Neutral dinuclear gold(I) complexes with N-phosphanyl, N-heterocyclic carbenes (NHCPs)

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ABSTRACT

Neutral dinuclear gold(I) complexes having general formula $[Au_2Cl_2(NHCP)]$ (NHCP = N-phosphanyl N-heterocyclic carbene) have been synthesized by two different synthetic procedures: i) transmetalation of the NHCP ligand from the corresponding dinuclear silver(I) complex; ii) deprotonation of the corresponding N-phosphanyl azolium/tetrahydropyrimidinium salt in the presence of the gold(I) precursor. Interestingly, although the silver complexes are invariably dinuclear dicationic species of formula $[Ag_2(NHCP)_2](OTf)_2$, both stoichiometries $[Au_2(NHCP)_2](OTf)_2$ and $[Au_2Cl_2(NHCP)]$ are potentially accessible with gold. Preference for either stoichiometry is dictated by the steric properties of the NHCP ligand as well as by a proper choice of the experimental conditions. On the other hand, preparation of copper(I) compounds with $[Cu_2Cl_2(NHCP)]$ stoichiometry leads to product mixtures and has not led up to now to pure neutral compounds. Both the silver(I) and gold(I) complexes have been structurally characterized.

1. Introduction

The organometallic and coordination chemistry of gold has witnessed a tremendous development in the 21st century, following the recognition of the outstanding properties of gold complexes as catalysts for a variety of technologically relevant reactions [1], but also as potential emitters in photo- and electrochromic devices [2] and as bioactive compounds [3]. Within the broad variety of gold complexes that has been prepared for use in these application fields, a subclass of compounds which currently raise considerable interest consists in polynuclear complexes. Such complexes can exhibit exceptional luminescence properties, particularly when the two gold centers interact with one another through so-called aurophilic interactions [2,4]. Moreover, the recognition that selected gold-catalyzed chemical reactions are actually catalyzed by two gold centers that work in concert [5] has made the development of tailored digold complexes appealing also for catalytic purposes [6].

In this connection, we [7] and others [8] have recently investigated on gold(I) complexes with N-phosphanyl, N-heterocyclic carbene ligands (NHCPs), a peculiar class of bidentate ligands recently developed by some of us [9]. In the frame of these investigations, we have succeeded in preparing and characterizing several dinuclear complexes of gold(I) with general formula $[Au_2(NHCP)_2](OTf)_2$. In this communication, we wish to disclose synthetic strategies that lead instead to gold(I)-NHCP complexes of general formula $[Au_2Cl_2(NHCP)]$. Such complexes are potentially attractive, in that the halide ligands can be readily exchanged with other anionic ligands or removed from the gold centers, thus giving rise to unsaturated species amenable to act as catalysts.
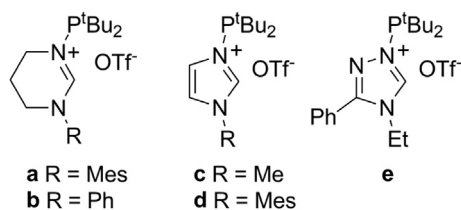
2. Results and discussion

