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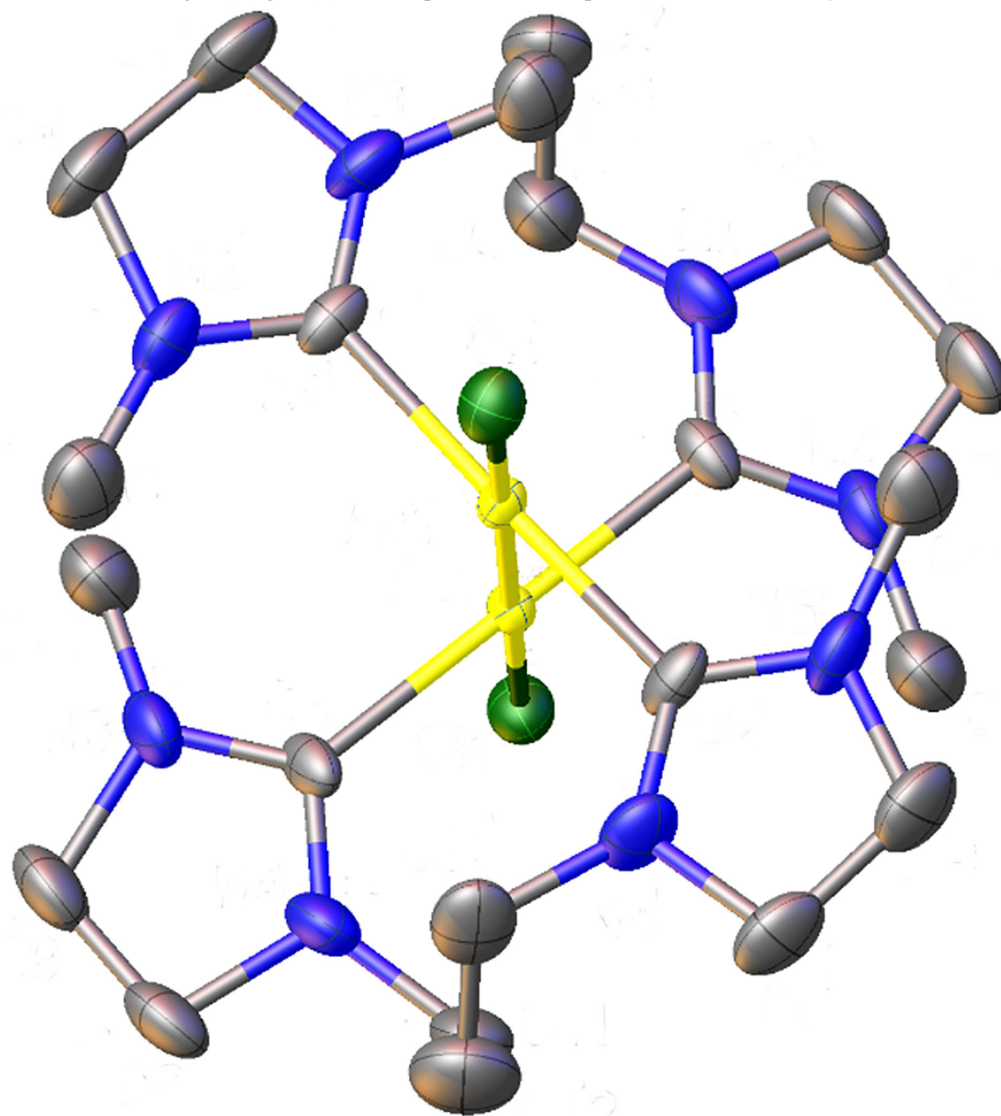
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Abstract:

A novel dinuclear gold(II) complex with two-fold rotational symmetry **2** of general formula $[\text{Au}_2\text{Cl}_2(\text{diNHC})_2](\text{PF}_6)_2$ (diNHC=di(N-heterocyclic carbene)) has been obtained in quantitative yield via chlorine (in the form of PhICl_2) oxidative addition to the parent gold(I) complex **1** $[\text{Au}_2(\text{diNHC})_2](\text{PF}_6)_2$. The novel compound has been characterized by ^1H and ^{13}C NMR and single crystal x-ray structure analysis. The oxidation of the two gold(I) centres to gold(II), with the formation of a covalent bond between them, imposes to the complex an axis of chirality, along the Au–Au bond, leading to a chiral propeller arrangement.

