Reactivity of 5-alkynyl-3,4-dihydro-2H-pyrroles with Au(III) Route to vinylgold(III) complexes, aurocycles by cyclisation of these complexes and ML complexes

Huy-Dinh Vu, Christelle Bouyry, Jacques Renault, Arnaud Bondon, Fabian Lambert, Thierry Roisnel, Philippe Uriac

▶ **To cite this version:**

Huy-Dinh Vu, Christelle Bouyry, Jacques Renault, Arnaud Bondon, Fabian Lambert, et al.. Reactivity of 5-alkynyl-3,4-dihydro-2H-pyrroles with Au(III) Route to vinylgold(III) complexes, aurocycles by cyclisation of these complexes and ML complexes. Journal of Organometallic Chemistry, 2019, 897, pp.228-235. 10.1016/j.jorganchem.2019.07.014 . hal-02278402

HAL Id: hal-02278402

https://univ-rennes.hal.science/hal-02278402

Submitted on 16 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Reactivity of 5-alkynyl-3,4-dihydro-*2H*-pyrroles with Au(III): route to vinylgold(III) complexes, aurocycles by cyclisation of these complexes and ML complexes.

Huy-Dinh Vu[1,3], Christelle Bouvry[1], Jacques Renault[1*], Arnaud Bondon[1], Fabian Lambert[2], Thierry Roisnel[2], and Philippe Uriac[1]

[1]*Univ Rennes, CNRS, ISCR [(Institut des Sciences Chimiques de Rennes)] - UMR 6226, F-35000 Rennes, France*
[2]*Univ Rennes, CNRS, ISCR [(Institut des Sciences Chimiques de Rennes)] – UMR 6226, ScanMat - UMS 2001, F-35000 Rennes, France*
[3]*Department of Chemistry, Vietnam National University of Forestry, Hanoi, Vietnam*

Corresponding Author

*E-mail: jacques.renault@univ-rennes1.fr

Abstract: The reaction of 5-alkynyl-3,4-dihydro-*2H*-pyrroles (**imine**) with $AuCl_3$ led to the synthesis of the vinyl gold(III) complexes **3** that could give the aurocycles **4** with an excess of $AuCl_3$. In the base presence the dimerization of **4** was observed leading to **5**. If $NaAuCl_4$ was used as gold(III) source a ligand exchange was observed leading to the complexes **6**. Nucleophilicity of both nitrogen atom and alkyne function as well as imine-enamine tautomerism were involved to explain the formation of **3**.

Key words

Gold(III) complexes, vinylgold complexes, aurocycles, cyclic imine.

1. Introduction

The interest in gold(III) complexes is ever increasing due to their optical (1) and catalytic properties (2). It is interesting to note that most of these complexes have aryl or hetero-aryl C-Au(III) bonds where the introduction of gold(III) was mainly achieved by trans-metalation (3) or oxidative addition (4). The design of complexes involving Au(III) and alkenes remain poorly explored although they were frequently proposed as reaction intermediates. The first vinylgold complex characterized using X-ray crystallography has been proposed by Hashmi *et al.* (5). and obtained by Ahn *et al.* (6). More recently the groups of Bochmann *et al* (7) and Tilset *et al* (8) have obtained [(C^N^C)Au(olefin)] complexes that were characterized by X-ray crystallography. We have previously published the synthesis of 5-alkynyl-3,4-dihydro-2*H*-pyrroles (9) and in this current work we report the preparation of gold(III) vinyl complexes with $AuCl_3$ and how their cyclization led to [(C^C)Au(X)(Y)] complexes (aurocycles) that are able to dimerize. To the best of our knowledge such aurocycles are rare (10) and only described with a biphenyl-ligand type (3a, 4a, 7b). When $NaAuCl_4$ was used, classical **ML** or **ML2** type gold (III) com-

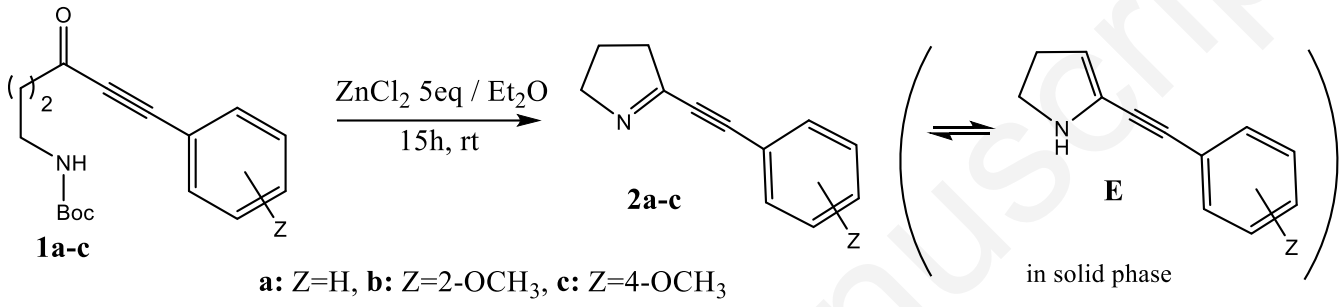
Accepted manuscript

plexes were obtained. After the ligands description, their reactivity *versus* $AuCl_3$ and $NaAuCl_4$ will be reported. Crystallographic data are given for each type of gold(III) complex obtained.

2. Results and discussion

*2.1. Synthesis of the ligands **2a-c**.*

For this study three 5-alkynyl-3,4-dihydro-*2H*-pyrroles **2a-c** were prepared in moderate yields (60-67%) (Scheme 1) from the *N*-Boc protected ynones **1a-c** using a 1M $ZnCl_2$ solution in diethylether (9). In all compounds the alkyne in position 5 was bearing an aryl group (Ar). It should be noted that on the infra-red spectra obtained with solid samples the compounds **2a-c** exhibited an intense NH vibration (see Sup info) attributed to the enamine tautomers **E**.

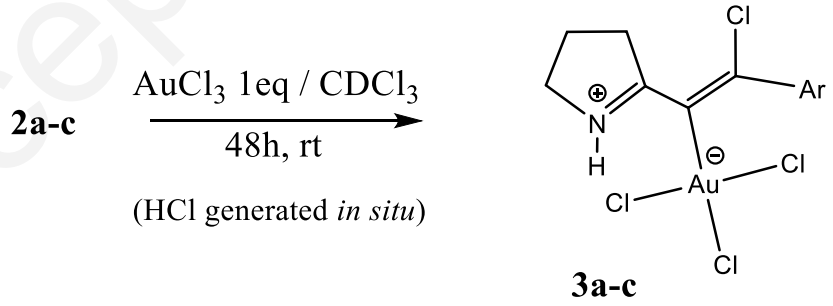


Scheme 1. Synthesis of imines **2a-c** (ligands)

*2.2 Synthesis of vinylgold(III) complexes **3a-c**.*

If $AuCl_3$ in halogenated solvent was employed the vinylgold(III) complexes **3a-c** were obtained from the cyclic imines **2a-c** (Scheme 2). The yields were always < 50% even though all starting material was consumed in the reaction (see Sup info).

The complexes were yellow-green (**3a**) or orange (**4b-c**) solids and were stable for several weeks at room temperature in air presence. It was observed that **2b** and **2c** formed precipitates quicker than **2a** probably because of the electrodonating effect of the methoxy substituent. By slow evaporation of the solvent [$(CD_3)_2CO$] crystals suitable for X-ray study were obtained with **3a**. Protodeauration was never observed even after water addition.



