Inorganic Chemistry Communications 33 (2013) 82–85

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Synthesis and characterization of novel gold(III) complexes with polydentate N-donor ligands based on the pyridine and triazole heterocycles

Marco Bortoluzzi [a],*, Alberto Scrivanti [a], Andrea Reolon [a], Emanuele Amadio [a], Valerio Bertolasi [b]

[a] Dipartimento di Scienze Molecolari e Nanosistemi, Dordoduro 2137, 30123 Venezia, Italy
[b] Dipartimento di Chimica e Centro di Strutturistica Diffrattometica, Università di Ferrara, via Borsari 46, 44100 Ferrara, Italy

ARTICLE INFO

Article history:
Received 14 March 2013
Accepted 8 April 2013
Available online 17 April 2013

Keywords:
Gold(III)
Chloro-complexes
N-donor ligands
Pyridine
Triazole

ABSTRACT

The coordination chemistry towards the Au(III) metal centre of the pyridine-triazole ligands 2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz^{Ph}**) and 2-[(4-pentyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz^{Pent}**) has been explored and complexes having formulae $AuCl_3(pytz^{Ph})$ (**1^{Ph}**) and $AuCl_3(pytz^{Pent})$ (**1^{Pent}**) have been isolated and characterised. Reaction of **1^{Ph}** with $AgClO_4$ allowed the preparation of the compound $[AuCl_2(pytz^{Ph})](ClO_4)$ (**2^{Ph}**). Reaction of **1^{Ph}** and **1^{Pent}** with $K[AuCl_4]\cdot 2H_2O$ led to the formation of the salts $[Hpytz^{Ph}][AuCl_4]$ (**3^{Ph}**) and $[Hpytz^{Pent}][AuCl_4]$ (**3^{Pent}**).

Polydentate N-donor ligands play a fundamental role in the coordination chemistry of gold(III). Some examples of species commonly present in the coordination sphere of this metal centre are polyfunctional amines such as ethylenediamine, diethylenetriamine and their derivatives, amido-ligands usually obtained from the deprotonation of the corresponding amines, pyridine-based compounds such as 2,2′-bipyridine, 1,10-phenantroline, 2,2′:6′:2″-terpyridine and 2,3,5,6-tetrakis(2-pyridinyl)pyrazine, a number of ligands containing imine moieties or 5-membered heterocycles such as pyrazoles, oxazoles and imidazoles [1].

The catalytic properties of many gold complexes, in particular as far as activation of unsaturated compounds and of the C–H bond is concerned, make the coordination chemistry of gold a current field of research [2]. Moreover, the synthesis of novel complexes is nowadays prompted by the anti-tumoral, anti-bacterial, anti-viral and anti-rheumatoid properties exhibited by several coordination compounds of gold [3].

The heterocycle 1,2,3-triazole is present in various polydentate N-donor ligands [4]. The relative abundance of triazole-based coordinating moieties can be ascribed to the ease of their preparation, usually based on the copper-catalysed Huisgen reaction between an organic azide and an alkyne [5]. The coordination chemistry of polydentate neutral ligands containing pyridine and triazole moieties towards some square-planar d^8 metal centres has been recently studied. In particular, 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine and 2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz^{Ph}**) have been recently used for the preparation of novel halogeno-, allyl- and homoleptic Pd(II) and Pt(II) complexes [6]. However, in the case of the isoelectronic gold(III) centre the only reported compound is the salt **[Hpytz^{Ph}][AuCl$_4$]**, which has also been structurally characterised [6c].

Our recent studies have been aimed at extending the coordination chemistry of the ligand **pytz^{Ph}** towards gold(III) and in this communication we wish to report the synthesis and a preliminary study on the reactivity of the complexes having formula $AuCl_3(pytz^{Ph})$ (**1^{Ph}**) and $[AuCl_2(pytz^{Ph})](ClO_4)$ (**2^{Ph}**). Furthermore, we have also expanded this study to ligands having an aliphatic substituent instead of a phenyl ring on the triazole moiety, by synthesising the species 2-[(4-pentyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz^{Pent}**).