Graphical Abstract:

Structural characterization of a novel dinuclear gold(II) complex with di(N-heterocyclic carbene) ligands, the formation of the gold(II)-gold(II) bond imposes to the complex coordination chirality.



Keywords (separated by '-') Gold(II) complex - N-heterocyclic carbene - Oxidative addition - Bidentate ligands

Footnote Information **Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10870-020-00840-7>) contains supplementary material, which is available to authorized users.



Quantitative Selection of the Axially Chiral Conformation in a Flexible Dinuclear Gold(I) di(N-Heterocyclic Carbene) Complex via Chlorine Oxidative Addition

Marco Baron¹ · Marzio Rancan^{1,2} · Lidia Armelao^{1,2} · Cristina Tubaro¹

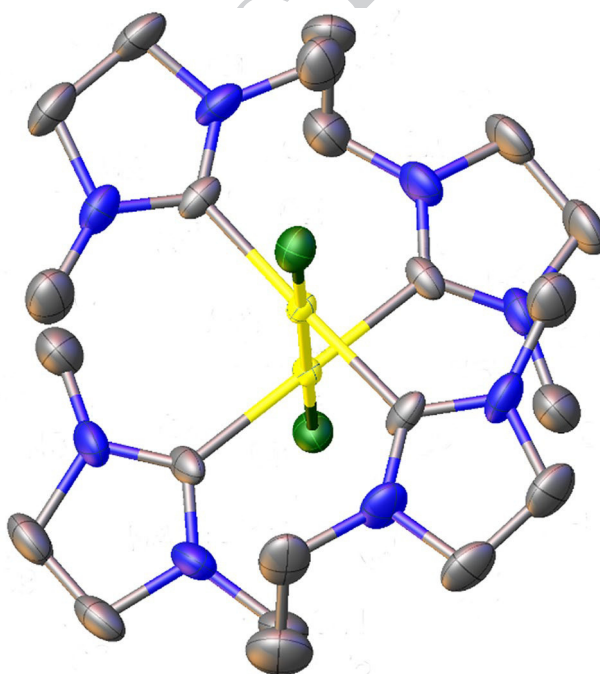
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Abstract

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A4 Extended author information available on the last page of the article

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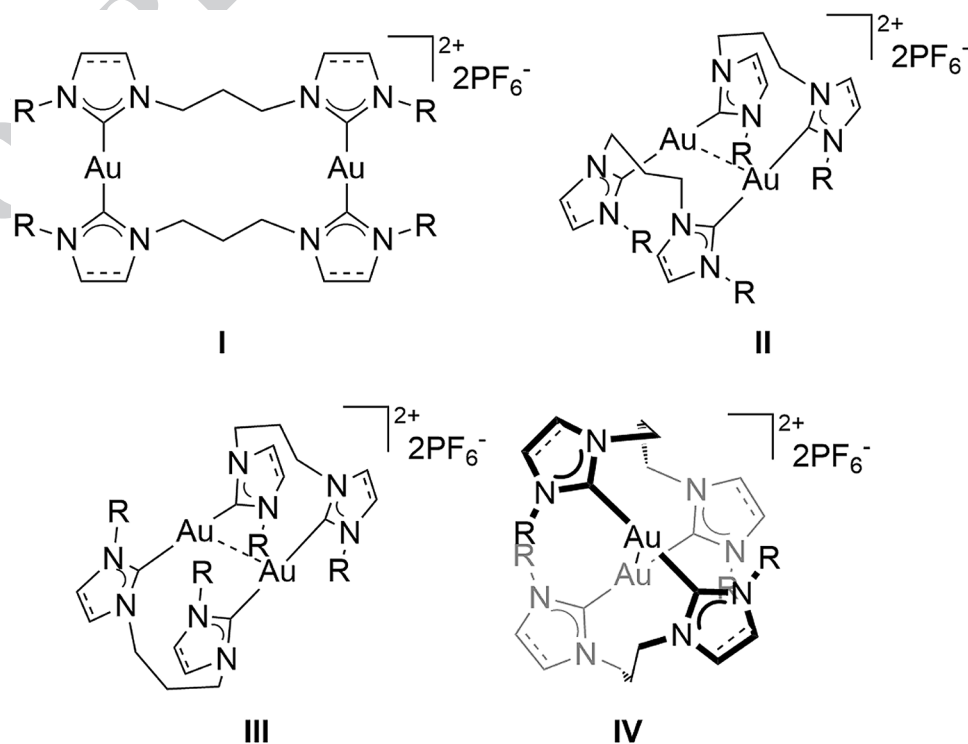
19 Introduction

