

Mononuclear Coinage Metals Complexes with Pyrazoles and Imidazoles. Syntheses, Characterizations and Catalytic Applications on MW Peroxidative Oxidation of Alkane of [3,5-dinitropyrazolyl-copper-triphenylphosphane]₂

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Abstract: Trinuclear derivatives of coinage metals based on pyrazoles and imidazoles as bridging ligands have received much attention in recent years for their unexpected pi-acid or pi-basic properties. This behavior resulted in the synthesis of new compounds with sophisticated optoelectronic features with applications in the field of sensing, of optical devices, and finally as semiconductor components of diodes. The chemistry of the trinuclear gold(I) cyclic compounds is strongly linked to the corresponding mononuclear derivatives whose applications have been less studied and sometimes ignored. While the reactivity of the trinuclear gold(I) derivative toward redox reactions is well known, those of silver(I) trinuclear derivatives and copper(I) are not well understood. The different reactivity are strongly influenced by the nature of the metal, in fact, the silver does not support the higher oxidation state, while copper easily passes in the oxidation state (+2). The gold(I) trinuclear derivative leads to the formation of stable gold(I) carbene complexes, silver carbenes with imidazoles are stable and isolated in high yield by the corresponding imidazolium salts but not from the corresponding trinuclear derivative, while the copper mononuclear pyrazole derivatives can be isolated only in the presence of PPh₃ as co-ligand. A dinuclear and a hexanuclear pyrazolate copper compounds having electron-withdrawing groups in the pyrazole were tested as catalysts in the MW peroxidative oxidation of cycloalkane, showing a better and faster conversion in the cyclohexyl ketone.

Key words: Carbenes; pyrazoles, imidazoles, metallacycles, gold(I), Ag(I) and Cu(I) derivatives, NHC complexes, oxidative addition; homogeneous catalysis, Cu catalyst, MW peroxidative oxidation of alkanes.

INTRODUCTION

The interest in coordination chemistry has impressively increased in the last decades. One research lines in progressively expansion is the family of the metallacycles containing pyrazole and imidazole as bridging ligands.^[1] 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.^[2]

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

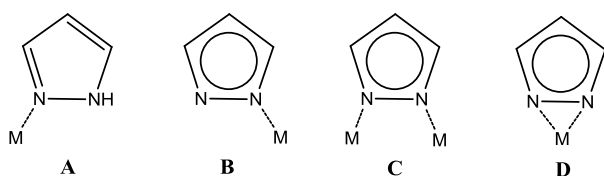


Figure 1

The imidazole is an aromatic heterocycle sterically and electronically comparable with the pyrazole. In the anionic form imidazole can act as a monodentate ligand to give mononuclear complexes^[3], while in the exo-bidentate coordination it can form polymers^[4] or metallacycles.^[5] Both type of exo-bidentate coordinations are possible as shown in figure 2, involving N,N' or N³,C² metal binding: the latter is typical in N-substituted imidazoles after deprotonation of the C² with a strong base.

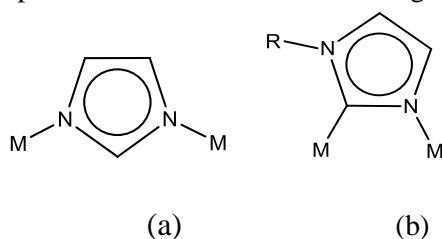


Figure 2

Oxidative addition to polynuclear Gold(I) compounds.

Trimeric pyrazolate and imidazolate gold(I) complexes can undergo oxidative-addition

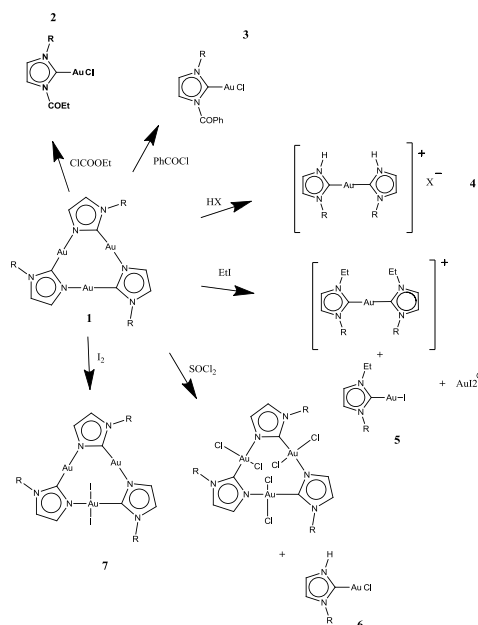
reactions of halogens at the metal centers giving mixed-valence $\text{Au}_2^{\text{I}}/\text{Au}^{\text{III}}$ metallacycles. Both steric and electronic factors influence the reactivity of the gold atoms in these compounds. The electronic communication between the gold atoms may be the origin of this 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. Complex $[\text{Au}(\mu\text{-C}(\text{OMe})=\text{N}(\text{Me}))_3]_3$ 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).