The preparation of the gold(I) complexes has been accomplished from the NHCP precursors depicted in Chart 1. As it will be outlined in more detail below, such precursors were either reacted directly with gold(I) species or employed first to prepare silver complexes of general stoichiometry $[Ag_2(NHCP)_2](OTf)_2$, which then transferred
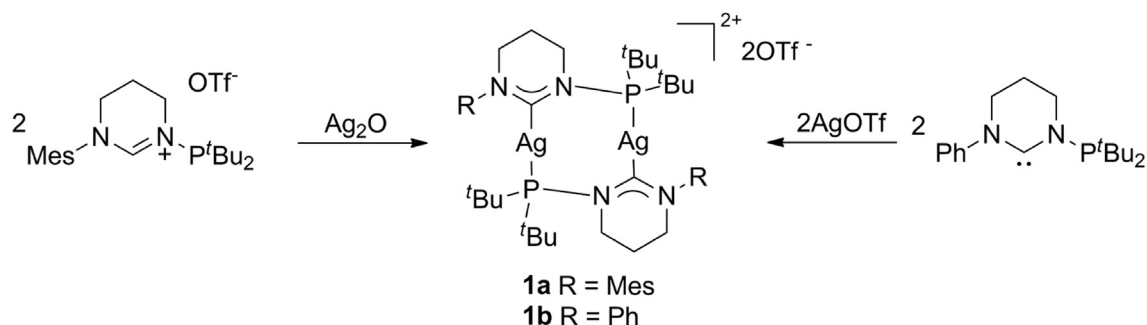
Chart 1. NHCP precursors employed in this study.

the ligand to gold(I) centers by transmetalation. Silver complexes of this kind, hereafter named **1c** and **1e**, stemming from imidazole or triazole-derived ligand precursors **c** and **e**, have been previosly reported by us [10] whereas complexes **1a** and **1b**, prepared employing tetrahydropyrimidine-derived ligand precursors **a** and **b**, are described for the first time herein.

2.1. Synthesis of silver(I) complexes with NHCP ligands based on tetrahydropyrimid-2-ylidene unit

The dinuclear silver(I) complexes **1a,b** having bridging NHCP ligands deriving from precursors **a** and **b** [11] were successfully prepared by two approaches, namely i) by reaction of the tetrahydropyrimidinium salt **a** with silver oxide in dichloromethane or ii) by reaction of silver triflate with the free carbene, produced upon deprotonation of salt **b** with LiHMDS (Scheme 1).
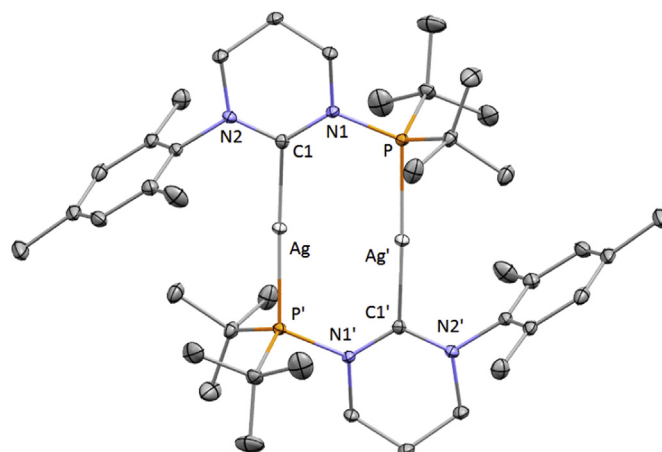

Fig. 1. ORTEP view of the cationic complex in **1a**, with the atomic numbering scheme. Ellipsoids are drawn at their 30% probability level. Hydrogen atoms and OTf⁻ anions are omitted for clarity. Symmetry transformation used to generate equivalent atoms, ' = −x+1, −y+2, −z+1'.

axis passing through the midpoint of the M···M separation. In both compounds the ligand coordinates in a bridging mode to two silver atoms, through the carbene carbon and the phosphorous atoms. The core structures strictly resemble those reported in Ref. [7a] and in Ref. [7b]. The coordination of the silver atoms is linear in both

Scheme 1. Synthesis of the silver(I) complexes **1a,b**.

The silver(I) complexes are off-white solids, soluble in most common organic solvents like chloroform, dichloromethane or CH_3CN. In the case of the synthesis of complex **1a**, the disappearance of the C2-H signal in the ^1H NMR spectrum is indicative of the deprotonation of the tetrahydropyrimidinium salt. The formation of the carbene complex in the two cases is further supported by the ^{13}C NMR spectra in which the carbene carbon resonance is found at δ 215 ppm, upfield shifted compared to the free carbene (ca. 250 ppm) [11]; furthermore, the complexity of the signal clearly indicates the coordination of the carbon to the silver center, because of the coupling with the spin active ^{107}Ag and ^{109}Ag nuclei. The same type of multiplicity (two sets of doublets) is also observed in the ^{31}P NMR spectra of the coordinated phosphanyl group of the ligands.