20 Dinuclear gold(I) complexes with one or two bridging
 21 di(N-heterocyclic carbene) ligands (diNHC) are an appeal-
 22 ing class of organometallic compounds, because they might
 23 show high-quality photoemission properties [1, 2], prom-
 24 ising antibacterial and anticancer activity [3, 4] and good
 25 catalytic performances in the activation of carbon–carbon
 26 multiple bonds [5, 6]. Focussing on complexes of the general
 27 formula $[\text{Au}_2(\text{diNHC})_2]^{2+}$, i.e. complexes with two bridg-
 28 ing ligands, they feature two peculiar features that govern
 29 their properties and reactivity: very high stability due to
 30 the formation of a metallamacrocyclic structure and ligand
 31 supported intramolecular aurophilic interaction. Aurophi-
 32 licity, first described by Schmidbaur in the eighties [7], by
 33 enhancing the probability of electronic transitions [8], is
 34 responsible for the solid state photoemission properties of
 35 the complexes. Moreover, also the reactivity of the com-
 36 plexes is influenced by this weak interaction. In particular,
 37 we have already demonstrated that dinuclear gold(I) diNHC
 38 complexes, in which intramolecular aurophilic interaction is
 39 present, can form stable gold(II) diNHC complexes in the
 40 oxidative addition reaction of halogens [9]. The oxidation
 41 state gold(II), bearing an electron configuration $5d^9$, is quite
 42 unusual for gold, as the oxidation states gold(I) and gold(III)
 43 are much more common (electron configuration $5d^{10}$ and $5d^8$

44 respectively). In the case of dinuclear gold(II) compounds,
 45 close Au–Au contacts of about 2.6 Å, which appear to rep-
 46 resent a true covalent Au–Au σ -bond, make these complexes
 47 exclusively diamagnetic [10]. A survey of reported dinuclear
 48 gold(II) complexes (Cambridge Structural Database, version
 49 5.40, including updates up to April 2019) [11], shows that
 50 the majority of structures involves phosphorus ylides [12],
 51 bis(diphenylphosphino)amines [13], 2-ferrocenyloxazolines
 52 [14], dithiolates [15], aminidate [16] and cyclometalated
 53 phenylphosphanes [17] as bridging bidentate ligands. Fewer
 54 studies refer to dinuclear unsupported gold(II) complexes
 55 [18–20], that means, complexes in which the two gold cen-
 56 tres are not bound by a bridging ligand. Finally, also a very
 57 limited number of mononuclear gold(II) complexes was
 58 found [11, 21–24]. The identification of molecular motifs
 59 able of forming gold(II) species is of particular interest for
 60 the development of novel homogeneous catalysts. In fact,
 61 systems in which this intermediate oxidation state is achiev-
 62 able have been found to better perform in organic transfor-
 63 mations whose substrate activation starts with an oxidative
 64 addition to the catalyst [25].

65 In this frame, we recently reported [26] that in the case
 66 of dinuclear gold(I) complexes, when a propylene bridge
 67 is used, a library of four main conformations is observed
 68 and may be present in solutions, Fig. 1. It is interesting to
 69 note, that even if the ligand is achiral, one of the possible

Fig. 1 Stretched-out (I), folded-syn (II), folded-anti (III) and twisted (IV) conformational isomers for propylene bridged complexes of general formula $[\text{Au}_2(\text{diNHC})_2](\text{PF}_6)_2$



70 conformers is chiral (IV), due to the dimetallic nature of
71 the complex having chiral propeller arrangement. Similar
72 structures have been reported with gold and also with other
73 metal centres [27–30].

