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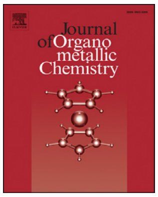

# Synthesis and thermotropic behaviour of bis(imidazolium) salts bearing long-chain alkyl-substituents and of the corresponding dinuclear gold carbene complexes

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## ABSTRACT

New propylene bridged bis(imidazolium) salts bearing at the wingtip positions a benzyl group functionalised with one or two long alkyl chains, as well as the corresponding dinuclear N-heterocyclic dicarbene gold(I) complexes of general formula $[Au_2(RIm{-}(CH_2)_3{-}ImR)_2](X)_2$ ($X = Br, PF_6, BF_4$) have been synthesised and thermally characterised. All the compounds are stable up to 200 °C and the bis(imidazolium) salts $[H_2(RIm{-}(CH_2)_3{-}ImR)](X)_2$ ($X = Br, PF_6$) behave as thermotropic liquid crystals in the temperature range 100–200 °C. By contrast, only the gold(I) diNHC complexes with eight aliphatic chains present mesomorphism, whereas those with four chains show numerous crystalline phases with structural disorder and presumably modified Au–Au distances, as indicated by solid state emission properties.

## 1. Introduction

Molecular thermotropic materials are a wide class of compounds that includes organic ionic liquids, liquid crystals and plastic crystals [1] and this kind of soft materials presents interesting physico-chemical properties that are influenced by temperature [2]. We have been involved for many years in the chemistry of bis(imidazolium) salts, to be used as di(N-heterocyclic carbene) (diNHC) ligand precursors, and in fact we have extensively studied the coordination properties of diNHC ligands towards a variety of late transition metal centres [3,4]; the interest towards the obtained complexes is inherent in their wide range of application covering in particular the fields of catalysis, medicine and photophysics [5]. However, imidazolium salts are interesting also by themselves because they are privileged molecular scaffolds for the preparation of thermotropic materials [1a,6–8]. Several reports deal indeed with the thermal behaviour of poly(imidazolium) salts [9,10], while those on liquid crystalline NHC metal complexes are rather limited [11]. The synthesis of a molecular material that combines the properties of thermotropic organic materials and of transition metal complexes could afford new materials for new effects and devices [12]. However, the coordination of a metal centre could deeply modify the properties of the organic substrate and the effects of the metalation are hardly predictable [13]. In this frame, the highly stable NHC metal complexes turned out to be promising architectures for the development of thermotropic organometallic species [14]. Here we report on the synthesis of novel bis(imidazolium) salts with a propylene bridge between two heterocyclic rings and long chain wingtip substituents. Moreover, the corresponding gold(I) diNHC complexes have also been synthesised with the aim of preparing luminescent thermotropic complexes, since propylene bridged di-NHC gold(I) complexes are efficient solid state emitters [4]. All the synthesised bis(imidazolium) salts and gold(I) complexes have been thermally characterised by TGA, DSC, SAXS and POM. Solid state photoluminescence

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measurements have moreover been carried out on selected gold(I) diNHC complexes.

## 2. Results and discussion

### 2.1. Synthesis of the bis(imidazolium) salts and of the gold(I) complexes

Compounds ($\mathbf{L^1}$–$\mathbf{L^7}$)·2HBr were synthesised in good yields via a single-step procedure (Scheme 1), in which functionalised benzyl bromides, preliminary obtained following a route already described in the literature [15–18], react with 1,3-di(1H-imidazol-1-yl)propane. The isolated bis(imidazolium) salts were characterised by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy as well as elemental analysis.

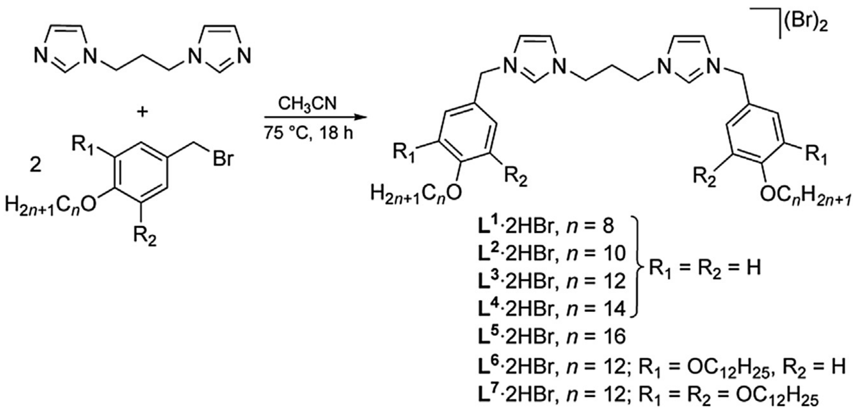
In particular the isolation of the bis(imidazolium) salt was confirmed by the presence in the $^1$H NMR spectra of a signal around $\delta$ 10.2 ppm, attributable to the hydrogen atom in position 2 of the heterocyclic ring. The elemental analyses confirm the purity of the prepared compounds, which are however hygroscopic and are isolated with different amounts of molecules of solvation.