Scheme 2. Synthesis of vinylgold(III) complexes **3a-c**

The $[M-H]^-$ ions were observed in HRMS (ESI) attesting the addition of $AuCl_3$ and HCl to the cyclic imines **2a-c.** In the crystal structure of **3a (**Figure 1) the Au^{III} atom, coordinated with three chloride ligands, presented a square-planar geometry like in the vinylgold complexes previously described (6a) showed in Scheme 3.

Accepted manuscript

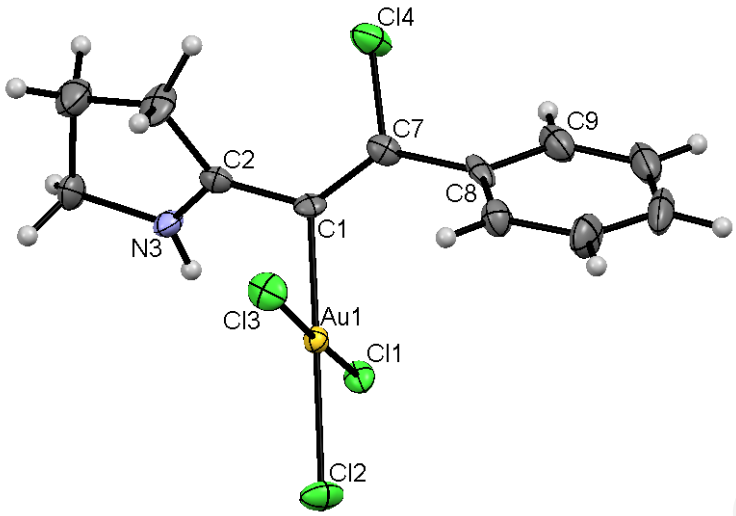


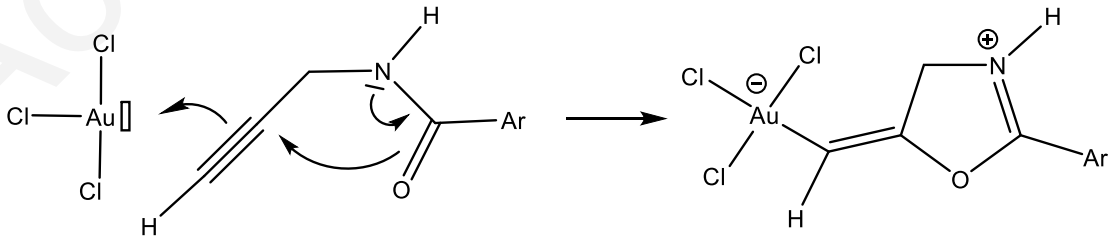
Figure 1. Molecular structures of vinylgold complex **3a**

ORTEP view of **3a** (50% probability). Key bond lengths (Å): Au-C1 = 2.030(7), Au-Cl3 = 2.2864(18), Au-Cl1 = 2.2856(18), Au-Cl2 = 2.343(2), C1-C7 = 1.335(10).

The C-Au bond length [2.030(7) Å] was close that of the vinylgold complex (6a) [2.004(19)]. The pyrrolidine, Ar and $AuCl_3$ were twisted with the following angles (degrees): Au1-C1-C2-N3 = -54.4(9), Cl1-Au1-C1-C7 = -83.1(6), C1-C7-C8-C9 = 138.7(8). The trans-formation of the alkyne moiety was clearly attested in ^{13}CNMR (disappearance of the sp carbon signals) and in IR (disappearance of the 2200cm^{-1} vibration). A broad signal near 12.5 ppm in ^{1}HNMR was in accordance with the imine protonation as well as the broad band near 3200 cm^{-1} in IR. The ^{13}CNMR shifts of the new sp^2 carbons were similar for the three compounds: C-Au: near 120 ppm and C-Cl: unshielded near 130 ppm.

2.3. Probable mechanism for the formation of the vinylgold(III) complexes

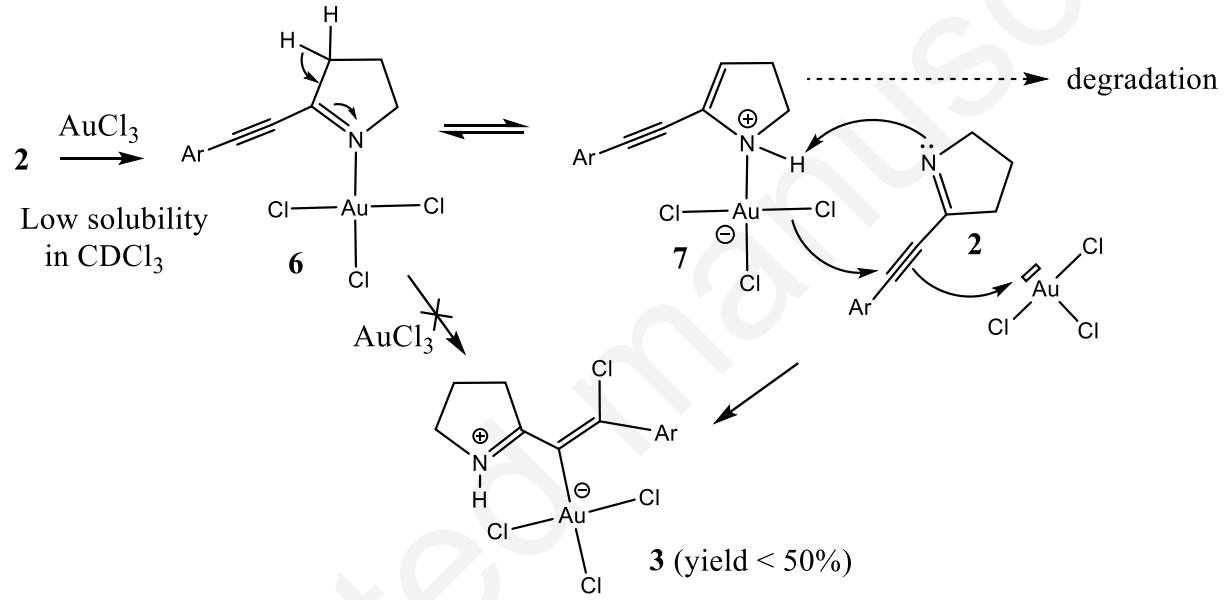
As shown below (Scheme 3) a vinylgold(III) complex was previously postulated by Hashmi *et al.* (5) and isolated by Ahn *et al.* (6a) in order to explain the preparation of oxazoles from acetylenic amides. The alkyne activation was mediated by $AuCl_3$ which enabled the nucleophilic attack of the oxygen atom of the amide moiety and finally cyclisation. In our case, a similar mechanism (Scheme 4) could be envisaged but the origin of HCl remained to be explained.