Scheme 1

Oxidative-addition with halogens was also investigated for complex $[\text{Au}(\mu\text{-N}^3, \text{C}^2\text{-bzim})_3]_3$. This substrate behaves similarly to most of the trinuclear gold(I) complexes since it adds Iodine at only one gold center to yield $[\text{Au}(\mu\text{-N}^3, \text{C}^2\text{-bzim})_3]_3\text{I}_2$.^[6] It consists of discrete trinuclear complexes with the gold atoms bridged by three 1-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 carbenate derivatives. A different behavior of complex $[\text{Au}(\mu\text{-N}^3, \text{C}^2\text{-bzim})_3]_3$ 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^[7d,f] or by ¹⁹⁷Au Mössbauer investigation.^[6] Moreover, an oxidation was

observed when complex $[\text{Au}(\mu\text{-N}^3, \text{C}^2\text{-bzim})]_3$ reacted with Me_3SiI ($\text{Au}^{\text{I}}/\text{Au}_2^{\text{III}}$) or SOCl_2 (Au_3^{III}).^[6,7] The behaviour of trinuclear gold(I) compound, $[\text{Au}(\mu\text{-Rim-N}^3, \text{C}^2)]_3$ where Rim is 1-benzylimidazole, have been investigated towards several reagents capable of oxidative addition (Scheme 2).



Scheme 2

NHC chemistry.

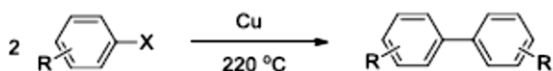
Öfele and Wanzlick first pioneered the metalation of imidazol-2-ylidenes, better known as N-heterocyclic carbenes (NHCs), from imidazolium salts in 1968.^[8,9] However, it was not until the isolation of the first free carbene by Arduengo, in 1991, that significant interest was given to the area.^[10] Complexes of N-heterocyclic carbenes with virtually every transition metal and many main group elements have been reported.^[8,11] 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.^[12,13] In 1997, Bertrand and colleagues reported the synthesis of a silver NHC from triazolium salts using silver acetate.^[14] Lin and Wang, in 1998, reported the syntheses of silver NHCs using Ag_2O .^[15] Danopoulos and colleagues reported the syntheses of silver NHC complexes using Ag_2CO_3 in

2000.^[16] 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). Several theoretical studies have been done involving N-heterocyclic carbene complexes of group 11 metals.^[12,13,17] Bond strengths of group 11 NHC complexes follow the pattern $\text{Au} > \text{Cu} > \text{Ag}$. 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.^[17] 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.

Homogeneous catalysis.

The term catalysis was first employed by Berzelius in 1836 to identify a new entity capable of promoting the occurrence of a chemical reaction by a "catalytic contact". Currently more than 95% of chemicals being produced via a process that includes at least one catalytic step.^[18] Traditionally catalysts 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 a different phase (heterogeneous catalysis). 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 makes the homogeneous catalysts intrinsically

more active and selective than traditional heterogeneous catalysts. Since the findings of the Ullmann reaction (Scheme 3), 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.^[19] 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 3: Ullmann reaction.

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 microanalyser at University of Camerino. Infrared spectra (4000 – 100 cm⁻¹) were recorded with PERKIN-ELMER SYSTEM 2000 FT-IR spectrophotometer. ¹H NMR spectra were recorded on an Oxford-400 Varian spectrometer. Chemical shifts, in ppm, for ¹H NMR spectra are relative to internal Me₄Si. 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 (N₂) 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.

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 F², SHELXL-97,[129] incorporated in SHELXTL-PC V 5.10.[130]

The structure was solved in the space group P $\bar{1}$ (# 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.

Syntheses of compounds

[Ag-C²,N³-(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 stirred for other 30 minutes. After that 169.87 g, of AgNO₃ (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.

1,3-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 %.

[1,3-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 CH₂Cl₂. To this solution solid Ag₂O (102 mg; 0.44 mmol) was added. The grey suspension was stirred for two hours at room temperature then CH₂Cl₂ 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 %.

[1,3-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 CH₂Cl₂. To this solution, a solution of Me₂SAuCl (37 mg; 0.1278 mmol) in 3 mL of CH₂Cl₂ 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%.

1,3-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 K₂CO₃ (5.26 g, 3.8 x 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 CH₂Cl₂. The methylenic solution was extracted with water (20 mL x 1 time). The organic phase was treated with Na₂SO₄ 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 %.

[1,3-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 CH₂Cl₂. To this solution solid Ag₂O (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 CH₃OH filtered over a celite bed and dried obtaining 71 mg of an oily product. Yield 64%.

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;

1.8×10^{-2} mol). The solution was stirred overnight and evaporated to dryness. A green oil was obtained. 630 mg (0.23×10^{-2} mol) of this oil were treated with 20 mL of CH_2Cl_2 and 263 mg of Ag_2O (0.1137×10^{-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 %.

[Cu(μ -N,N-3,5-(NO₂)₂pz)₂(PPh₃)₂], compound 9.

To a mixture of Ph_3P (0.174 g; 0.66 mmol) and $\text{Cu}(\text{BF}_4)_2$ (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

[Ag(μ -N,N-3,5-(NO₂)₂pz)(PPh₃)], 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 %.

[Cu(μ -N,N-3,5-(CF₃)₂pz)₂(PPh₃)], compound 11.

To a mixture of Ph_3P (0.155 g; 0.58 mmol) and $\text{Cu}(\text{BF}_4)_2$ (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 %.

[Ag(μ -N,N-3,5-(CF₃)₂pz)(PPh₃)], compound 12.

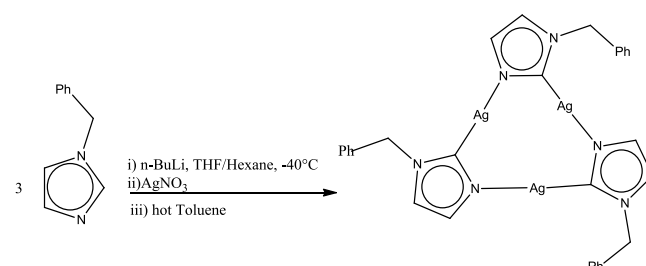
Ph_3P (0.067 g; 0.25 mmol) dissolved in 10 mL of dry THF, solid AgBF_4 was added (0.05 g; 0.25 mmol). The solution was stirred for one hour and a methanolic solution of the sodium pyrazole salt (0.051 g; 0.25 mmol) was added. The suspension was stirred over night at room temperature. The white suspension 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 %.

