* **2007**, *251*, 1889–1902.

89. Bindoli, A.; Rigobello, M. P.; Scutari, G.; Gabbiani, C.; Casini, A.; Messori, L., *Coord. Chem. Rev.,* **2009**, *253*, 1692–1707.

90. Santini, C.; Pellei, M.; Papini, G.; Morresi, B.; Galassi, R.; Ricci, S.; Tisato, F.; Porchia, M.; Rigobello, M. P.; Gandin, V.; Marzano, C., *J. Inorg. Biochem.*, **2011**, *105,* 232–240.

91. Rackman, O.; Nichols, S. J.; Leddman, P. J.; Berners Price, S. J.; Filipovska, A.; *Biochem. Pharmacol.,* **2007**, *74,* 992–1002.

92. Caruso, F.; Rossi, M.; Tanski, J.; Pettinari, C.; Marchetti, F., *J. Med. Chem.,* **2003**, *46,* 1737–1742.

93. Vergara, E.; Casini, A.; Sorrentino, F.; Zava, O.; Cerrada, E.; Rigobello, M. P.; Bindoli, A.; Laguna, M.; Dyson, P. J.,

ChemMedChem, **2010**, *5,* 96–102.

94. Maiore, L.; Cinellu, M. A.; Michelucci, E.; Moneti, G.; Nobili, S.; Landini, I.; Mini, E.; Guerri, A.; Gabbiani, C.; Messori, L., *J. Inorg. Biochem.,* **2011**, 105, 348–385.

95. Casas, J. S.; Castellano, E. E.; Couce, M. D.; Crespo, O.; Ellena, J.; Laguna, A.; Sànchez, A.; Sordo, J.; Taboada, C., *Inorg. Chem.,* **2007**, *46*, 6236–6238.

96. Vergara, E.; Cerrada, A.; Casini, O.; Zava, M.; Laguna P. J.

Dyson,Organometallics, **2010**, *29*, 2596–2603.

97. McKeage, M. J.; Papathanasiou, P.; Salem, G.; Sjaarda, A.; Swiegers, G. F.; Waring, P.; Wild, S. B., *Met.-Based Drugs,* **1998**, *5*, 217–223.

98. Berners-Price, S. J.; Bowen, R. J.; Galettis, P.; Healy, P. C.; McKeage, M. J., *Coord. Chem. Rev.,* **1999**, *185–186*, 823–836.

99. Nell, M. J.; Wagener, M.; Zeevaart, J. R.; Kilian, E.; Mamo, M. A.; Layh, M.; Coyanis, M.; van Rensburg, C. E., *Appl. Radiat. Isot.,* **2009**, *67*, 1370–1376.

100. McKeage, M. J.; Berners-Price, S. J.; Galettis, P.; Bowen, R. J.; Brouwer, W.; Ling, D.; Zhuang, L.; Baguley, B. C., *Cancer Chemother. Pharmacol.,* **2000**, *46*, 343–350.

101. Kouroulis, K. N.; Hadjikakou, S. K.; Kourkoumelis, N.; Kubicki, M.; Male, L.; Hursthouse, M.; Skoulika, S.; Tyurin, A. K. V. Y.; Dolganov, A. V.; Milaeva, E. R.; Hadjiliadis, N., *Dalton Trans.,* **2009**, 10446–10456.

102. Halcrow, M. A., *Dalton Trans.,* **2009**, 2059–2073.

103. Marzano, C.; Gandin, V.; Folda, A.; Scutari, G.; Bindoli, A.; Rigobello, M. P., *Free Radical Biol. Med.,* **2007**, *42*, 872–881.

104. Gandin, V.; Fernandes, A. P.; Rigobello, M. P.; Dani, B.; Sorrentino, F.;. Tisato, F; Bjoernstedt, M.; Bindoli, A.; Sturaro, A.; Rella, R.; Marzano, C., *Biochem. Pharmacol.,* **2010**, *79*, 90–101.