Scheme 3. Formation of vinylgold (III) complex from acetylenic amides

When the reaction was performed in $CHBr_3$ the addition of HBr was not observed. In this case, the solvent did not provide HBr (or HCl). When the reaction was performed in anhydrous

CH_2Cl_2 or laboratory grade CH_2Cl_2 the yields were close: 47% with anhydrous CH_2Cl_2 and 43% with laboratory grade CH_2Cl_2. Yields with $CHBr_3$, $CHCl_3$ or $CDCl_3$ under argon or air atmosphere were always close to 45%. That excluded a reaction between H_2O and $AuCl_3$ inducing HCl liberation. Therefore, we concluded that HCl was generated by a reaction between the imines and $AuCl_3$ as reported in Scheme 4. Addition of the dissolved part of $AuCl_3$ to the imine **2** gave the complex **6** (observed by ^1H NMR). Then, imine-enamine tautomerism enabled formation of the postulated intermediate **7** acting as HCl source. This mechanism could also explain the *trans* addition which was also recently reported with ethynylpyridines and HX (11). As $AuCl_3$ was both acting for alkyne activation (**2b**, **2c**>**2a**) and Cl^- source, the yields were always <50% and the conversion of the starting material was complete. Two complementary experiments were in favor of this mechanism. First, **6a** (*vide infra*) did not react with $AuCl_3$. Moreover the use of $HAuCl_4$ as possible gold and HCl source resulted in the formation of a mixture impossible to analyze.



Scheme 4. Formation of vinylgold (III) complex from imines

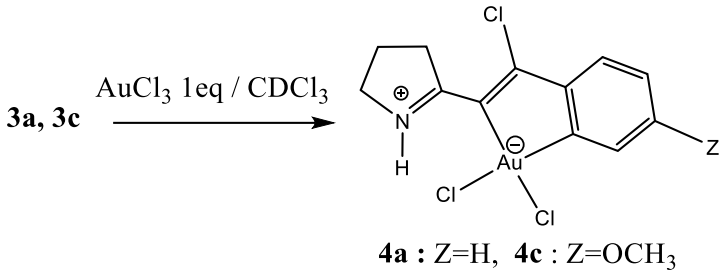
Some others alkenyl gold(III) complexes have been prepared by Bochman *et al* by insertion of allenes or alkynes into their [(C^N^C)Au(H)] complexes (12). In this case, the regio- and stereoselective *trans*-auration process was mediated by a radical. A diene-diylgold(III) complex prepared by Helaja *et al* (13) has been obtained by H migration. One can also notice that the $AuCl_3$ addition on dimethylacetylen was previously reported and discussed by R. Hüttel and H. Forkl (14).

*2.4. Synthesis of aurocycles **4a**, **4c** and of dimer **5a**.*

During our reactivity study of **2a** with $AuCl_3$ the reaction has been performed with two equivalents of $AuCl_3$. In this condition a mixture of **2a**, **3a** and a new compound **4a** was obtained. In fact, the excess of $AuCl_3$ did not improve the formation of **3a** but induced its cyclisation into the aurocycle **4a.** Then the complexes **3a-c** were allowed to react with one equivalent of $AuCl_3$ in $CDCl_3$ over 48-72h at RT. With **3a** and **3c** a 50/50 mixture of the complexes **3** and **4** was obtained (scheme 5). The cyclisation of **3b** did not occur because of the steric hindrance

Accepted manuscript

between Cl and OCH_3. The yields of this cyclisation were always <50% and the aurocycles were quite difficult to separate from the starting vinylgold complexes (see experimental part) by crystallization.



Scheme 5. Synthesis of aurocycles **4a** and **4c**

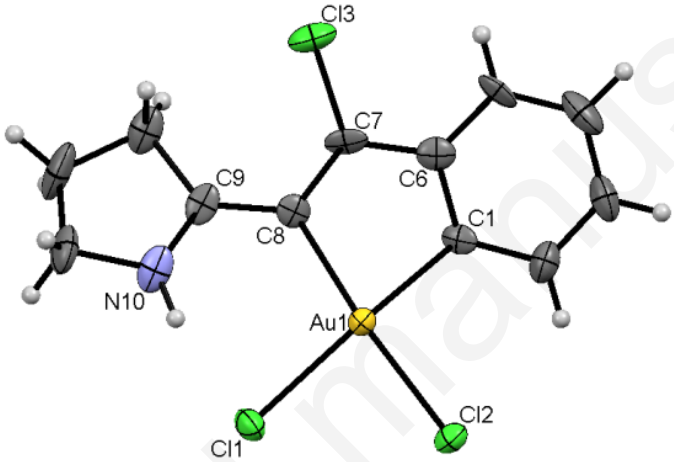


Figure 2. Molecular structure of aurocycle **4a**

ORTEP view of **4a** (50% probability). Key bond lengths (Å) and angles (deg) : Au1 - C1 = 2.022(10), Au1-C8 = 2.067(11), Au1-Cl2 = 2.346(3), Au1-Cl1 = 2.410(3), Cl3-C7 = 1.733(11), C1-C6 = 1.406(15), C6-C7 = 1.436(17), C7-C8 = 1.381(15), C8-C9 = 1.445(15); C1-Au1-C8 = 81.6(4), C1-Au1-Cl2 = 93.0(3), C8-Au1-Cl2 = 173.0(3), C1-Au1-Cl1 = 176.8(3), C8-Au1-Cl1= 100.5(3), Cl2-Au1-Cl1 = 85.01(10), C7-C8- Au1 = 110.9(8), C6-C1-Au1 = 114.7(8).

The HCl elimination was attested in MS and ^{1}H NMR by the disappearance of one aromatic proton and confirmed by the X-ray structure of **4a** (Figure 2) and **4b** (see supplementary information). The bond lengths measured for **4a** are very close to those reported for aurocycles with to aryl ligands (3b, 7b): Au-C1 and Au-C8 (2.022, 2.046) *versus* 1.97(3), 2.00(2) and 2.028, 2.046). The aurocycle and the pyrroline ring were twisted around chirality axis C8-C9. The ^{13}C NMR spectra (15) were particularly modified with the transformation of one CH into quaternary carbon. One could also notice that the ^1J CH values (167-169Hz) of the carbon in *ortho* position of Au were modified by the C-Au^{III} bond formation.

In the presence of D_5-pyridine or K_2CO_3 the loss of HCl induced the formation of the neutral homodimer **5a** (Fig 3) which showed distinct internal and external methylene shifts. This type of dimer was previously reported with **2a** and $PdCl_2$ (9). The formation of heterodimers was not observed.

Accepted manuscript

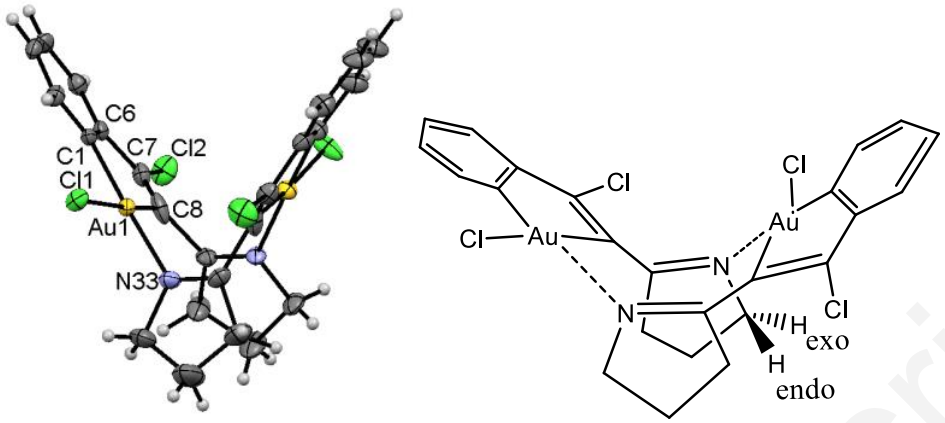
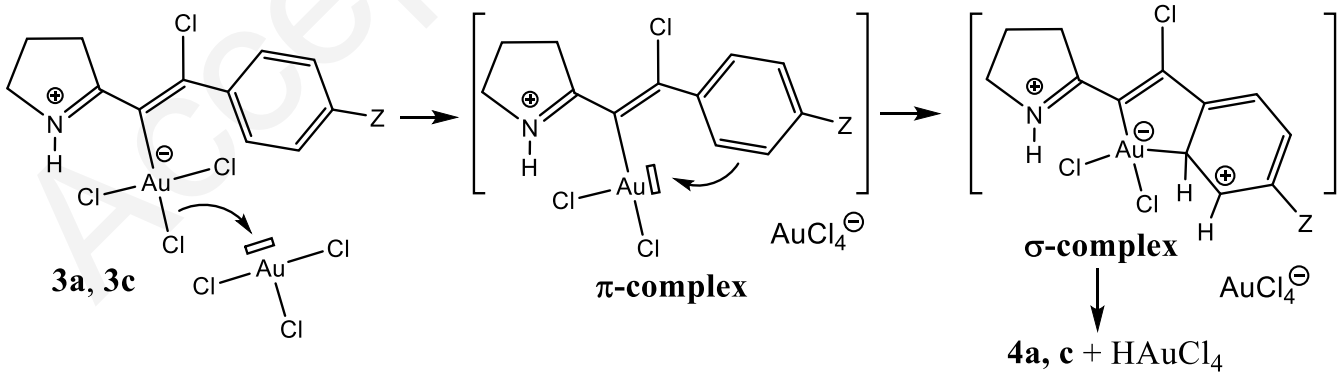