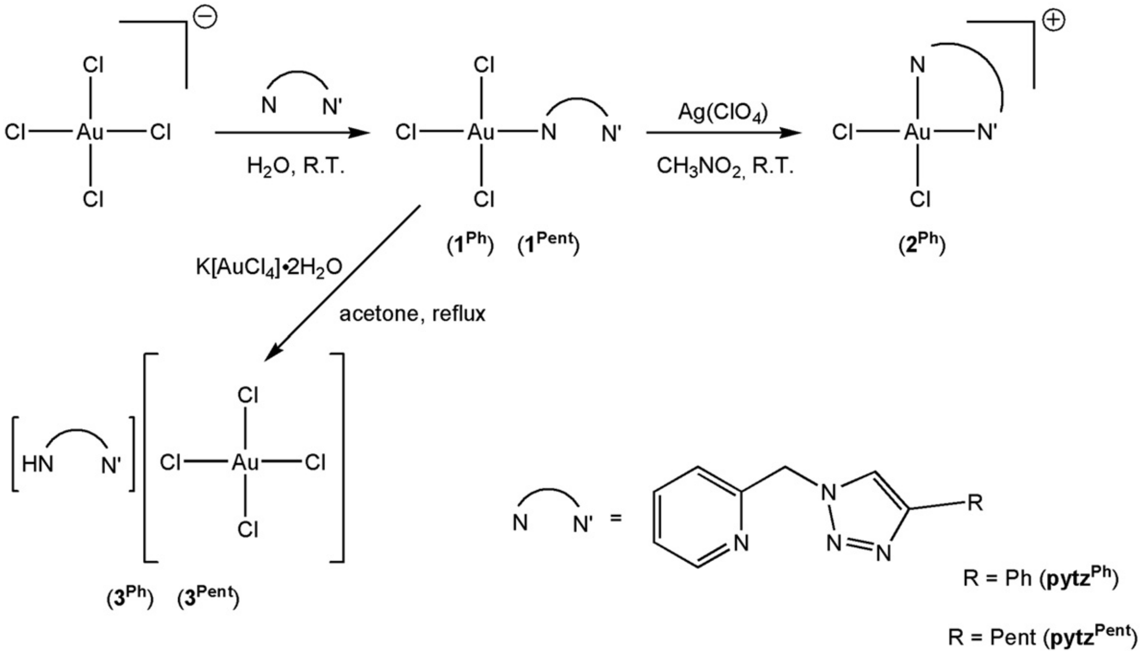
The ligand **pytz^{Ph}** was prepared by reacting 2-(azidomethyl)pyridine with phenylacetylene according to a literature procedure [6]; **pytz^{Pent}** was obtained analogously by reacting 2-(azidomethyl)pyridine with 1-heptyne in THF/H_2O. Details about the synthesis and characterization of **pytz^{Pent}** are collected in the Supplementary file.

Neutral complexes having general formula $AuCl_3(pytz^R)$ ($R = Ph$, Pent) were synthesised by adding a slight excess of the appropriate ligand dissolved in methanol to an aqueous solution of $K[AuCl_4]\cdot 2H_2O$ (see Scheme 1). While $[AuCl_3(pytz^{Ph})]$ (**1^{Ph}**) immediately precipitates as a pale yellow solid, $AuCl_3(pytz^{Pent})$ (**1^{Pent}**) was obtained as a yellow oil after removal of the solvent at reduced pressure. Yields were >95% in both the cases. Displacement reactions on gold(III) bromo-complexes as precursors [7] led instead to quite unstable species, which quickly decomposed with the formation, among all, of the $[AuBr_2]^-$ anion.

---

* Corresponding author. Tel.: +39 0412348651; fax: +39 0412348517.
E-mail address: markos@unive.it (M. Bortoluzzi).

1387-7003/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2013.04.015



Scheme 1. Synthesis of $\mathbf{1^{Ph}}$, $\mathbf{1^{Pent}}$, $\mathbf{2^{Ph}}$, $\mathbf{3^{Ph}}$ and $\mathbf{3^{Pent}}$.

Characterization data for $\mathbf{1^{Ph}}$ and $\mathbf{1^{Pent}}$ are reported in Table S1. Details about the characterization methods are collected in the Supplementary file. Elemental analysis data are in agreement with the proposed formulae. Conductivity measurement on acetone solutions confirmed that both the products are neutral.

In the aromatic region of the ^{1}H NMR spectrum of $\mathbf{1^{Pent}}$ (see Supplementary file) only one set of resonances for the pyridine and triazole rings is present and one singlet attributable to the methylene group is observable at 6.00 ppm (the corresponding ^{13}C NMR resonance falls at 59.2 ppm). In the aliphatic region the signals of the pentyl chain are easily observable. There is no meaningful change among the ^{1}H NMR spectra of $\mathbf{1^{Pent}}$ recorded in the range 298–193 K. In particular, the $-CH_2-$ signal remains a sharp singlet, this suggesting the coordination of the N-donor ligand to the gold centre through only one nitrogen atom. The ^{1}H NMR resonance of pyridine-H_6 proton is 8.58 ppm, a value close to the 8.56 ppm of the free ligand. On the contrary, the chemical shift of triazole-H_5 is meaningfully high-frequency shifted with respect to $\mathbf{pytz^{Pent}}$, this suggesting the interaction of the ligand with Au(III) through the triazole moiety.