RESULTS AND DISCUSSIONS

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.

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 Fackler method^[21] as following (scheme 4).



Scheme 4.

The compound **1** was characterized by ¹H NMR and IR spectroscopies, elemental analysis etc.

Moreover the crystal structure was determined by X-ray Crystal diffraction. 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 and 4, respectively. The crystal structure data and structure refinement are listed in table 1 (tables in appendix).

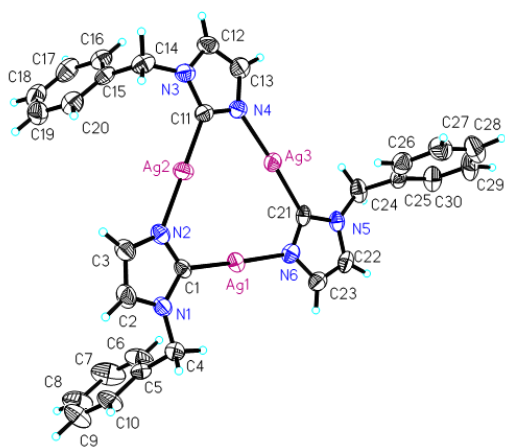


Figure 3

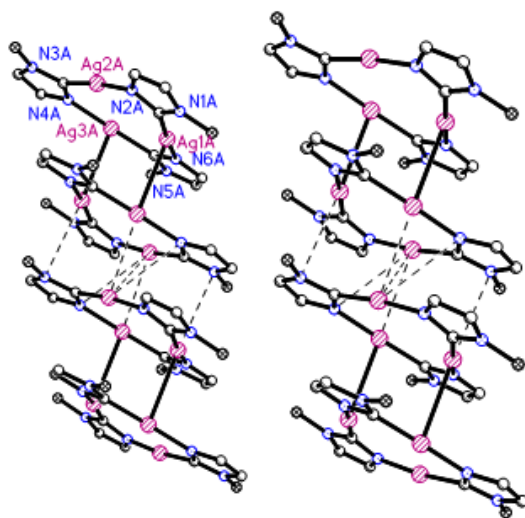


Figure 4

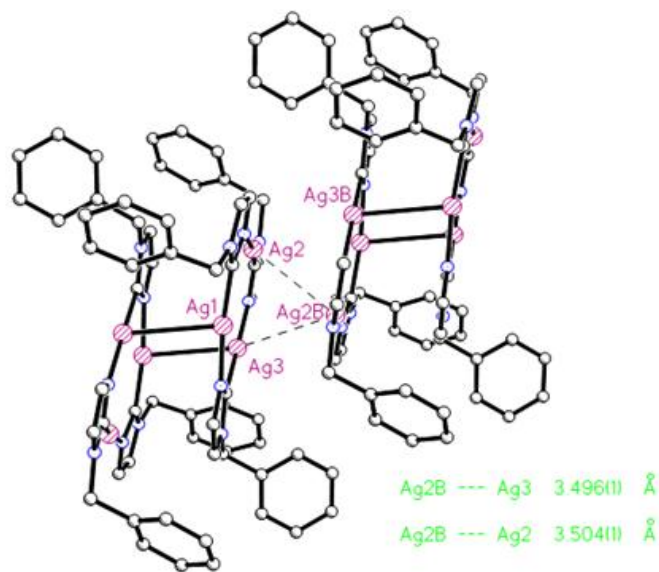
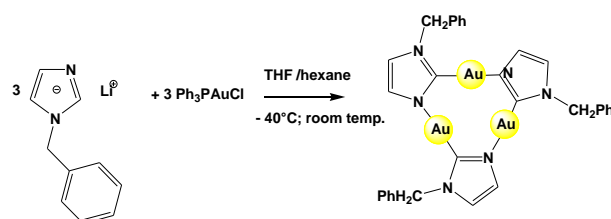
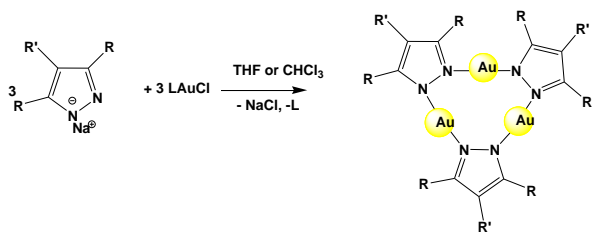


Figure 5. Depiction of the secondary interactions in the dimer of trimers of compound **1**.