Figure 3. Molecular structures of complex dimeric aurocycle **5a**

ORTEP view of **5a** (50% probability). A molecule of $CHCl_3$ has been omitted for clarity. Key bond lengths (Å) and angles (deg): Au1-C8 = 2.000(4), Au1-C1 = 2.030(5), Au1-N33 = 2.105(5), Au1-Cl1 = 2.3568(12), C6-C7 = 1.467(7); C8-Au1-C1 = 77.6(2), C8-Au1-N33 = 99.24(19), C1-Au1-N33 = 176.61(19), C1-Au1-Cl1 = 95.80(15), C8-Au1-Cl1 = 172.57(13), N33-Au1-Cl1 = 87.45(13), C6-C1-Au1 = 114.1(4).

*2.5. Mechanism for the formation of **4a**, **4c**.*

The intramolecular formation of this new type of aurocycle was favored by the spatial proximity of the gold(III) and the nucleophilic phenyl ring. Then, $AuCl_3$ activated the cyclisation and trapped the hydrochloride acid which was formed (Scheme 6). This auration reaction has been previously reported (16) but, as it was difficult to control, exchange (3) or oxidation (4) reactions were preferred to prepare arylgold compounds.

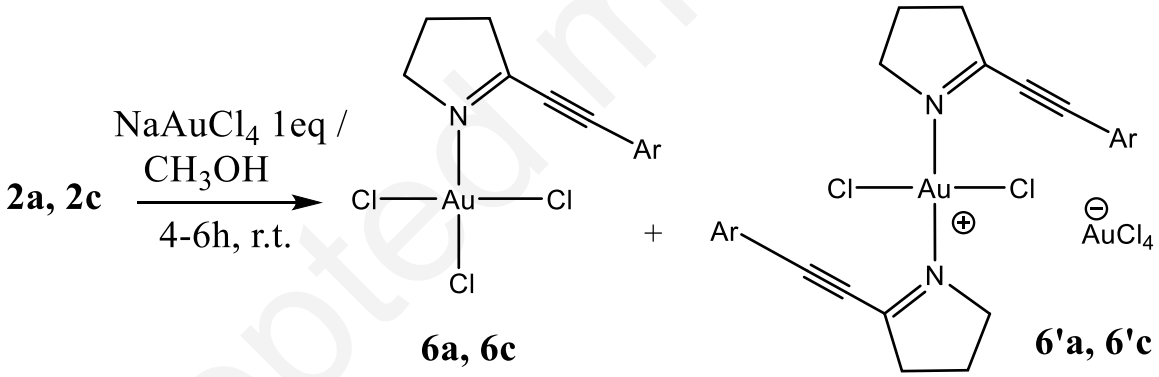


Scheme 6. Proposal of synthesis mechanism of **4a**, **4c**

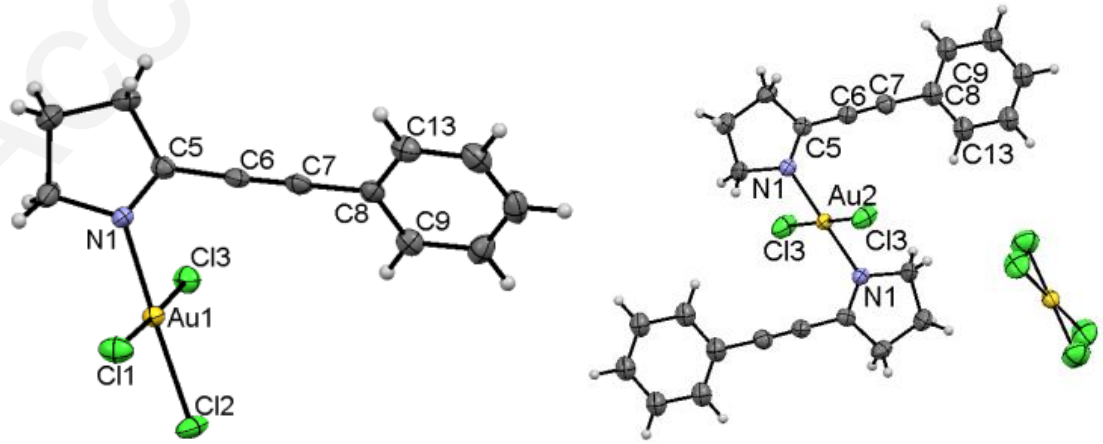
Accepted manuscript

*2.6. Synthesis of the ML (and **ML2**) complexes **6a**, **6c** (and **6'a**, **6'c**)*

In a previous study, we demonstrated the excellent ability of **2a** to give complexes with ZnI_2 and $PdCl_2$ (9). With these divalent metal complexes of **ML2** type were obtained. In the case of $PdCl_2$ both *cis* and *trans* complexes were crystallized. In the presence of one equivalent of $NaAuCl_4$, $2H_2O$ the cyclic imine **2a** gave the corresponding gold(III) complexes **6a + 6'a** (70/30) in a 70% yield (Scheme 7). The ligand exchange reactions were performed in CH_3OH (or CD_3OD) at room temperature and the **ML** type complex was obtained in good yield. A yellow precipitate was observed which was dissolved in $CDCl_3$. When CD_2Cl_2 was used, the presence of another compound **6a'** was noted. As **6a'** was insoluble in $CDCl_3$ (see experimental section) pure **6a** suitable for X-ray study (Fig 4) was obtained as pale-yellow crystals by slow evaporation of solvent. A small amount of **6a'** was obtained after complete elimination of **6a** using $CDCl_3$ and some crystals obtained by slow evaporation in the NMR tube enabled us to establish the **ML2** structure of **6a'** (Fig 4). The low solubility of **6a'** can be explained by its ionic structure with $AuCl_4^-$ as anion. The spatial structure of **6a** and **6'a** were similar to those reported for other neutral gold (III) trihalide complexes involving nitrogen (17), arsenic (18), phosphorous (18,19), or for complexes with amino acids (20). The same structure was also founded in NHC complexes (21). A NHC complex with *trans* geometry like **6a'** was also previously described (22). With **2c** a 80/20 mixture of **6c** and **6'c** was also obtained in 77% yield. The complex **6c** was a yellow-orange solid less soluble than **6a.** The separation of these two complexes remained difficult because of their low solubility.