74 When more species are in equilibrium, the capability
75 to orchestrate the system via chemical [31, 32] or physi-
76 cal stimuli [33] to achieve selection mechanisms is of para-
77 mount importance, especially if we want to exploit the fea-
78 tures of a specific conformer. In this study, it is demonstrated
79 that we can quantitatively drive the different conformers in
80 order to select the chiral conformation of a dinuclear gold
81 complex supported by diNHC ligands bearing a propyl-
82 ene linker between the coordinating units. The selection is
83 based on the oxidative addition of chlorine (in the form of
84 iodobenzene dichloride) to a gold(I) complex leading to the
85 clean and exclusive formation of a novel dinuclear gold(II)
86 diNHC complex. The ligand used in this study is based on
87 imidazolidin-2-ylidene donors [34].

88 Experimental

89 Synthesis and Crystallization

90 All manipulations were carried out using standard Schlenk
91 techniques under an atmosphere of argon. The reagents were
92 purchased by Aldrich as high-purity products and gener-
93 ally used as received; all solvents were used as received as
94 technical grade solvents. Complex **1** [35] and iodobenzene
95 dichloride [36] were synthesized according to literature pro-
96 cedures. NMR spectra were recorded on a Bruker Avance
97 300 MHz (300.1 MHz for ^1H and 75.5 for ^{13}C); chemical
98 shifts (δ) are reported in units of parts per million (ppm)
99 relative to the residual solvent signals.

100 For the synthesis of **2**, complex **1** (10.0 mg,
101 $9.05 \cdot 10^{-3}$ mmol) was dissolved in acetonitrile (10 mL), sub-
102 sequently iodobenzene dichloride (6.0 mg, $2.17 \cdot 10^{-2}$ mmol)
103 was added and the reaction mixture was stirred at room tem-
104 perature for 1 h. Afterwards the solvent volume was reduced
105 to 2 mL under vacuum and a yellow solid was precipitated
106 by adding diethyl ether (10 mL). The product was isolated
107 by filtration and dried under vacuum (yield 95%). Com-
108 pound **2** was characterized by means of ^1H and ^{13}C NMR
109 spectroscopy.

110 ^1H NMR (300.1 MHz, CD_3CN , 298 K): δ 1.85 (m, 4H,
111 CH_2), 3.07 (s, 12H, CH_3), 3.25–4.08 ppm (m, 24H, N- CH_2).
112 ^{13}C NMR (75.5 MHz, CD_3CN , 298 K): δ 24.2 (CH_2),
113 37.3 (CH_3), 46.5 (N- CH_2), 50.6 (N- CH_2), 53.1 (N- CH_2),
114 184.7 ppm (NCN).

115 Single crystals of **2** were obtained from a NMR sample of
116 the complex in CD_3CN by slow evaporation of the deuter-
117 ated solvent. A suitable crystal was recovered directly from

the NMR tube, fixed on the top of a Lindemann glass capil- 118
lary with perfluorinated oil and moved to the diffractometer. 119

Refinement

120
121 Crystal data, data collection, and structure refinement details
122 are summarized in Table 1. H atoms could not be located in
123 difference Fourier maps and were placed in calculated, ideal
124 positions and treated using a riding-model approximation.
125 Methyl H atoms were refined as part of rigid rotating groups,
126 with a C–H distance of 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$
127 while methylene H atoms were placed in calculated posi-
128 tions and refined using a riding model, with C–H distances
129 of 0.97 and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In the main moiety,
130 DFIX restraints were applied to C3–C4, C8–C9, C6–N1
131 bonds and EADP constrains to C5, C6 and C10 atoms. The
132 anion PF_6^- was split in two parts the occupancies of which
133 were constrained to sum to 1.0 while the relative occupan-
134 cies of these two sites were refined freely. The disorder was
135 refined with same distance (SADI) restraints for P...F and
136 F...F in order to restrain the model to an octahedral geometry
137 and with anisotropic displacement (EADP) constrains for P
138 and F atoms. Rigid-bond restraints (RIGU) were applied. A
139 Flack parameter close to 0.5 suggested the compound was
140 an inversion twin, hence the TWIN and BASF instructions
141 of Shelx were applied; the twin domain ratio was refined to
142 48:52. Finally, a void analysis using the program PLATON
143 [37] revealed the presence a total solvent accessible volume
144 of 921 \AA^3 with a total electron-count/cell of 200 electrons.
145 These values are consistent with the presence of approxi-
146 mately ten molecules of acetonitrile in the unit cell voids as
147 diffuse electron density. The SQUEEZE routine of PLATON
148 was applied [37], that is, the contribution of the unidentified
149 solvent to the structure factors was assessed by back-Fourier
150 transformation and the data were corrected accordingly. The
151 refinement using the modified dataset improved the overall
152 structure.