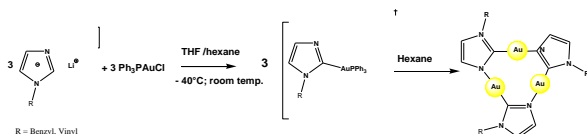
A comparison with the crystal structure of the $[\text{Au}-\text{C}^2\text{N}^3-(1\text{-benzylimidazolite})]_3$ can be discussed.^[22] The gold(I) trinuclear compound crystallizes in $C2/c$ monoclinic space group but also in this case the formation of dimer of trimers was observed with aurophilic distance 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 polymorph of $[\text{Au}(\mu\text{-C}(\text{OMe})=\text{NMe})_3]$ ^[22] and for $\{[3,5\text{-}(i\text{-pr})_2\text{Tz}]\text{Au}\}_3$.^[23]





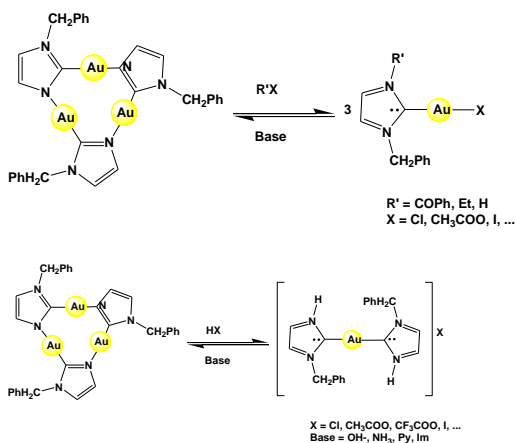
Scheme 5 Examples of synthesis paths to obtain trinuclear cyclic gold(I) compounds from carbeniates, imidazoles and pyrazoles.

During the synthesis of the Gold(I) analogous the formation of an intermediate have been occurred and a further stirring with hexane was needed. The hexane facilitates the removal of the PPh₃ allowing the cyclization by coordination to the N₃. (Scheme 6)



Scheme 6

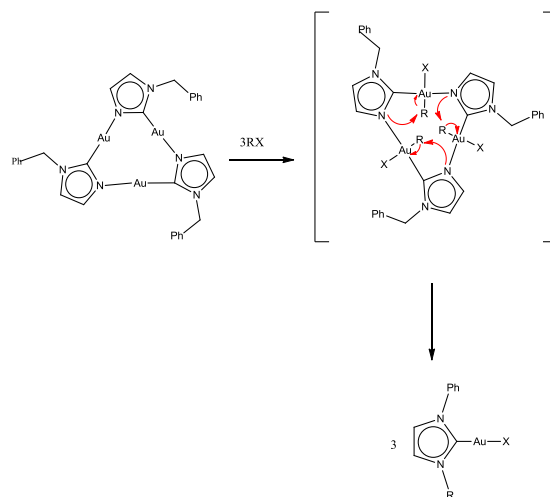
The formation of mononuclear carbenic derivatives by starting from the gold(I) trinuclear derivative can also be achieved by adding alkyl or acyl halides or acids (scheme 7)



Scheme 7

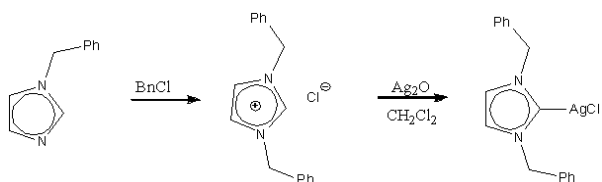
This reactivity was ascertained for the gold(I) trinuclear cyclic compound where the ligand is 1-benzyl imidazole or 1-vinylimidazole but it has never been tested for the silver analogous, compound **1**. We wanted to test this reactivity starting with the reaction of compound **1** with benzyl chloride in CH₂Cl₂ with a mole ratio of 1 :

3. 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, whose 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 that could not be attributed to the imidazolium salt. This can be due to the fact that the silver(I) does not support oxidative addition that it could be the first step of the reaction followed by a reductive elimination with formation of the monocarbene derivative in the case of gold.^[6] (Scheme 8) To confirm this thesis we also performed the synthesis of the corresponding silver carbene complex to test its stability (Scheme 9). The synthesis proceeds by the formation of the imidazolium salt and further treatment with Ag₂O following a literature method already published.^[24] The imidazolium salt, compound **2**, and the corresponding silver carbene, compound **3**, were characterized by ¹H and ¹³C NMR, IR spectroscopies, elemental analysis and ESI mass spectrometry.



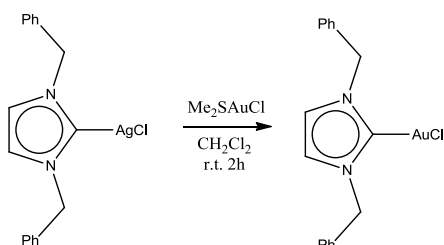
Scheme 8

The silver carbene resulted pretty stable so we stated that the reason why we could not afford the carbenic specie from the trinuclear cyclic compound is the fact that Ag could not support higher oxidation states than (I).



Scheme 9

We were also able to get crystals of compound **3** by layering hexane on a solution of CH_2Cl_2 . (data of the crystal structure collected in Table 2) We determined the crystal structures that showed the presence of a dimer of the carbenes through Ag-Cl interaction. 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 10

The transmetalation 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 . 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.

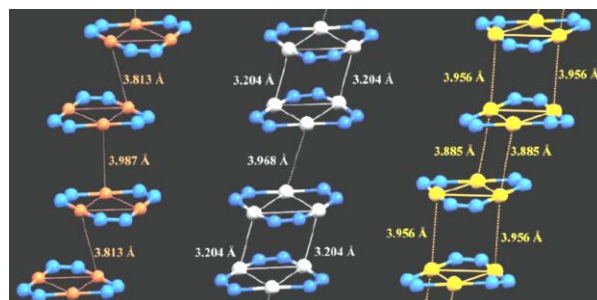
The transmetalation reaction of scheme 10 was successful in the case of gold(I) but failed when the exchanging metal was copper(I). In fact the reaction with CuCl and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ did not afford to the corresponding copper(I)carbene. The direct reaction between the imidazolium salt and CuCF_3SO_3 , upon previous treatment with potassium tert-butoxide, was performed according to a procedure reported in literature^[25] or by adding the Cu_2O to the imidazolium salt.^[26]