Scheme 7. Synthesis of complexes **ML** and **ML2**



Accepted manuscript

Figure 4. Molecular structures of complex **ML 6a** and **ML2 6a'**

ORTEP view of **6a (ML)** (50% probability). Key bond lengths (Å) : Au1-N1 = 2.015(3), Au1-Cl2 = 2.2662(11), Au1-Cl1 = 2.2716(11), Au1-Cl3 = 2.2810(11), N1-C5 = 1.288(6), C5-C6 = 1.429(6), C6-C7= 1.198(6), C7-C8 = 1.432(6), C8-C9 = 1.391(7). ORTEP view of **6a' (ML2)** (50% probability). A molecule of CH_2Cl_2 has been omitted for clarity. Key bond lengths (Å): Au2-N1=2.005(3), Au2-N1_#2 = 2.005(3), Au2-Cl3 = 2.2674(13), N1-C5 = 1.283(5), C5-C6 = 1.412(6), C6-C7 = 1.191(6), C7-C8 = 1.434(7).

3. Conclusion

In conclusion, we have shown that some types of gold(III) complexes were obtained from 5-alkynyl-3,4-dihydro-2*H*-pyrroles and fully characterized. The particularly interesting reactivity of this ligand with Au(III) can be explained by the addition of three chemical properties: the alkyinophilicity of the gold(III), the basicity of the imine and the imine-enamine tautomerism. Introduction of chirality in the aurocycles is now in progress.

4. Experimental section

4.1. Materials and instrumentation

All reagents were of high quality and were purchased from commercial suppliers; they were either used without further purification or were purified/dried according standard procedures. ^{1}H and ^{13}C NMR were recorded at 300 and 75 MHz or 500 and 100 MHz respectively (using TMS as an internal standard); shifts (δ values) are given in parts per million (ppm), coupling constants (*J* values) are given in Hertz (Hz), and multiplicity of signals are reported as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintet), sext (sextet), m (multiplet), * (broad signal), dt (doublet of triplet), td (triplet of doublet).UV spectra were recorded using a Specord 205 (Analitkjena) and IR spectra with a Perkin–Elmer (Spectrum 2) apparatus using a Universal ATR Sampling Accessory. HRMS analyses were obtained with a Waters Q-TOF 2 or a Micromass ZABSpec TOF or a Bruker MicrO-TOF QII or a LTQ Orbitrap XL instrument for ESI. X-ray crystallographic data were collected with an APEXII crystal diffractometer. Thin-layer chromatography was performed using pre-coated silica gel plate (0.2 mm thickness). Numerous reactions were performed in deuterated solvent to check the reactions.

*4.2. Ynones **1a-c***

The preparation and the structural data of the ynone **1a** were described in ref 9.

4.2.1. tert-Butyl [6-(2-methoxyphenyl)-4-oxohex-5-yn-1-yl]carbamate **1b**

^{1}H NMR ($CDCl_3$): δ = 7.50 (dd, *J*=7.6, 1.7 Hz, 1H), 7.45 (td, *J*=8, 1.7 Hz, 1H), 6.95 (t, *J*=7.5 Hz, 1H), 6.93 (t, *J*=7.5 Hz, 1H), 4.69 (s*, *N*H), 3.91 (s, 3H), 3.21 (q, *J*=7.5 Hz, 2H), 2.74 (t, *J*= 7.2 Hz, 2H), 1.95 (quint, *J*=7 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 187.4, 161.5, 156.0, 135.0, 132.6, 120.6, 110.8, 109.0, 91.9, 88.6, 79.3, 55.8, 42.7, 39.8, 28.4, 24.6. HRMS (ESI): $[M+Na]^+$ $C_{18}H_{23}NO_4Na$ calc.340.15193, found. 340.152. IR ν-alkyne: 2197 cm^{-1}

4.2.2. tert-Butyl [6-(4-methoxyphenyl)-4-oxohex-5-yn-1-yl]carbamate **1c**

^{1}H NMR ($CDCl_3$): δ = 7.53 (d, *J*=8.9 Hz, 2H), 6.90 (d, *J*=8.9 Hz, 2H), 4.67 (s*, *N*H), 3.85 (s, 3H), 3.20 (q, *J*=6.6 Hz, 2H), 2.72 (t, *J*= 7.2 Hz, 2H), 1.92 (quint, *J*=7 Hz, 2H), 1.45 (s, 9H). ^{13}C

Accepted manuscript

NMR ($CDCl_3$): δ = 187.2, 161.7, 156.0, 135.1, 114.4, 111.6, 92.3, 87.7, 79.3, 55.4, 42.6, 39.9, 28.4, 24.5. HRMS (ESI): $[M+Na]^+$ $C_{18}H_{23}NO_4Na$ calc.340.15193, found. 340.1519. F°C: 91. Infra-red: ν-alkyne: 2194 cm^{-1}

*4.3. Imines **2a-2c***

4.3.1. General Procedure for the Preparation of Imines **2a–c** *from Ynones* **1a-c**

Ynone **1** (4 mmol) was dissolved in a 1M solution of $ZnCl_2$ in diethyl ether (5 eq) under a nitrogen atmosphere. The solution was stirred for 15 h at room temperature and then a 1M aqueous solution of Na_2CO_3 (100 mL) was added and stirring was maintained for 30 min. The white precipitate of $ZnCO_3$ was filtered off and washed with diethyl ether (5x40 mL). Combined organic were washed with 0.1 M aqueous solution of Na_2CO_3 (50 mL) then with a Na_2SO_4 saturated aqueous solution. The organic layer was dried with Na_2SO_4 and concentrated under vacuum to give the crude product, which was purified by chromatography over silica gel. Remark: a 2M solution of NH_4OH can be used in place of Na_2CO_3 but the yields are lower.

The preparation and the structural data of the imine **2a** were described in ref 9.

4.3.2. 5-[(2-Methoxyphenyl)ethynyl]-3,4-dihydro-2H-pyrrole **2b**

Yield from **1b**: 62%. ^{1}H NMR ($CDCl_3$): δ = 7.48 (dd, *J*=7.6, 1.7 Hz, 1H), 7.34 (td, *J*=8, 1.7 Hz, 1H), 6.92 (t, *J*=7.5 Hz, 1H), 6.90 (t, *J*=7.5 Hz, 1H), 4.01 (txt, *J*=7.2, 2.2 Hz, 2H), 3.89 (s, 3H), 2.77 (txt, *J*= 7.2, 2.2 Hz, 2H), 1.95 (quint, *J*=7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 160.6, 159.8, 134.1, 130.9, 120.5, 111.0, 110.7, 89.1, 88.7, 62.0, 55.8, 39.9, 22.5. HRMS (ESI): $[M+H]^+$ $C_{13}H_{14}NO$ calc.200.10699, found. 200.1065. IR: ν-alkyne: 2197 cm^{-1} and ν-NH: 3375 cm^{-1} (enamine).