Results and Discussion

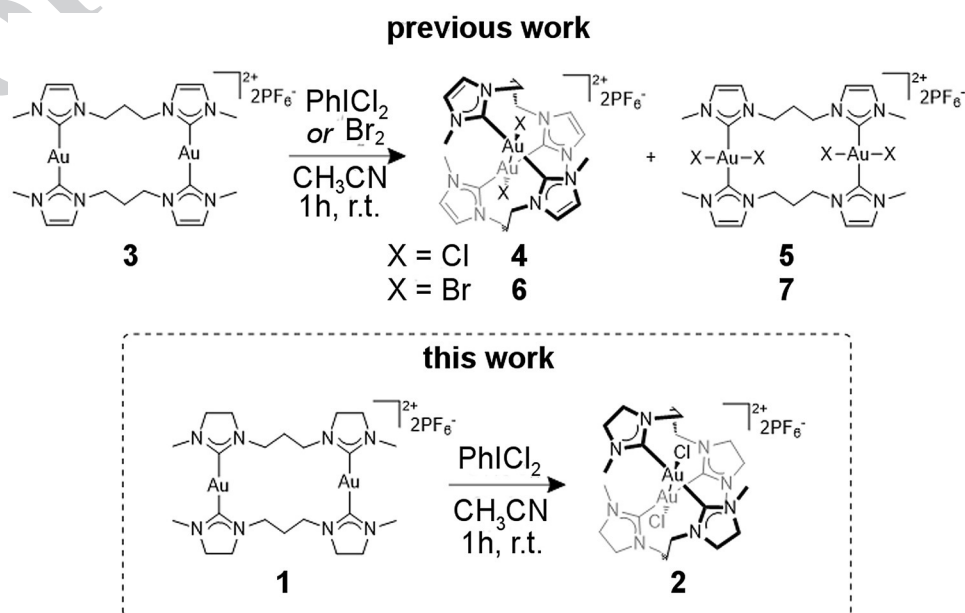
153
154 In a previous study [42], we showed that the chlorine and
155 bromine oxidative addition to the gold(I) diNHC complex
156 **3**, bearing imidazol-2-ylidene coordinating units and a pro-
157 pylene linker, leads to a mixture of a gold(II) and a gold(III)
158 complex in a 1:9 and 0.5:9.5 ratio for the chlorine and bro-
159 mine addition, respectively (Fig. 2). In the case of the bro-
160 mine addition, it was possible to unambiguously demonstrate
161 by single crystal diffraction, that the gold(II) compound has
162 a chiral propeller conformation. This suggested that the halo-
163 gen oxidative addition can drive a conformational flexible
164 complex, with four possible conformations (Fig. 1), towards
165 a specific conformational arrangement, even if the selectivity

Table 1 Experimental details

Chemical formula	$C_{27}H_{47.5}Au_2Cl_2F_{12}N_{10.5}P_2$
M_r	1274.02
Crystal system, space group	Tetragonal, $P4_12_12$
Temperature (K)	303
a, c (Å)	11.9792 (3), 30.1944 (19)
V (Å ³)	4332.9 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	7.04
Crystal size (mm)	0.23 × 0.15 × 0.1
Diffractometer	Xcalibur, Eos, Gemini
Absorption correction	Multi-scan <i>CrysAlis PRO</i> 1.171.38.43b (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm
T_{min}, T_{max}	0.534, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13702, 4425, 3682
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.625
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0553, 0.1179, 1.14
No. of reflections	4425
No. of parameters	201
No. of restraints	272
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 46.7695P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	1.22, -2.17
Absolute structure	Refined as an inversion twin
Twin domain ratio	48:52
CCDC code	1901763

Computer programs: *CrysAlis PRO* 1.171.38.43b, *ShelXT* [38], *SHELXL* [39], *Olex2* [40], *PLATON* [41]

Fig. 2 Oxidative addition of chlorine and bromine to complex **3** (above) and oxidative addition of chlorine to complex **1** (below)



