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Synthesis of dinuclear N-heterocyclic dicarbene Au(III)/Au(III) and Au(II)/Au(II) complexes via oxidative addition of chlorine or bromine to Au(I)/Au(I) species

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ABSTRACT

Oxidative addition of chlorine to dinuclear N-heterocyclic dicarbene gold(I) complexes of formula $[Au_2(RIm{-}Y{-}ImR)_2](PF_6)_2$ (R = Me, Y = $(CH_2)_{1-4}$; R = Cy, Y = CH_2) affords in high yield stable Au(III)/Au(III) and Au(II)/Au(II) complexes. The nature of the products depends on the bridge between the two carbene moieties. With Y = methylene, ethylene and butylene, Au(III)/Au(III) dinuclear dicarbene complexes are formed. Only in the case of the propylene bridge the main product is an Au(II)/Au(II) complex. The same reaction output is now proposed also in the oxidative addition of bromine, as fully supported by the X-ray structure of complex $[Au_2Br_2(MeIm{-}(CH_2)_3{-}ImMe)_2](PF_6)_2$.

1. Introduction

In recent years, there has been an increasing interest in gold chemistry, as a consequence of the promising applications of gold compounds in the fields of nanotechnology, medicine and catalysis [1–3]. In this context, the research activity on the synthesis and characterisation of new gold complexes has been extended to N-heterocyclic carbene (NHC) complexes [4,5]. The majority of these studies involves mononuclear NHC–gold(I) and, to a minor extent, gold(III) complexes [5]. In fact, the inherent instability of the gold(III) centre towards reduction to gold(I) or gold(0) does not easily allow extending its coordination set.

For this reason, the safest, simplest and most general synthetic procedure to gold(III) carbene complexes involves oxidative addition of halogen to the corresponding gold(I) carbene complexes [6–8]. Other protocols, such as the reaction of a gold(III) precursor with the free carbene or the transmetallation of the carbene ligand between the corresponding Ag(I) complex and a gold(III) precursor may easily result in gold(III) reduction.

We have recently reported the synthesis of N-heterocyclic dicarbene dinuclear gold(III) complexes *via* oxidative addition of bromine to the corresponding gold(I) complexes [9]. These last ones differ mainly for the length of the bridge between the carbene units and for the wingtip substituents at the nitrogen atoms of the heterocyclic ring (Chart 1). The type of obtained products, as well as their stability in solution towards the reductive elimination of Br_2, was significantly different, mostly depending on the length of the bridging group connecting the two carbene units. Various molecular structures were determined by single crystal X-ray analysis (Chart 2) for the dicarbene complexes: bis-dicarbene Au(III)/Au(III) (dinuclear, type A, and polymeric, type B), mono-dicarbene Au(III)/Au(III) (dinuclear, type C), and bis-dicarbene mixed valence Au(III)/Au(I) (dinuclear, type D).

In this paper, as an extension of our study, we report on the addition of chlorine, generated *in situ* from $PhICl_2$, to the same dinuclear dicarbene gold(I) complexes, in order to verify the possible influence of a different oxidant on the output of the reaction. It can be anticipated that a dinuclear Au(II)–Au(II) complex is formed with the propylene bridged dicarbene. This observation has prompted in turn a re-evaluation of the related oxidative addition of bromine to the same Au(I) complex.

2. Results and discussion

2.1. Synthesis of gold(III) di(NHC) complexes

The gold(III) dicarbene complexes were synthesised by reaction of the gold(I) analogues with $PhICl_2$ in Au/Cl_2 1/1.2 molar ratio in acetonitrile at room temperature for 12 h (Scheme 1). Because of the corrosive and difficult to handle nature of gaseous chlorine, we

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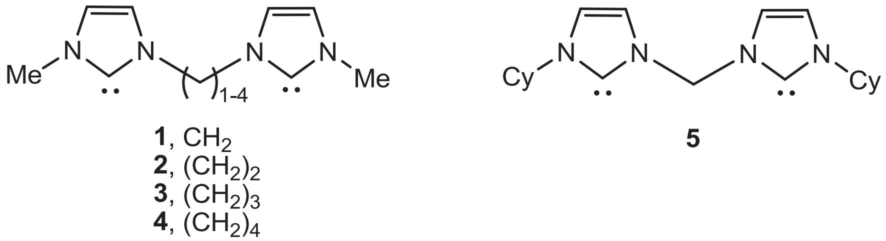


Chart 1. Dicarbene ligands **1**–**5** employed in this study.