4.3.3. 5-[(4-Methoxyphenyl)ethynyl]-3,4-dihydro-2H-pyrrole **2c**

Yield from **1c**: 67%. ^{1}H NMR ($CDCl_3$): δ = 7.50 (d, *J*=7.6 Hz, 2H), 6.89 (d, *J*=7.5 Hz, 2H), 4.04 (txt, *J*=7.2, 2.2 Hz, 2H), 3.84 (s, 3H), 2.75 (txt, *J*= 7.2, 2.2 Hz, 2H), 1.98 (quint, *J*=7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 160.5, 159.8, 133.9, 114.1, 113.7, 92.9, 83.9, 61.9, 55.3, 39.9, 22.5. HRMS (ESI): $[M+H]^+$ $C_{13}H_{14}NO$ calc.200.10699, found. 200.1071. Infra-red: ν-alkyne: 2195 cm^{-1} and ν-NH: 3359 cm^{-1} (enamine).

4.4. Vinylgold(III) complexes **3a-c**

The yields were very depending on the work-up and on the quantities of imines (<100-150mg was the best).

4.4.1. (E)-Trichloro[2-chloro-1-(3,4-dihydro-2H-pyrrol-1-ium-5-yl)-2-phenylvinyl] aurate (III) **3a**

To a suspension of $AuCl_3$ (101.2mg; 0.33mmol) in 3 mL of halogenated solvent (not anhydrous, deuterated or not) 56.4mg (1eq) of **2a** were added. This suspension was agitated during 48h and the formation of a yellow-green solid was observed. After filtration and washing with 1mL of solvent this solid was dissolved in CD_3COCD_3 and the solution again filtered on Celite in order

Accepted manuscript

to eliminate a little black residue. With $CDCl_3$ a 43% yield was obtained. By slow evaporation of the NMR solvent suitable crystals for X-ray were obtained. With anhydrous CH_2Cl_2 a 47% yield was obtained and with usual CH_2Cl_2 the yield was reduced to 41%.

^{1}H NMR (CD_3COCD_3): δ = 12.15 (s*, 1H), 7.86 (m, 2H), 7.48 (m, 3H), 4.49 (tt, *J*=7.8, 2.2, 2H), 3.72 (tt, *J*=8, 2.2 Hz, 2H), 2.61 (quint, *J*=8, 2H). ^{13}C NMR (CD_3COCD_3): δ = 189.1, 139.7, 131.5, 131.0, 129.6, 129.3, 120.7, 55.2, 39.7, 21.1. HRMS (ESI): $[M-H]^-$ $C_{12}H_{11}N^{35}Cl_4Au$ calc.505.93167 found. 505.9319. UV: λ 302nm (ε=10252), λ: 212nm (ε =23665). IR: ν-NH^+: 3197cm^{-1}, ν-C=N: 1590 cm^{-1}

4.4.2. (E)-Trichloro[2-chloro-1-(3,4-dihydro-2H-pyrrol-1-ium-5-yl)-2-(2methoxyphenyl] vinyl)aurate(III) **3b**

To a suspension of $AuCl_3$ (32mg; 1.05mmol) in 3 mL of $CDCl_3$ 56.4mg (1eq) of **2b** were added. This suspension was agitated during 48h and the formation of a yellow-green solid was observed. After filtration and washing with 1mL of solvent this solid was dissolved in CD_3COCD_3 and the solution again filtered on Celite. Yield: 35%.

^{1}H NMR (CD_3COCD_3): δ = 12.15 (s*, 1H), 7.60 (dd, *J*=7.6, 1.7 Hz, 1H), 7.43 (td, *J*=8, 1.7 Hz, 1H), 7.08 (d, *J*=8 Hz, 1H), 7.00 (txd, *J*=7.5, 1 Hz, 1H), 4.46 (txt, *J*=7.2, 2.2 Hz, 2H), 3.86 (s, 3H), 3.70 (txt, *J*= 7.2, 2.2 Hz, 2H), 2.59 (quint, *J*=7 Hz, 2H). ^{13}C NMR (CD_3COCD_3): δ = 188.7, 158.3, 132.5, 131.6, 131.4, 128.8, 121.8, 120.9, 112.9, 56.1, 55.0, 39.9, 21.2. HRMS (ESI): $[M-H]^-C_{13}H_{13}NO^{35}Cl_4Au$ calc.535.94224 found. 535.9429.

4.4.3. (E)-Trichloro[2-chloro-1-(3,4-dihydro-2H-pyrrol-1-ium-5-yl]-2-(4-methoxyphenyl)

vinyl) aurate (III) **3c**

To a suspension of $AuCl_3$ (152mg; 0.5 mmol) in 3 mL of $CDCl_3$ 100mg (1eq) of **2c** were added. This suspension was agitated during 48h and the formation of an orange solid was observed. After filtration and washing with 1mL of solvent this solid (140mg) was dissolved in CD_3COCD_3 and the solution again filtered on Celite. After solvent evaporation 130mg of **4c** were obtained. Yield: 48%.

^{1}H NMR (CD_3COCD_3): δ = 10.80 (s*, 1H), 7.84 (dd, *J*=9 Hz, 2H), 7.43 (td, *J*=8, 1.7 Hz, 1H), 7.03 (d, *J*=9 Hz, 2H), 4.46 (txt, *J*=7.8, 2.3 Hz, 2H), 3.89 (s, 3H), 3.70 (txt, *J*= 7.8, 2.3 Hz, 2H), 2.59 (quint, *J*=8 Hz, 2H). ^{13}C NMR (CD_3COCD_3): δ = 187.8, 161.2, 131.0, 130.4, 118.1, 113.7, 54.9, 54.0, 38.9, 20.3. On a 100MHz spectrum recorded in CD_3CN signals at 130.5, 131.2, 133.3 could be observed. HRMS (ESI): $[M-H]^-C_{13}H_{13}N^{35}OCl_4Au$ calc.535.94224 found. 535.9428. UV: λ: 295nm (ε =12967), λ: 200nm (ε =40733). IR: ν-NH^+: 3179cm^{-1}, ν-C=N: 1633, 1601 cm^{-1}

4.5. Aurocycles **4a, 4c**

4.5.1. (E)-Dichloro[2-chloro-1-(3,4-dihydro-2H-pyrrol-1-ium-5-yl)-2-phenylvinyl] aurate(III) **4a**

To a suspension of140mg of $AuCl_3$ (0.46mmoles) in 5 mL of $CDCl_3$ were added 235 mg of **3a** (1eq). After 72h of stirring out of light the mixture was filtered giving 345mg of a solid which was dissolved in CD_3COCD_3 and filtered again in order to eliminate a black residue. This solu-

Accepted manuscript

tion was constituted by a 50/50 mixture of **3a** and **4a** (see sup info). By slow evaporation 40mg of creme **4a** was formed (yield: 17%). The separation of **3a** and **4a** remained extremely difficult. Crystals of **4a** were obtained by slow evaporation in the NMR solvent.

^{1}H NMR 500MHz (CD_3COCD_3): δ = 8.03 (dd, *J*=8.7, 1.1, 1H), 7.25 (td, *J*=8.5, 1.1, 1H), 7.11 (td, *J*=8.5,1.1Hz,1H), 7.07 (dd, *J*=8.5,1.1Hz,1H), 4.83 (tt, *J*=7.8, 2.1, 2H), 3.49 (tt, *J*=7.8, 2.1 Hz, 2H), 2.53 (quint, *J*=8 Hz, 2H). ^{13}C NMR 500MHz (CD_3COCD_3): δ = 189.0, 140.5, 132.3, 131.7, 130.4, 130.1, 121.5, 55.9, 40.4, 21.9.^{1}J of the carbon near Au: 167Hz. HRMS (ESI): [M-H]$^{-}$$C_{12}H_{10}NO^{35}Cl_4Au$ calc.469.95499 found. 469.9549. UV λ: 315nm (ε =1635), λ: 229nm (ε =24318), λ: 200nm (ε =27528).