The structures of the silver(I) complexes were determined by X-ray diffraction methods. The ORTEP views of complexes **1a** and **1b** are reported in Figs. 1 and 2 respectively, while the most significant bond distances and angles are collected in Table 1.

Cationic compounds in **1a** and **1b** are both symmetric with the inversion centre located at the midpoint of the M···M distance in the case of **1a**, while in the case of **1b** the complex has a twofold

structures being the P-M-C$_{carbene}$ bond angle 175.50(6) and 178.10(7)° in **1a** and **1b** respectively. Differently from what observed in one of the structures reported in Ref. [7b] no interaction is present between the silver atoms of the complexes and the oxygen atom of the triflate anions; in fact in the crystal packing of both structures the triflate anions are far from the complexes being at a distance of 5.163 and 3.341 Å in **1a** and **1b** respectively. The C$_{carbene}$-Ag and the P-Ag bond distances are in the range expected for silver complexes with NHC or phosphane ligands (see Ref. [7] and references cited therein). The Ag···Ag separation is very short in both structures, being 2.7468(3) and 2.7459(4) Å in **1a** and **1b** respectively. These interatomic distances are shorter with respect to those observed in Ref. [7]; moreover they are shorter than the sum of the covalent radii for silver compounds [2.90 Å] and even shorter than that observed in the pure metal [2.88 Å], suggesting a closed shell d^{10}-d^{10} interaction [12]. A difference between the two structures is the higher degree of planarity in the core of **1a** with respect to that in **1b**. In fact, the five membered system consisting of Ag,Ag,P,N,C atoms presents an envelope conformation with the nitrogen atom deviating from the planarity by 0.109 Å in **1a** and 0.163 Å in **1b**.

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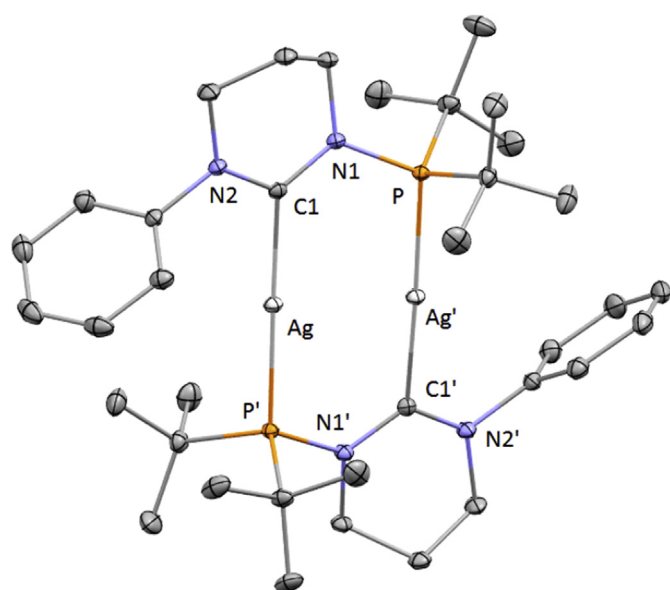
Fig. 2. ORTEP view of the cationic complex in **1b**, with the atomic numbering scheme. Ellipsoids are drawn at their 30% probability level. Hydrogen atoms, OTf⁻ anions and acetonitrile solvent molecules are omitted for clarity. Symmetry transformation used to generate equivalent atoms, ' = −x+1, y, −z+3/2'.

Table 1
Selected bond distances (Å) and angles (°) for compounds **1a** and **1b**.