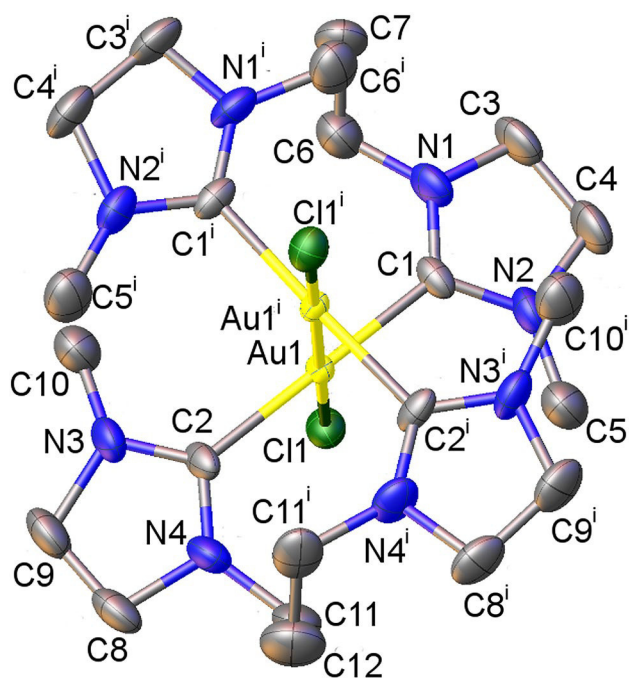


Fig. 3 ORTEP-style view of the molecular structure of complex **2**. PF_6^- anions and hydrogen atoms have been omitted for clarity, ellipsoids are drawn at the 50% probability level. Symmetry code $i=y, x, -z+1$

Table 2 Selected geometric parameters (\AA , $^\circ$)

Au1–Au1 ⁱ	2.5602 (12)	Au1–C1	2.041 (16)
Au1–Cl1	2.378 (4)	Au1–C2	2.039 (16)
Cl1–Au1–Au1 ⁱ	179.49 (12)	C1–Au1–C2	175.6 (7)
C1–Au1–Au1 ⁱ	91.9 (5)	C2–Au1–Au1 ⁱ	92.2 (5)

Symmetry code(s): (i) $y, x, -z+1$

is not complete. Here, we report that using a similar diNHC ligand, where the imidazol-2-ylidene coordinating units are replaced by imidazolin-2-ylidene donors, the chlorine oxidative addition gives the gold(II) complex **2** in the axially chiral arrangement as the only product and in quantitative yield establishing 100% selectivity. In this case, no gold(III) analogue is observed. Hence, the presence of a different donor in the carbene ligand changes the reactivity of the parent gold(I) complex in the halogens oxidative addition reaction leading to a clean and quantitative selection of the chiral propeller conformation.

The new complex **2** crystallises in the tetragonal space group $P4_12_12$. The asymmetric unit contains half of the gold(II) complex molecule and a disordered PF_6^- anion; the other half of the molecule and anion are symmetry equivalents (Fig. 3). The molecular structure of **2** is depicted in Fig. 3 and selected bond distances and angles for the metal centre are reported in Table 2.

The structure consists of two gold(II) centres in a square planar coordination environment. Each gold(II) atom is coordinated by two carbene donors situated *trans* to one another, a chlorine atom, and the fourth coordination site is occupied by the other gold centre with a direct gold(II)–gold(II) covalent bond. The presence of the metal–metal bond makes the dinuclear complex diamagnetic, by coupling the otherwise unpaired electron of the two $5d^9$ gold centres. The Cl1–Au1–Au1ⁱ–Cl1ⁱ ($i=y, x, -z+1$) fragment is almost linear, with the Cl1–Au1–Au1ⁱ angle close to 180° ($179.49(12)^\circ$). The Au1–Au1ⁱ and Au1–Cl1 distances, 2.5602(12) and 2.378(4) \AA , respectively, compare well with literature data for other dinuclear gold(II) complexes obtained via chlorine oxidative addition [43]. Similarly, also the Au(II)–C_{carbene} bond distances, 2.041(16) and 2.039(16) \AA for Au1–C1 and Au1–C2, respectively, fit with literature data [42, 44].