4.5.2. (E)-Dichloro[2-chloro-1-(3,4-dihydro-2H-pyrrol-1-ium-5-yl)-2-(4-methoxyphenylvinyl] aurate(III) **4c**

To a suspension of $AuCl_3$ (140mg, 0.46mmoles) in 5 mL of $CDCl_3$ were added 235 mg of **3c** (1eq). After 72h of stirring out of light the mixture was filtered giving 345mg of a solid which was dissolved in CD_3COCD_3 and filtered again in order to eliminate a black residue. This solution was constituted by a 50/50 mixture of **3c** and **4c** (see sup info). By slow evaporation 40mg of orange **4c** was formed (yield: 17%). The separation of **3c** and **4c** remained extremely difficult. Crystals of **4c** were obtained by slow evaporation in the NMR solvent.

^{1}H NMR (CD_2Cl_2): δ = 7.79 (d, *J*=2.5, 1H), 7.24 (d, *J*=8.7, 1H), 6.73 (dd, *J*=2.5, 8.7, 1H), 4.01 (qt, *J*=8, 1.7Hz, 2H), 3.85 (s, 3H), 3.65 (tq, *J*= 8, 1.7 Hz, 2H), 2.37 (quint, *J*=8, 2H). ^{13}C NMR 500MHz (CD_2Cl_2): δ = 183.0, 161.1, 151.6, 139.7, 133.6, 130.1, 116.8, 113.5, 55.8, 50.4, 39.9, 21.95. HRMS (ESI): [M-H]$^{-}$$C_{13}H_{12}NO^{35}Cl_4Au$ calc.499.96556 found. 499.9552. UV λ: 343nm (ε =4320), λ: 240nm (ε =24866), λ: 200nm (ε =40303).

4.6. Dimer **5a**

The dimer **5a** was obtained using two procedures.

a) The dimer **5a** could be quantitatively prepared in the NMR tube by addition of some drops of D5-pyridine on a solution of 10mg of **4a** in CD_3COCD_3. This complete formation of **5a** was attested by the separation of the protons of the three CH_2 groups.
b) **5a** can also be prepared by agitation of **4a** (10mg) in a mixture of $CDCl_3$ (1mL and D_2O+Cs_2CO_3 (0.5mL). Neutralization of **4a** induced the complete formation of the dimer 5a and its dissolution in $CDCl_3$. Crystals of **5a** suitable for X-ray analysis were obtained by slow evaporation in the NMR tube.

^{1}H NMR ($CDCl_3$): δ = 7.86 (dd, *J*=7.7, 1 Hz, 1H), 7.17 (dd, *J*=7.5, 1 Hz, 1H), 7.04 (dd, *J*=7.5, 1.5 Hz, 1H), 7.00 (dd, *J*=7.5, 1.5 Hz, 1H), 4.40 (m, 1H), 3.79 (m,1H), 3.49 (m, 1H), 2.80 (m, 1H), 2.41 (m, 1H), 2.15 (m, 1H). ^{13}C NMR 500MHz ($CDCl_3$, 100MHz) : δ = 182.6, 148.5, 144.0, 143.9, 138.4, 131.9, 129.0, 128.1, 125.5, 60.8, 38.9, 22.5.

Accepted manuscript

4.7. Complexes ML and ML2

4.7.1. Dichloro-N,N'-di[5-(phenylethynyl)-3,4-dihydro-2H-pyrrole]tetrachloroaurate(III) **6a**

To a solution of 130mg of $NaAuCl_4$, $2H_20$ (0.33mmol) in CH_3OH (or CD_3OD) 65mg of **2a** (1eq) were added. After some minutes a yellow solid precipitated. The reaction was allowed to react for 4 hours with stirring and then filtrated. The yellow precipitate was washed with 1mL of CH_3OH and dried under vacuum. 110mg of solid were obtained. It was a 73/27 mixture of **6a** and **6'a** with a 58% yield. This solid was dissolved in $CDCl_3$ (3 + 1 mL) and after evaporation of the solvent 54 mg of pure **6a** were obtained (Yield: 29%).

^{1}H NMR ($CDCl_3$): δ = 7.73 (dt, *J*=7, 1.4 Hz, 2H), 7.57 (tt, *J*=7.5, 1.4 Hz, 1H), 7.46 (tt, *J*=7.4, 1.3 Hz, 2H), 4.35 (tt, *J*=7.65, 2.2 Hz, 2H), 3.17(tt, *J*=8, 2.1 Hz, 2H), 2.39 (qt, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 168.0, 133.5, 132.6, 129.0, 118.6, 110.8, 81.8, 61.7, 39.9, 21.6. Infra-Red: ν -alkyne: 2201 cm^{-1} HRMS (ESI): $C_{12}H_{11}{}^{35}NCl_4Au$ calc.505.93167, found. 505.9321. UV: λ = 319nm (ε =21788), λ = 303nm (ε =23051), λ = 233nm (ε =30300).

Remark: If the precipitate solid was dissolved in CD_2Cl_2 the presence of another compound **6a'**was noted with similar NMR data (mixture of **6a** and **6'a**): ^{1}H NMR (in CD_2Cl_2 of the fraction insoluble in $CDCl_3$): δ = 7.51 (dt, *J*=7.3, 1.5 Hz, 2H), 7.46 (tt, *J*=7.5, 1.(Hz, 1H), 7.29 (tt, *J*=7.5, 1.5 Hz, 2H), 4.42 (tt, *J*=8, 2.2 Hz, 2H), 3.37 (tt, *J*=8.4, 2.1 Hz, 2H), 2.51 (quint, *J*=8.2 Hz, 2H). ^{13}C NMR (mixture in CD_2Cl_2): δ = 133,0, 132.5, 129.3, 81.8, 62.1, 39.7, 21.6. HRMS (ESI): $[C_{24}H_{22}N_2{}^{35}Cl_2Au]^+$ calc. 605.08201, found. 605.0818.

Crystals of **6a** and **6'a** were obtained by slow evaporation of the NMR solvent.

4.7.2. Dichloro-N,N'-di[5-(4-methoxyphenylethynyl)-3,4-dihydro-2H-pyrrole] tetrachloroaurate(III) **6c**

To a solution of 160mg of $NaAuCl_4$, $2H_20$ (0.4mmol) in CD_3OD (3 mL) 79mg of **2c** (1eq) were added. After some minutes an orange solid precipitated. The reaction was allowed to react for 3 hours with stirring and then filtrated. The yellow precipitate was washed with 1mL of CH_3OH and dried under vacuum. 173mg of solid were obtained. It was a 80/20 mixture of **6c** and **6'c** with a 86% yield. This solid was dissolved in $CDCl_3$ (1 mL) and after evaporation of the solvent 96 mg of pure **6a** were obtained (Yield: 48%). The **ML2** complex **6c'** was only obtained as mixture.

ML complex 6c: ^{1}H NMR ($CDCl_3$): δ = 7.72 (d, *J*=9 Hz, 2H), 7.02 (d, *J*=9 Hz, 2H), 4.32 (tt, *J*=7.6, 2.1 Hz, 2H), 3.91 (s, 3H), 3.18 (tt, *J*=7.8, 2.1 Hz, 2H), 2.38 (quint, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 163.2, 133.7, 114.8, 110.3, 82.1, 61.6, 55.7, 39.8, 21.7. Infra-Red: ν alkyne: 2198 cm^{-1} HRMS (ESI): $[C_{13}H_{13}NO^{35}Cl_4NaAu]^+$, calc. 523.96205, found 523.9621. UV: λ = 346nm (ε =14848), λ = 231nm (ε =18975).