	1a	**1b**
Ag···Ag'	2.7468(3)	2.7459(4)
Ag-C$_{carbene}$	2.136(2)	2.134(2)
Ag-P	2.3960(6)	2.3857(6)
C$_{carbene}$-N1	1.344(3)	1.364(3)
C$_{carbene}$-N2	1.329(3)	1.321(3)
P-Ag-C$_{carbene}$'	175.50(6)	178.10(7)
N1-C$_{carbene}$-N2	118.98(19)	118.6(2)

2.2. Synthesis of gold(I) complexes with NHCP ligands based on the tetrahydropyrimid-2-ylidene unit

The silver(I) complexes **1a,b** were used as transmetalating agents for the transfer of the NHCP ligand towards gold(I) centers, in acetonitrile as solvent and with a Ag:Au 1:2 molar ratio. While the reaction starting from the silver complex **1a** yielded complex **2a** as unique product (Scheme 2), transmetalation with **1b** afforded a mixture of two products: the neutral digold complex **2b** and the dicationic digold complex **3b**, analogue to the starting silver complex (Scheme 2). The last reaction could be however driven towards the formation of **2b** as sole product by adding 4 equivalents KCl and using dichloromethane as solvent. Successful transmetalation was indeed confirmed by the ³¹P NMR spectra, which present a singlet at δ ca. 140 ppm, slightly downfield shifted with respect to the doublet observed for the silver complexes at δ ca. 137 ppm. Furthermore, the ¹H NMR spectra of complexes **2a,b** are very similar, as regards the number and the pattern of the signals, to those of the silver complexes **1a,b**, although all signals are downfield shifted. The main difference on going from the dicationic dinuclear species (**1a,b** or **3b**) to the neutral ones **2a,b** regards the signal of the *t*-butyl protons: in complexes **1a,b** (or **3b**) it resonates at ca. 1.2 ppm, while in complexes of type **2** at ca. 1.6 ppm. This could be ascribable to the different charge of the complex and to the different trans effect of chlorides compared to NHCs.

The structure of the obtained complexes has been further confirmed by the X-ray diffraction analysis; the molecular structure of complex **2a** is reported in Fig. 3 and it will be discussed in the subsequent Section.
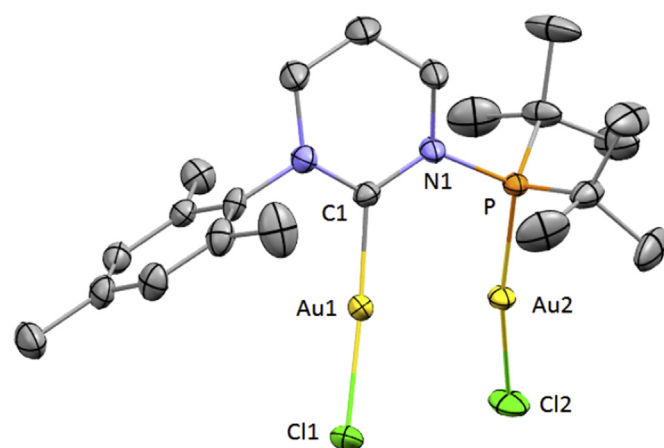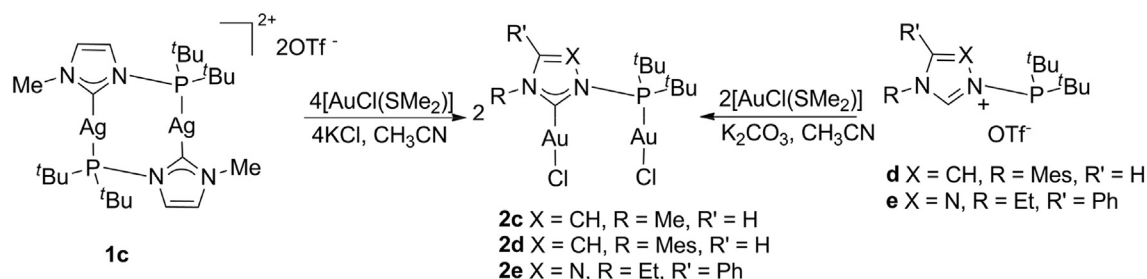