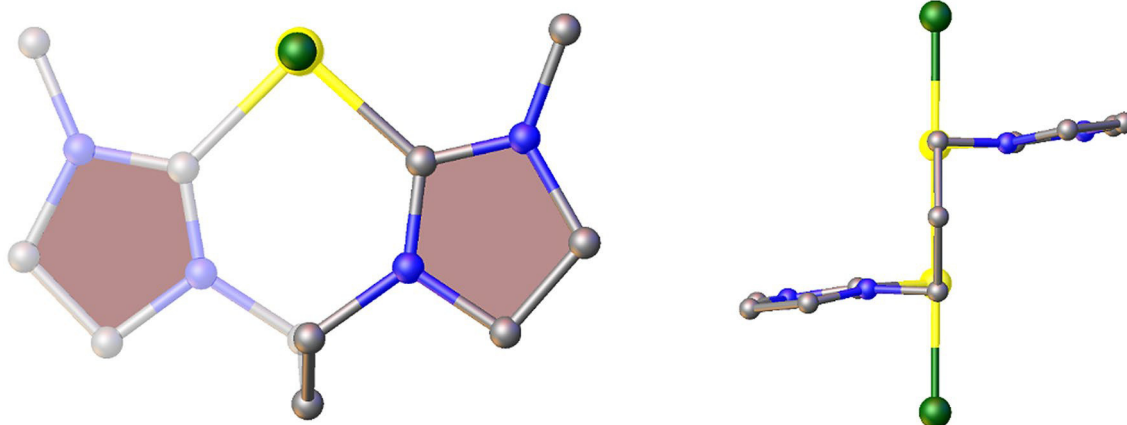


Fig. 4 Depiction of part of the molecular structure of complex **2** highlighting the bridging coordination mode of the di(NHC) ligand and the relative orientation of the carbene rings. View along the

Au–Auⁱ axis (left) and view along the C7–C12 axis (right). Colour code for atoms: gold (yellow), chlorine (green), carbon (grey) and nitrogen (blue)

200 The mean planes defined by the two imidazol-2-ylidene
 201 rings of the same ligand are almost parallel, forming a dihe-
 202 dral angle of 4.6(13) (Fig. 4). In **2**, each bidentate ligand is
 203 coordinated in a bridging fashion between the two gold centres
 204 forming a sixteen membered metallamacrocyclic ring.

205 The arrangement of the macrocyclic ring is very intriguing.
 206 The covalent bonded gold(II) centres are located at
 207 opposite sides of the ring resulting in a chiral propeller con-
 208 formation of the complex (Fig. 5) with an axis of chirality
 209 along the Au–Au bond. The compound is isolated as a race-
 210 mate with the right- (*P*) and the left-handed (*M*) conforma-
 211 tion both present in solution and in the solid state. For the
 212 measured crystal, inversion twinning with a domain ratio of
 213 48:52 was observed.

214 The crystal packing of **2** is reported in Fig. 6. The Au
 215 complexes are arranged with the Cl1–Au1–Au1ⁱ–Cl1ⁱ axis
 216 running approximately parallel to the crystallographic *c* axis.

217 Along this crystallographic direction, the cationic part of the
 218 complexes, the gold(II) centres, and the anionic part thereof,
 219 the chloride ligands and the PF₆[−] anions, are organized in
 220 alternate layers. Nevertheless, in the molecular packing,
 221 hydrogen bonding interactions are not detected.

222 Conclusions

223 In this study, we reported on the synthesis of a novel
 224 dinuclear gold(II) complex **2** obtained by oxidative addi-
 225 tion of chlorine to the parent dinuclear gold(I) complex **1**.
 226 The employment of a ligand bearing imidazolin-2-ylidene
 227 instead of imidazol-2-ylidene donors leads to the gold(II)
 228 complex as the only product of the reaction in quantitative
 229 yield, avoiding the formation of the gold(III) complex. The
 230 structural characterization of the dinuclear gold(II) complex