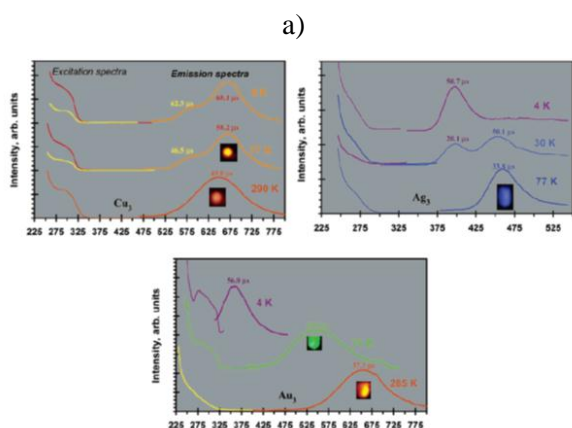
In both cases it was not possible to isolate the Cu(I) carbene species and a blue and pasty suspension was obtained.

Given the excellent results, the synthesis of the 4,5-Dichloro-, 4,5-Dicyano imidazolium chloride were attempted according to the method previously adopted.^[15] 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 9 also the 1,3-dibenzyl-benzimidazolium, compound **5**, and the 1,3-dibenzoyl-imidazolium salts, , compound **7**, were used to obtain the corresponding silver carbene compounds (compounds **6** [1,3-dibenzyl-benzimidazolyl-2-yl-silver chloride]₂ and compound **8** 1,3-dibenzoyl-imidazolium-silver chloride respectively). However the formation of the silver derivative, compound **8**, is still under debate.

Pyrazolate Au, Ag and Cu derivatives.

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 5 or scheme 7. 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.^[25] (Figure 3)



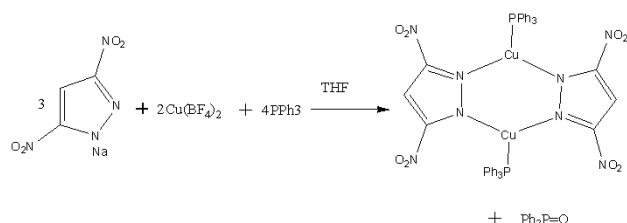


b)

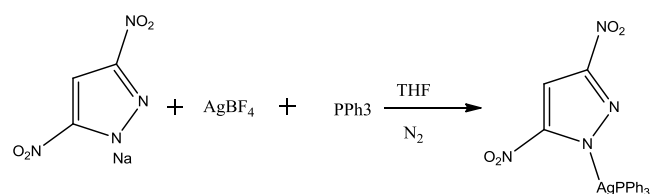
Figure 6. a) Columnar packings and intermolecular metallophilic interactions for compounds $[\text{Cu-3,5-pz}(\text{CF}_3)_2]_3$ (left), $[\text{Ag-3,5-pz}(\text{CF}_3)_2]_3$ (central), $[\text{Au-3,5-pz}(\text{CF}_3)_2]_3$ (right). b) Thermochromic emission spectra for Cu_3 , Ag_3 and Au_3 solid state 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 11c.^[21,27] However when the synthesis of $\text{Au}(\text{I})$ or $\text{Cu}(\text{I})$ was approached according to the classic methods, no cycles were obtained and the kinetically and thermodynamically stable mononuclear derivatives were 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 was obtained only by reacting the 3,5-dinitropyrazolate salt with $\text{Cu}(\text{BF}_4)_2$ in the presence of a co-ligand such as a phosphane (acting also as reducing agent). (Scheme 11a) 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

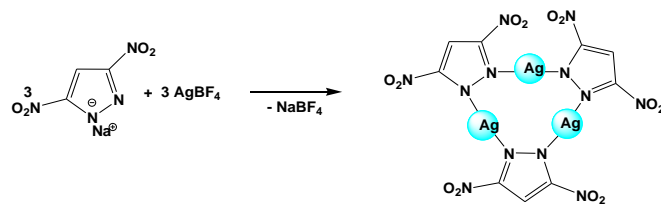
where the phosphane is coordinated to a metal cation is clear as in the ^{31}P -NMR a signal at 3.76 ppm is present as well as in the IR spectrum the peak at 1097 cm^{-1} is typical for P-quaternary carbon stretching. Moreover the $\text{C}_4\text{-H}$ stretching band in compound **9** falls at 3154 cm^{-1} , 14 cm^{-1} bluishifted if compared to the cyclic silver derivative $[\mu\text{-N,N-3,5-pz}(\text{NO}_2)_2\text{-Ag}]_3$ (3140 cm^{-1}) and 14 cm^{-1} redshifted if compared to the $[(3,5\text{-pz}(\text{NO}_2)_2\text{-AuPPh}_3)]$ at 3168 cm^{-1} .



a)



b)



c)

Scheme 11

In the ESI MS peaks due to the $[\text{Cu}(\text{PPh}_3)_2]^+$ 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 7 and the crystal data in table 3. Representative bond distances and angle in Table 4. The dinuclear nature of compound $[\text{Cu-(3,5-(NO}_2)_2\text{pz)}(\text{PPh}_3)]_2$ 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 N₅N₆C₄C₅C₆ ring up to 0.3376(4) for Cu2 with respect to N₁N₂C₁C₂C₃ 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.