In order to better give insight into the coordination mode of the ligand towards the $AuCl_3$ fragment, we optimised the possible isomers of $\mathbf{1^{Pent}}$ (coordination through pyridine-N, triazole-N_2 and triazole-N_3) by DFT calculations (computational details are reported in the Supplementary file). The species where the ligand is bonded to the gold centre by the triazole-N_3 atom (Fig. 1) is significantly more stable than the other isomers, in agreement with the experimental NMR observations.

The ^{1}H NMR spectrum of $\mathbf{1^{Ph}}$ is considerably different from that of $\mathbf{1^{Pent}}$. The presence of two sets of signals suggests the presence of two isomers, namely $\mathbf{1^{Ph}a}$ and $\mathbf{1^{Ph}b}$, in the relative molar ratio of 0.8:1. In particular, in the aromatic region eight signals attributable to two *ortho*-substituted pyridine rings are observable together with two singlets corresponding to the hydrogen atoms in position 5 of two triazole moieties. Two singlets in the spectral region between 6.6 and 6.0 ppm are also present, which correspond to two distinct methylene groups and have been attributed to the proper isomer by NOESY experiments. As for $\mathbf{1^{Pent}}$, no meaningful change of the NMR spectra was observed by lowering the temperature to 193 K. The presence of two isomers of $\mathbf{1^{Ph}}$ is confirmed also by the ^{13}C {^{1}H} NMR spectrum. In particular, two resonances at 153.1 and 147.7 ppm have been attributed to the pyridine carbon atom in position 6, while two signals at 124.1 and 123.6 ppm correspond to the triazole-CH. The methylene groups give two signals at 55.8 and 54.3 ppm. It is to be noted that the ^{1}H NMR chemical shift value of the pyridine-H_6 in $\mathbf{1^{Pent}}$ (8.58 ppm) is closer to that reported for the $\mathbf{1^{Ph}b}$ isomer of the phenyl-substituted derivative (8.85 ppm), this suggesting a similar coordination mode. The chemical shift of the same proton in $\mathbf{1^{Ph}a}$ is instead quite high-frequency shifted (9.43 ppm) and implies the coordination of the ligand by the pyridine nitrogen atom.

From DFT calculations the isomers of $\mathbf{1^{Ph}}$ with the Au-N_3(triazole) or the Au-N(pyridine) bonds resulted the most stable and have comparable energies, while the coordination through the triazole-N_2 has been excluded. The most stable isomers are probably the species observed by means of NMR spectroscopy and the optimised geometries are reported in Fig. 1.

The apparently higher coordinating ability of the triazole moiety in $\mathbf{pytz^{Pent}}$ with respect to $\mathbf{pytz^{Ph}}$ is fairly attributable to the increased basicity induced by the alkyl group. In fact, the computed proton affinity (PA) for the triazole-N_3 in $\mathbf{pytz^{Pent}}$ is about 3 kcal mol^{-1} higher than that calculated for the same nitrogen atom in $\mathbf{pytz^{Ph}}$. In this connection it is noteworthy that a similar PA difference has been computed in the past between 3-methyl-pyridine and pyridine [8].

The complexes $\mathbf{1^{Ph}}$ and $\mathbf{1^{Pent}}$ were reacted with one equivalent of $AgClO_4$ in CH_3NO_2 with the aim of preparing coordination compounds in which the N-donor ligands act as bidentate, but only with the phenyl-substituted ligand it was possible to isolate in high yield (ca. 90%) the compound $[AuCl_2(pytz^{Ph})](ClO_4)$ ($\mathbf{2^{Ph}}$) (see Scheme 1).

The relevant characterization data are collected in Table S1. Elemental analysis data for $\mathbf{2^{Ph}}$ are in agreement with the proposed formulation and the complex behaves as 1:1 electrolyte in CH_3NO_2 [9]. The IR spectrum shows signals attributable to the C═N and Cl–O stretchings and in the far-IR region a band at 370 cm^{-1} and a shoulder around 378 cm^{-1} have been attributed to the Au–Cl stretching [10].

The ^{1}H NMR spectrum of $\mathbf{2^{Ph}}$ in $(CD_3)_2CO$ at 298 K shows in the aromatic region four signals attributable to the pyridyl moiety alongside the singlet corresponding to the triazole-H_5 proton and the