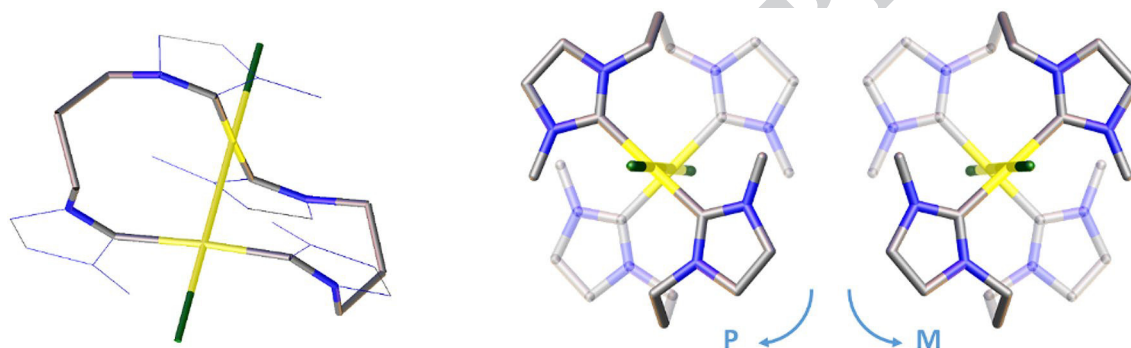
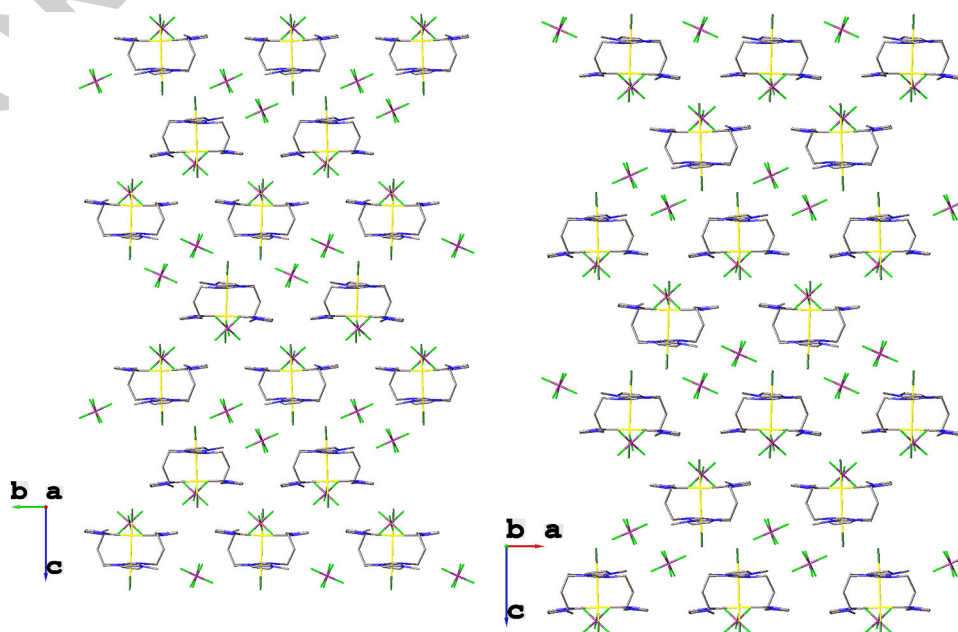


Fig. 5 Molecular structure of complex **2** highlighting the eight-shape of the sixteen-membered metallamacrocyclic ring (left). Representation of the *P* and *M* enantiomers of complex **2**. Colour code for atoms: gold (yellow), chlorine (green), carbon (grey) and nitrogen (blue)

Fig. 6 Crystal packing of **2**, view along the *a* (left) and *b* (right) axis. Colour code for atoms: gold (yellow), chlorine (green), carbon (grey), nitrogen (blue), phosphorus (purple) and fluorine (light green)



231 showed that the two gold(II) centres are covalently bonded
 232 (AuI–AuI¹ 2.5602(12) Å). The formation of the gold(II)-
 233 gold(II) bond imposes a propeller like conformation with
 234 a two-fold axis to the metallamacrocyclic structure of the
 235 complex. The twisted arrangement of the bidentate ligand
 236 allows the two gold(II) centres to be at the proper distance
 237 for a covalent bond. Hence, the oxidative addition can oper-
 238 ate as driving force to select a specific isomer in a complex
 239 mixture of possible conformational isomers. In particular,
 240 the ability to select a chiral compound is very intriguing
 241 concerning its potential application in asymmetric catalysis.

243 Compliance with Ethical Standards

244 **Conflict of interest** The authors declare that they have no conflict of
 245 interest.

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