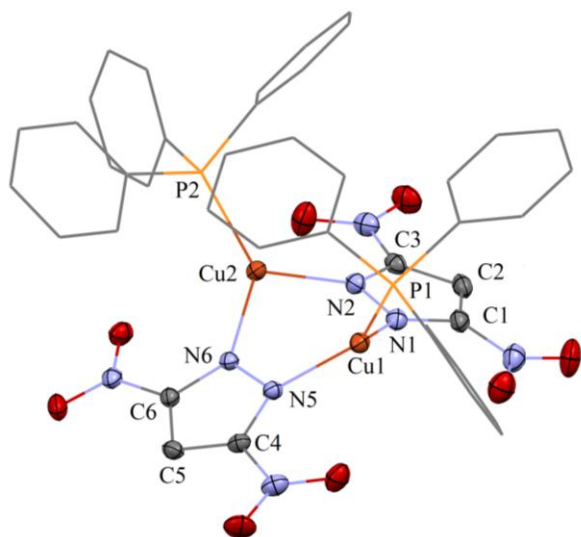


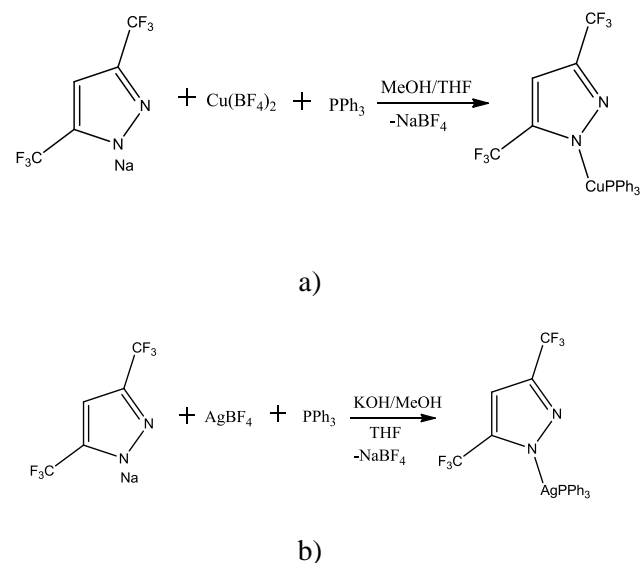
Figure 7

The reaction of the 3,5-(NO₂)₂pz sodium salt with silver tetrafluoroborate affords to the trinuclear cycle, but in the presence of a coordinating ligand such as the PPh₃, the mononuclear compound **10** can be obtained. (Scheme 11b) The substitution of the NO₂ groups in positions 3 and 5 with CF₃ 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 12) By comparing the ³¹P 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 C4-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(PPh₃)₂]⁺ already observed for compound **9**, also the semi oxidized product was obtained such as [Cu(PPh₃)(PPh₃=O)]⁺ at 587 and 605 m/z, respectively.

Catalytic studies.

Compound **9** was also tested as catalyst for the peroxidation of alkane, according to a fertile collaboration with Profssa Martins and professor Pompeiro of Instituto Superior Tecnico at Lisbon in Portugal to whom I am very grateful for the preliminary data I could insert in this thesis.

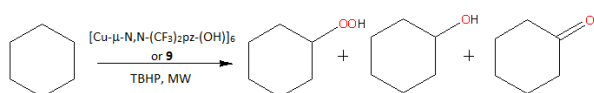


Scheme 12

Compound **9** was studied comparatively with an hexanuclear cyclic copper(I) compound having as bridging ligand the 3,5-(CF₃)₂pyrazolate and hydroxyl groups. The molecular structure of this latter compound resembles those already published by Mohamed et al.^[28] In this [Cu-μ-N,N-(CF₃)₂pz-(OH)]₆ compound a highly hydrated cavity is present on the contrary of what already observed in the previous compounds where Cl⁻, Br⁻, I⁻ and NO₂⁻ were found as encapsulated anions.

Catalytic studies on compound **9** and [Cu- μ -N,N-(CF₃)₂pz-(OH)]₆.

Compounds [Cu- μ -N,N-(CF₃)₂pz-(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. (final products, Scheme 13) The formation of CyOOH was proved by using the method purposed by Shul'pin.^[29] The addition of PPh₃ 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 PPh₃, with the formation of phosphane oxide) and in a corresponding decrease of cyclohexanone (Scheme 3.13).



Scheme 13

A very high yield, up to 58% (**9**) or 51% ([Cu- μ -N,N-(CF₃)₂pz-(OH)]₆) of oxygenated products, is obtained at optimized conditions: 0.5 h (**9**) or 1.5 h ([Cu- μ -N,N-(CF₃)₂pz-(OH)]₆) of MW irradiation at 100°C (see Figure 6 and Table 5 in the appendix), using 0.2% molar ratio of copper catalyst relatively to the substrate, in the presence of 2,2,6,6-tetramethyl-piperidinyloxy 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 9 and 10. The increase from 1 to 5 μ mol of **9** on the reaction medium leads to a yield increment from 22 to 37%, whereas 10 μ mol of **9** allow to reach the maximum yield faster (in 1 hour, instead of the 2 hours of MW irradiation needed for 5 μ mol 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-(CF₃)₂pz-(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 μ mol of **9**, respectively

(Figure 9). The same behaviour is observed for the Cu(I) catalytic system.

The catalytic activity of [Cu- μ -N,N-(CF₃)₂pz-(OH)]₆ and **9** is also sensitive to the temperature as depicted in figure 11 for **9**.