105. Zhou, Y.; Ling, X. L.; Li, S. W.; Li, X. Q.; Yan, B., *J. Gastroenterol.,* **2010**, *16*, 2291–2297.

106. ELbjerami, O.; Rashdan, M. D.; Nesterov, V.; Rawashdeh-Omary, M. A., *Dalton Trans.* **2010**, *39*, 9465-9468.

107. Vickery, J. C.; Olmstead, M.M.; Fung, E. Y.; Balch, A. L., *Angew. Chem. Int. Ed. Engl*., **1997**, *36*, 1179.

108. Yang, C.; Messerschmidt, M.; Coppens, P.; Omary, M.A., *Inorg Chem.*, **2006**, *45,* 6592-6594.

109. Galassi et al., *Inorg chem.,* **2013**, *52*, 14124-14137.

110. Murray, H. H.; Raptis, R.G.; Fackler, J.P., *Jr. Inorg. Chem.,* **1988**, *27*, 26–33; b) Zhang, C.-Y.; Feng, J-B.; Gao, Q.; Xie, Y-B, Acta Cryst*.,* **2008** E64..

111. Dias, H. V. R.; Polach, S. A.; Wang, Z. J., *Fluorine Chem*., **2000**, *103*, 163

112. Leclercq, L.; Simard, M.; Schmitzer, A.R., *J. Mol Struct.,* **2009**, *918*, 101-107.

113. Garrison,J.C.; Youngs,W.J., *Chem Rev.,* **2005**, *105*, 3978-4008.

114. Schneider, S.K.; Hermann, W.A.; Herdtweck, E., *Z. Anorg. Allg. Chem*., **2003**, *629*, 2363-2370.

115. Frey, G.D.; Dewhurst, R.D.; Kausar, S.; Donnadieu, B.; Bertrand, G.,

Organomet Chem., **2008**, *693*, 1674–1682.

116. Garner, M.E.; Niu, W.; Chen, X.; Ghiviriga,I.; Abboud, K.A.; Tan, W.; Veige, A.S.,*Dalton Trans.,* **2015**, *44*, 1914–1923.

117. Patila, Y.S.; Deallya, A.; Hackenberga, F.; Kapsb, L.; Mller-Bunza, H.; Schobertb, R.; Tacke, M.,*Helvetica Chimica acta,* **2011**, *94,* 1551-1561.

118. Arduengo, III, A.J.; Dias, H.V.R.;. Harlow, R:L.; Kline, M.; *J. Am Chem Soc.,* **1992**, 5530-5534.

119. Citadelle, C.A.; Le Nouy, E.; Bisaro, F.; Slawin, A.M.Z.; Cazin, C.S.J., *Dalton trans*.,**2010**, 39, 4489-4491.

120. Galassi, R.; Burini, A.; Ricci, S.; Pellei, M.; Rigobello, M.P.; Città, A.; Dolomella, A, Gandin, V.; Marzano, C., *Dalton Trans.,* **2012**, *41,* 5307.

121. Mohamed, A. A.; Ricci, S.; Burini, A.; Galassi, R.; Santini, C.; Chiarella, G. M.; Melgarejo, D. Y.; Fackler, J. P., *Inorg. Chem.,* **2011**, *50,* 1014-1020.

122. (a) Shul'pin, G.B., Transition Metals for Organic Synthesis, (eds., M.

Beller and C.Bolm), 2nd edition, vol. 2, Wiley-VCH, New York, 2004, 215. b) Shul'pin, G.B.; Nizova, G.V., React. Kinet. Catal. Lett., 1992, 48, 333–338; (c) Shul'pin, G.B.; Matthes, M.G.;

Romakh, V.B.; Barbosa, M.I.F.; Aoyagi, J.L.T.; Mandelli, D., Tetrahedron, 2008, 64, 2143–2152. d) Shul'pin, G.B., Dalton Trans., 2013, 42, 12794–12818. e) Shul'pin, G.B., Org. Biomol. Chem., 2010, 8, 4217–4228; f) Shul'pin, G.B., Mini-Rev. Org. Chem., 2009, 6, 95–104.