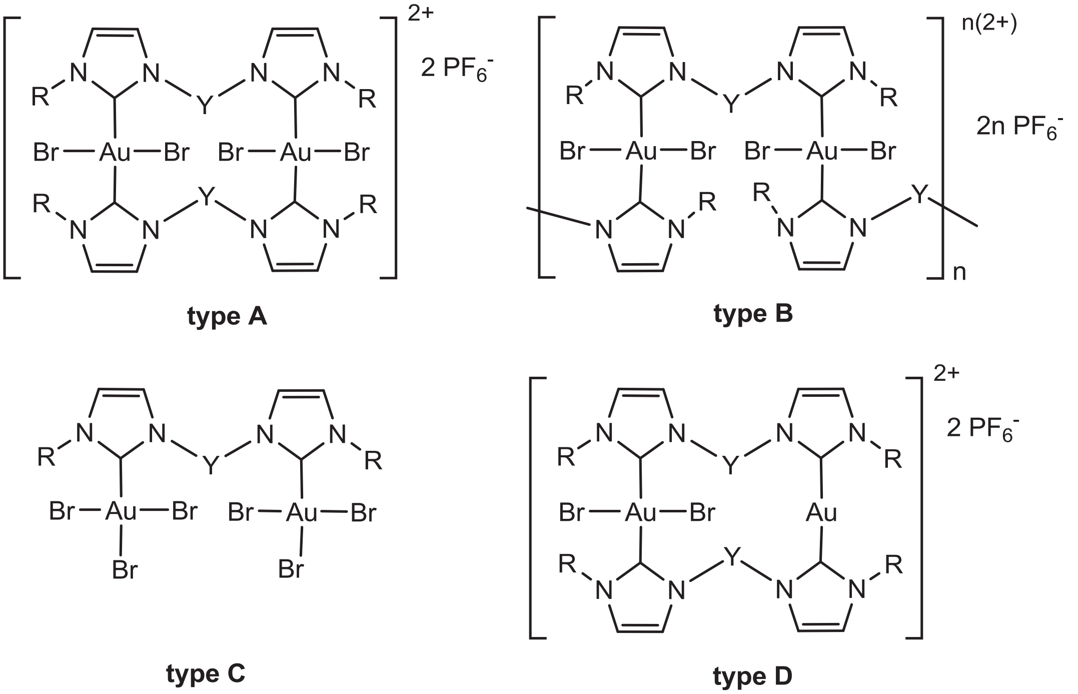
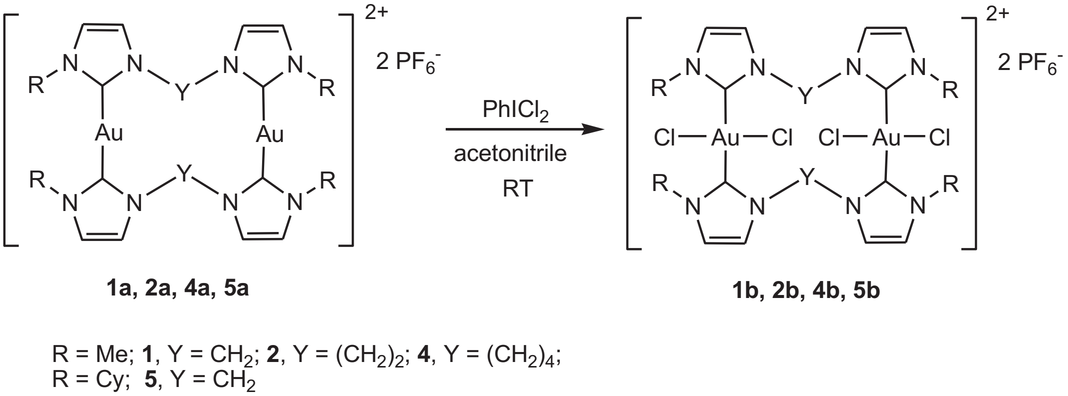


Chart 2. Type of gold complexes obtained in the addition of bromine.

used as oxidant solid $PhICl_2$, which is widely employed as a safer and easier source of Cl_2.

The complexes **1b**, **2b**, **4b** and **5b** are light yellow solids, soluble in common polar organic solvents (acetonitrile, dimethylsulfoxide). The features of the ^1H NMR signals are similar to those of the dinuclear dicarbene gold(I) complexes, thus suggesting that the symmetric dinuclear structure is maintained upon oxidation. The ^1H signals of the two hydrogen atoms of the imidazole backbone are slightly shifted downfield in comparison with the corresponding gold(I) complexes and the same downfield shift is observed also in the ^{13}C NMR spectra for the corresponding C_4 and C_5 carbon atoms. Finally, an upfield shift is observed for the carbene carbon resonance, from ca. 180 ppm for NHC–Au(I) to ca. 154 ppm for NHC–Au(III) complexes. These observations are the consequence of the greater delocalisation of the electronic density from the C_4–C_5 double bond to the carbene carbon atom, induced by the higher Lewis acidity of the gold(III) *vs.* gold(I) metal centre [7].



Scheme 1. Synthesis of the gold(III) dicarbene complexes.