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-(CF₃)₂pz-(OH)]₆ and **9** (Figure 8). A similar behavior was previously found.^[30]

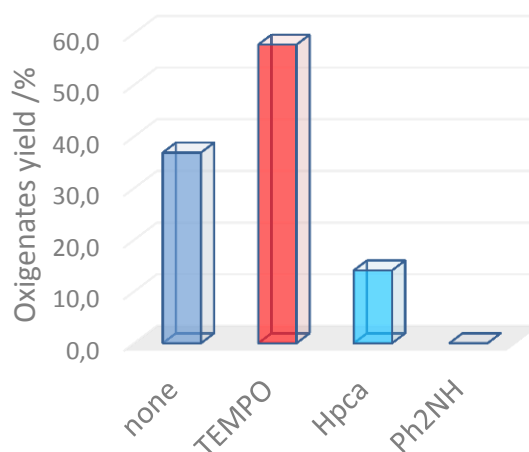


Figure 8.

Addition of a radical trap (*e.g.*, Ph₂NH, Figure 5) 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 5.

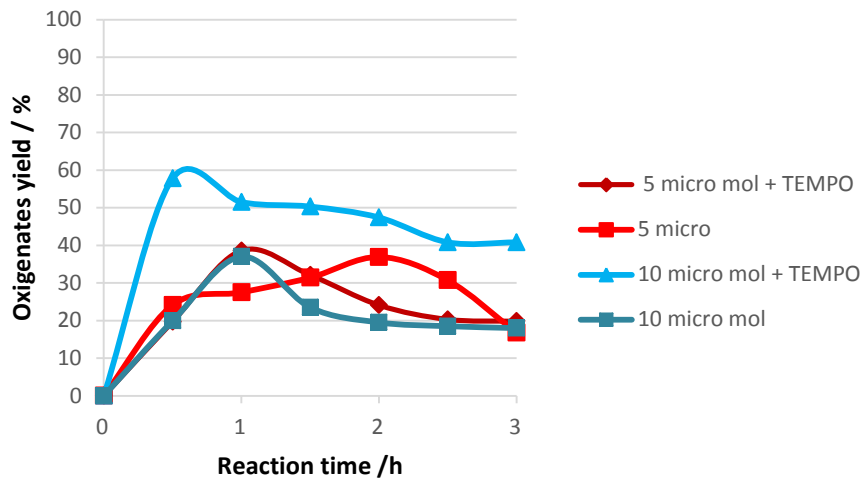


Figure 9

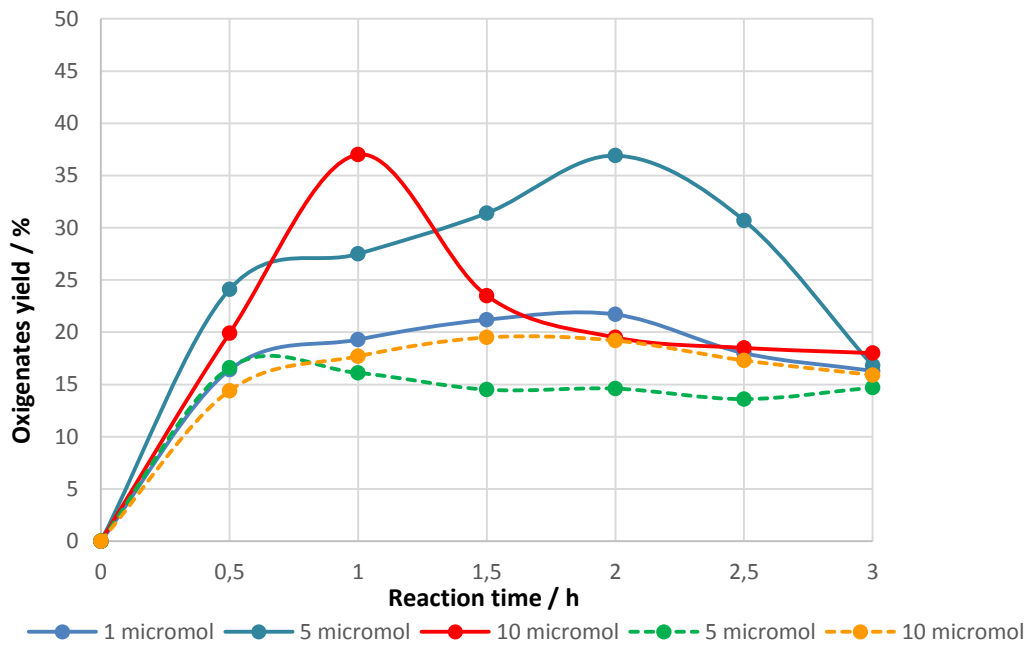


Figure10

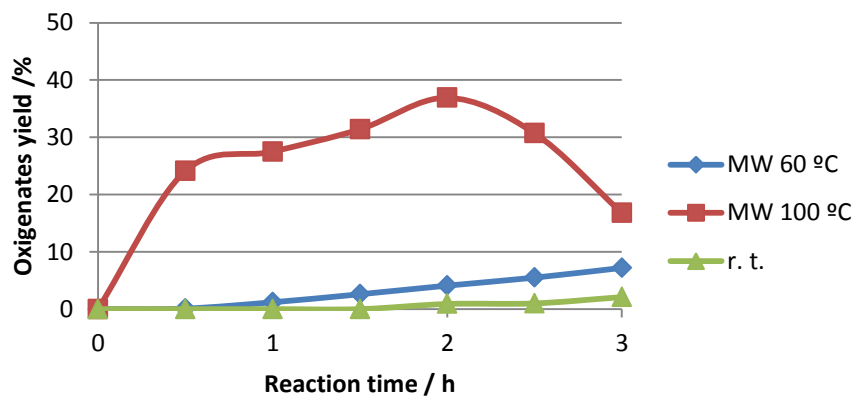
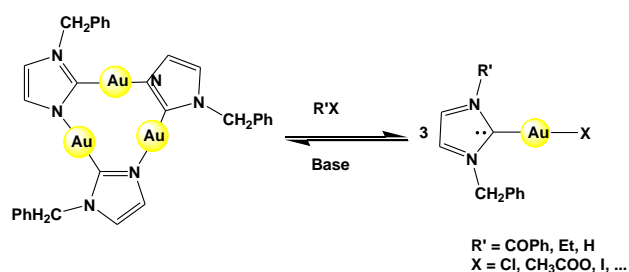