123. (a) Martins, L. M. D. R. S.; Pombeiro, A. J. L., *Coord*. *Chem. Rev.*,

2014, *265*, 74−88. b) Milunovic, M. N. M.; Martins, L. M. D. R. S.;

Alegria, E. C. B. A.; Pombeiro, A. J. L.; Krachler, R.; Trettenhahn, G.; Turta, C.; Shova, S.; Arion, V. B. *Dalton Trans.*, **2013**, *42*,

14388−14401. c) Sutradhar, M.; Kirillova, M. V.; Guedes da Silva,

M. F. C.; Martins, L. M. D. R. S.; Pombeiro, A. J. L., *Inorg. Chem.,*

2012, 51, 11229−11231. d) Silva, T. F. S.; Martins, L. M. D. R. S.;

Guedes da Silva, M. F.; Kuznetsov, M. L.; Fernandes, A. R.; Silva, A.; Santos, S.; Pan, C.-J.; Lee, J.-F.; Hwang, B.-J.; Pombeiro, A. J. L., *Chem. Asian J.*, **2014**, *9*, 1132−1143. e) L.M.D.R.S. Martins, A.

Martins, E.C.B.A. Alegria, A.P. Carvalho, A.J.L. Pombeiro, *Appl. Catal. A*: Gen. 2013, 464, 43–50; f) Martins, L.M.D.R.S.; Peixoto de Almeida, M.; Carabineiro, S.A.C.; Figueiredo, J.L.; Pombeiro, A.J.L., *ChemCatChem,* **2013**, *5*, 3847–3856.

124. (a) Timokhin, I.; Pettinari, C.; Marchetti, F.; Pettinari, R.; Condello, F.; Galli, S.; Alegria, E.C.B.A.; Martins, L.M.D.R.S.; Pombeiro, A.J.L., *Cryst. Growth Des.,* **2015**, *15*,(5), 2303-2317. b) Fernandes, R. R.; Lasri, J.; Kirillov, A. M.; da Silva, F. M. C. G.; Silva, J. A. L.;

Fraústo da Silva, J. J. R.; Pombeiro, A. J. L., *Eur. J. Inorg. Chem.,*

2011, 3781−3790. c) Fernandes, R. R.; Lasri, J.; da Silva, M. F. C. G.; da Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L., *J. Mol. Catal. A: Chem.,* **2011**, 351, 100−111. d) Peixoto de Almeida,

M.; Martins, L. M. D. R. S.; Carabineiro, S. A. C.; Lauterbach, T.; Rominger, F.; Hashmi, A. S. K.; Pombeiro, A. J. L.; Figueiredo, J. L., *Catal. Sci. Technol.,* **2013**, *3*, 3056−3069. e) Martins,

L.M.D.R.S.; Nasani, R.; Saha, M.; Mobin, S.M.; Mukhopadhyay, S.; Pombeiro, A.J.L., *Molecules,* **2015**, *20*, 19203-19220.

125. Arduengo, A.J.III; Dias,H.V.R.; Calabrese, J.C.; Davidson, F.,

Organometallics, **1993**, *12,* 3405.

126. SMART V 5.050 (NT) *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (1998).

127. SAINT V 5.01 (NT) *Software for the CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (1998).

128. Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1990.

129. Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure,* University of Göttingen, Germany, 1997.

130. SHELXTL 5.10 (PC-Version), *Program library for Structure*

Solution and Molecular Graphics; Bruker Analytical X-ray

Systems, Madison, WI (1998).

131. SADABS. *Program for absorption corrections using Siemens CCD based on the method of Robert Blessing*; Blessing, R.H. Act