Gold(I) carbene complexes $[Au_2L_2](Br)_2$ (**[1–6]-Br**) were obtained in good yields (36–85%) with a well-established procedure (Scheme 2), i.e. by deprotonation in dimethylformamide of the bis(azolium) salts ($\mathbf{L^1}$–$\mathbf{L^6}$)·2HBr with a mild base (NaOAc) in the presence of $AuCl(SMe_2)$ as gold precursor [19]. The final anion metathesis step with $KPF_6$ or $KBF_4$ allows the isolation of products **[1–6]-PF$_6$** (61–78% yield) and **[1–6]-BF$_4$** (65–95% yield). The adopted experimental procedure allows to obtain **[1–6]-Br** as spectroscopically pure complexes, as indicated by the presence in the NMR spectra of a single set of signals attributed to the cation of the expected compound, though characterised by unsatisfactory elemental analyses; the C/H/N ratio is correct, but the absolute values are rather low, probably because of a reduction of the gold precursor to gold(0). Nevertheless, the compounds could be purified by anion metathesis with $KPF_6$, while the same procedure with $KBF_4$ does not significantly improve their purity. The complexes have been synthesised with $PF_6^-$ or $BF_4^-$ anions because it is well known that the thermal properties of organometallic species depend on the associated counterion, as a consequence of intermolecular or anion/cation interactions [9f,20]. In the case of proligand $\mathbf{L^7}$·2HBr, the experimental conditions reported in Scheme 2 afforded reduction of the gold(I) precursor $AuCl(SMe_2)$ to gold(0) instead of the desired gold(I) diNHC complex. The formation of the complex **7-Br** is most likely prevented by the rather low solubility of its bis(imidazolium) proligand even at high temperature. In general, gold(I) complexes with four aliphatic chains are moderately soluble in DMSO and $CHCl_3$, while complexes with eight aliphatic chains (**6-PF$_6$** and **6-BF$_4$**) are insoluble in DMSO but are highly soluble in $CHCl_3$. In the $^1$H NMR spectra of the obtained products the disappearance of the C2–H signal is indicative of the deprotonation of the bis(imidazolium) salt. The formation of the carbene complex is also confirmed by the signal of the carbene carbon around $\delta$ 180 ppm, in the typical range of C2 coordinated to a gold(I) centre [4,21]. The dinuclear structure of the dicarbene complexes has been established by mass spectrometry measurement (ESI-MS) which displays the peaks relative to the $[Au_2L_2X]^+$ ($X = PF_6^-$ or $BF_4^-$) and $[Au_2L_2]^{2+}$ fragments.

### 2.2. Thermal properties of the complexes with long-chain wingtip substituents

The carbene ligand precursors ($\mathbf{L^1}$–$\mathbf{L^6}$)·2HBr are soft fine-crystalline powders in the pristine state and melt to a fluid mesophase, maintained until decomposition around 200 °C (Table 1). POM textures include oily strips, homeotropic zones and strongly birefringent zones, from which the mesophase was readily identified as smectic, likely a smectic A phase (Fig. 1a and b), whose assignment was clearly confirmed by SAXS patterns. The small-angle region of patterns contains two sharps reflections in the spacing ratio 1:2 that correspond to the first and second order reflections of the lamellar period *d*. The wide-angle region consists, instead, of a broad scattering halo which clearly shows that the alkyl chains and bis(imidazolium) cores have liquid like lateral arrangements (Fig. 1a and b).

The smectic phase arises from the nanosegregation in sublayers of antagonistic ligand segments. In that way, ionic layers formed by bis(imidazolium) cations and counterions alternate with layers of molten aliphatic tails and intermediate strata containing the benzyl segments and the aliphatic spacers, respectively. The periodicity of the alternation thus corresponds to a single molecular layer. As a consequence the layer thickness *d* is related to the molecular volume $V_{mol}$ and to the average layer portion covered by a single molecule, i.e. the molecular area *S*, through the ratio $S = V_{mol}/d$. The molecular volume $V_{mol}$ can be calculated by using the partial volumes of the various segregating segments (alkyl chains, bis(imidazolium) core and benzyl groups), that do not vary significantly between different molecular architectures and are readily deduced from reference dilatometric measurements [15,17]. The increase of *d* with chain length for the compounds having two long-alkyl chains (*bicatenar compounds*) comes down to *S* values ranging between 28 and 37 Å$^2$ with Br$^-$ counteranions, and around 40 Å$^2$ with $PF_6^-$ (Fig. 2). These areas are intermediate between the cross-section



**Scheme 1.** Synthesis of the bis(imidazolium) salts ($\mathbf{L^1}$–$\mathbf{L^7}$)·2HBr.