Figure 11

CONCLUSIONS

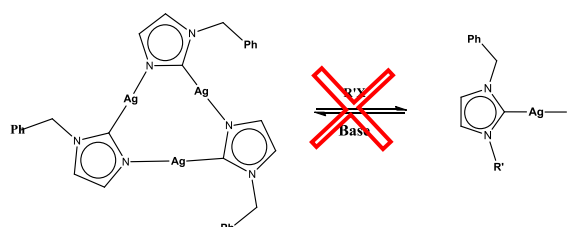
In this chemistry project the following aims have been achieved:

- 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.

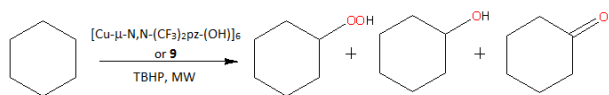


- 3) For a better understanding of this reactivity also the silver and gold(I) carbene derivatives have been synthesized with 1,3-dibenzylimidazolium and 1,3-dibenzyl-benzoimidazolium salts. The carbene derivatives were obtained in good yield and crystals for the X-ray crystal structure determination 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 NO_2 and CF_3 , 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 PPh_3 as coligand, $[\text{Cu-N}_2\text{N-(3,5(NO}_2)_2\text{pz)-PPh}_3]_2$, 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 $[\text{Cu-N,N-(3,5(NO}_2)_2\text{pz)-PPh}_3]_2$ was compared to that of an hexanuclear Cu(II) derivative having as bridging ligand the 3,5-(CF₃)₂pyrazole. Between them the $[\text{Cu-N,N-(3,5(NO}_2)_2\text{pz)-PPh}_3]_2$ shows better activity both in terms of yield of conversion as well as in time of conversion.

APPENDIX

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

Identification code	compound 1
Empirical formula	C ₃₀ H ₂₇ Ag ₃ N ₆
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 → c = 91.965(2)°
Volume	1409.2(3) Å ³
Z	2
Density (calculated)	1.874 Mg/m ³
Absorption coefficient	2.095 mm ⁻¹
F(000)	780
Crystal size	0.20 x 0.05 x 0.05 mm ³
Theta range for data collection	1.71 to 27.81°
Index ranges	-10 ≤ h ≤ 10, - 16 ≤ k ≤ 7, -12 ≤ l ≤ 18
Reflections collected	9206
Independent reflections	5841 [R(int) = 0.0287]
Completeness to theta =	87.5 %

27.81°	
Absorption correction	Empirical
Max. and min. transmission	0.9422 and 0.7449
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5841 / 0 / 352
Goodness-of-fit on F²	1.049
Final R indices [I > 2σ(I)]	R1 = 0.0371, wR2 = 0.0685
R indices (all data)	R1 = 0.0610, wR2 = 0.0751
Largest diff. peak and hole	0.769 and -0.583 e.Å ⁻³

Table 2. Preliminary data on the crystal structure of compound **3**.

Bond precision : C-C	= 0.0038 Å
Wavelength	= 0.71073 Å
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) Å ³
Space group	P - 1
Hall group	-P 1
Moiety formula	C ₁₇ H ₁₆ AgClN ₂
Sum formula	C ₁₇ H ₁₆ AgClN ₂ · C 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
N_{ref}	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. Details for the X-ray data collection for compound **9**.

Formula	C ₄₂ H ₃₂ Cu ₂ N ₈ O ₈ P ₂
Molecular weight	965.77
Crystal system	Triclinic
Space group	<i>P</i> -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-Kα)/mm⁻¹	1.163
Reflections collected	28774
Unique reflections	10015
Observed reflections [I > 2σ(I)]	7113 [R _{int} = 0.0486]
R, wR [I > 2σ(I)]	R = 0.0400; wR = 0.0860
R, wR [all data]	R = 0.0673; wR = 0.0969

$$R = \sum |F_o - F_c| / \sum |F_o|; wR = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

Table 4. 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 5 Selected data for the MW-assisted oxidation of cyclohexane by t-BuOOH (aq. 70%) catalysed by **9** or [Cu-μ-N,N-(CF₃)₂pz-(OH)]₆.

Entry	Catalyst	Catalyst/ substrate (%)	Co- catalyst	Temperature (°C)	Reaction time (h)	Yield (%) ^b			CyOH / CyO
						CyO	CyOH	Total	
1		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	9	0.2	-		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			-		0.5	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	[Cu- μ -N,N-(CF ₃) ₂ pz-(OH)] ₆		-	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
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			-	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 ₂ NH	100	0.5	0.0	0.0	0.0	-

^a Reaction conditions: cyclohexane (5 mmol), catalyst (1-10 μmol), *t*-BuOOH (70% in H₂O, 10 mmol), 60 - 100 °C, TEMPO (when used, 2.5 mol% vs. substrate), Hpca (when used, 20 mol% vs. substrate), Ph₂NH (when used, 10 mmol). ^b Moles of products [cyclohexanol (CyOH) + cyclohexanone (CyO)] per 100 mol of cyclohexane, as determined by GC after treatment with PPh₃.

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