ML2 complex 6c': ^{1}H NMR (CD_2Cl_2): δ = 7.49 (d, *J*=9 Hz, 2H), 6.76 (d, *J*=9 Hz, 2H), 4.35 (m, 2H), 3.82 (s, 3H), 3.34 (m, 2H), 2.49 (m, 2H).

Accepted manuscript

5. Accession codes

CCDC 1871903, CCDC 1871904, CCDC 1871905, CCDC 1871906, CCDC 1871907, CCDC 1871908 contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgements

The authors acknowledge S. Ferron for UV Data.

Supporting information

NMR Spectra, X-ray data (**4a, 4c, 5a, 6a, 6'a**), Infra-red spectra (**2c, 3a, 4a, 6a**) and UV spectra (**3a, 3c, 4a, 4c, 6a, 6c**).

References

(1) For a recent example: Tang, M.-C., Lee, C.-H., Ng, M., Wong, Y.-C., Chan, M.-Y., Yam, V. W.-W. Angew. Chem. Int. Ed., 57 (2018) 5463-5466 and references cited.

(2) Some examples: a) Alcaide, B., Almendros, P. Accounts of Chemical research, 47(2014) 939-952. b) L. Fensterbank, L., Malacria, M. Accounts of Chemical research, 47 (2014) 953-965. c) Zhang, Y., Peng, H., Zhang, M., Cheng, Y., Zhu, C. Chem. Com., 47 (2011) 2354-2356. d) Kung, K. K.-Y., Lo, V. K.-Y., Ko, H.-M., Li, G.-L., Chan, P.-Y., Leung, K.-C., Zhou, Z., Wang, M.-Z., Che, C.-M., Wong, M.K. Adv. Synth. Catal., 355 (2013) 2055-2070. e) Zhukhovtskiy, A. V., Kobylianskii, I., Wu, C.-Y., Toste, D. J. Am. Chem. Soc., 140 (2018) 466-474

(3) a) David, B., Monkowius, U., Rust, J., Lehmann, C.W., Hyzak, L., Mohr, F. Dalton Trans., 43 (2014) 11059-11066. b) Price, G.A., Flower, K.R., Pritchard, R.G. Brisdon, A.K., Quayle, P. Dalton Trans., 40 (2011) 11696-11697. c) Usón, R., Vicente, J., Cirac, J.A., Chicote, M.T. J. Organomet. Chem., 198 (1980) 105-112. d) Ball, L.T., Lloyd-Jones, G.C., Russell, C. J. Am. Chem. Soc., 136 (2014) 254-264.

(4) a) Guenther, J., Mallet-Ladeira, S., Estévez, L., Miqueu, L.K., Amgoune, A., Bourissou, D. J. Am. Chem. Soc., 136 (2014) 1778-1781. b) Joost, M., Estévez, L., Miqueu, K., Amgoune, A., Bourissou, D. Angew. Chem. Int. Ed., 54 (2015) 5236-5240. c) Wu, C.-W., Horibe, T., Jacobsen, C.B., Toste, D. Nature, 517 (2015) 449-454.

(5) Hashmi, A.S.K., Weyrauch, J.P., Frey, W., Bats, J.W. Org. Lett., 6 (2004) 4391-4394.

(6) a) Egorova, O.A., Seo, H., Kim, Y., Moon, D., Rhee, Y.M., Ahn, K.H. Angew. Chem. Int. Ed., 50 (2011) 11446-11450. b) Seo, H., Jun, M.E., Egorova, O.A., Lee, K.-H., Kim, K.-T., Ahn, K.H. Org. Lett.14 (2012) 5062-5065.

(7) a) Savjani, N., Roşca, D.-A., Schormann, M., Bochmann, M. Angew. Chem. Ed. Int., 52 (2013) 874-877. b) Chambrier, I., Rocchigiani, L., Hughes, D.L., Budzelaar, P.M.H., Bochmann, M. Chem. Eur. J., 24 (2018) 11467-11474.

(8) a) Langseth, E., Scheuermann, M.L., Balcells, D., Kaminski, W., Goldberg, K.I., Eisenstein, O., Heyn, R.H., Tilset, M. Angew. Chem. Ed. Int., 52(2013) 1660-1663. b) Langseth, E., Nova, A., Tråseth, E.Aa., Rise, F., Øien, S., Heyn, R.H., Tilset M. J. Am. Chem. Soc., 136 (2014) 10104-10115.

(9) Vu, H.-D., Renault, J., Roisnel, T., Robert, C., Jéhan, P., Gouault, N., Uriac, P. Eur. J. Org. Chem., 2015, 4868-4875.

Accepted Manuscript

(10) Kumar, R., Nevado, C. Angew. Chem. Ed. Int., 56 (2017) 1994-2015.
(11) Muragishi, K., Asahara, H., Nishiwaki, N. ACS Omega, 2 (2017) 1265-1272.
(12) a) Pintus, A., Rocghigiani, L., Fernandez-Cestau, J., Budzelaar, P.H.M., Bochmann, M. Angew. Chem. Ed. Int., 55 (2016) 12321-12324. b) Roşca, D.A., Smith, D.A., Hughes, D.L., Bochmann, M. Angew. Chem. Ed. Int., 51 (2012) 10643-10646.
(13) Melchiomma, M., Nieger, M., and Helaja, J. Chem. Eur. J. 16 (2010) 8262-8267.
(14) Hüttel, R., Forkl, H. Chem. Ber., 105(1972) 2913-2921.
(15) Pazderski, L., Pawlak, T., Sitkowski, J., Kozerski, L., Szlyk, E. Magn. Reson. Chem., 47 (2009) 932-941.
(16) a) de Graaf, P.W.J., Boersma, J., van der Kerk, G.J.M. J. Organomet. Chem., 105 (1976) 399-406. b) Karash, M.S., Isbell, H.S. J. Am. Chem. Soc. 1931, 3053-3059.
(17) a) Schouteteen, S., Allen, O.R., Haley, A.D., Ong, G.L., Jones, G.D., Vicic, D.A. J. Organomet. Chem., 691 (2006) 4975-4981. b) Gibson, C.S., Colles, W.M. J. Am. Chem. Soc., 53 (1931) 2407-2415.
(18) Godfrey, S.M., Ho, N., McAuliffe, C.A., Pritchard, R.G. Angew. Chem. Ed. Int. Engl., 35 (1996) 2344-2345.
(19) Teets, T.S., Nocera, D.G. J. Am. Chem. Soc., 131 (2009) 7411-7420.
(20) Glišić, B.Đ., Ryschlewska, U., Djuran, M. Dalton Trans., 41 (2012) 6887-6901.
(21) a) Gaillard, S., Slawin, A.M.Z., Bonura, A.T., Stevens, E.D., Nollan, S.P. Organometallics, 29 (2010) 394-402. b) Schuh, E., Werner, S., Otte, Monkowius, U., Mohr, F. Organometallics, 35 (2016) 3448-3451. c) Orbisaglia, S., Jacques, B., Braunstein, P., Hueber, D., Pale, P., Blanc, A., de Frémont, P. Organometallics, 32 (2013) 4153-4164.
(22) Rodriguez, J., Bourissou, D. Angew. Chem. Ed. Int., 57 (2018) 386-388.

Accepted manuscript