Fig. 3. ORTEP view of complex **2a**, with the atomic numbering scheme. Ellipsoids are drawn at their 30% probability level. Hydrogen atoms and acetonitrile solvent molecule are omitted for clarity.
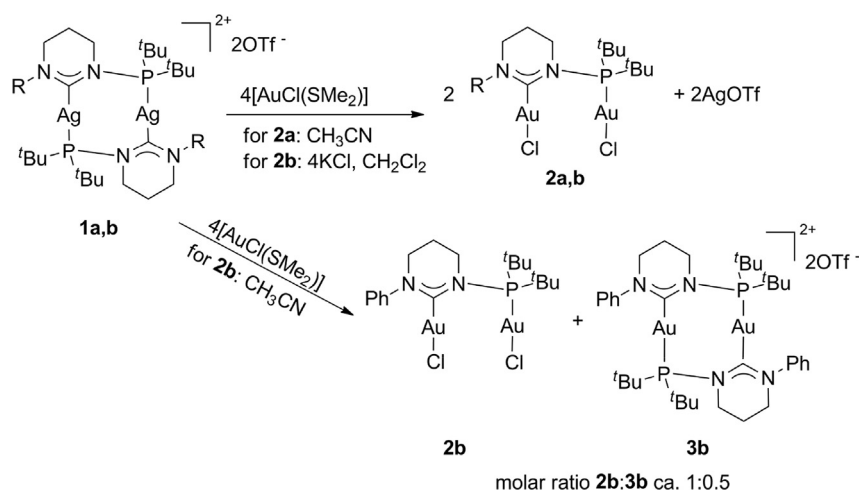
Scheme 2. Synthesis of the gold(I) complexes **2a,b**.

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2.3. Different approaches for the synthesis of neutral gold(I) complexes with NHCP ligands

The preparation of neutral gold(I) complexes similar to those reported in the previous section was also attempted with five-membered ring NHCPs, deriving from azolium salts **c-e**. With these type of carbenes, transmetalation of the NHCP ligand from the corresponding silver complex to gold(I) generally affords dinuclear bis(NHCP) complexes of structure $[Au_2(NHCP)_2](OTf)_2$. However, in the case of saturated NHCPs derived from imidazo-lin-2-ylidenes we previously observed the formation of product mixtures containing complexes with both stoichiometries [7b]. Consequently, we argued that the reaction selectivity could be shifted towards the desired stoichiometry by adding KCl to the reaction mixture, as in the case of complex **2b**. Indeed, this strategy proved useful; for example, in the case of precursor **c** the reaction of the dinuclear silver complex **1c** with [AuCl(SMe$_2$)] cleanly afforded the neutral dinuclear gold(I) complex **2c** (Scheme 3).
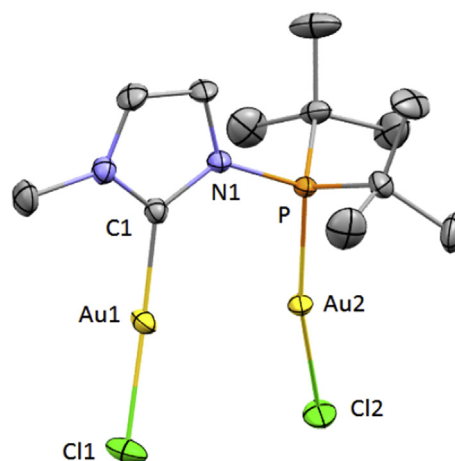

Fig. 4. ORTEP view of compound **2c**, with the atomic numbering scheme. Ellipsoids are drawn at their 30% probability level. Hydrogen atoms are omitted for clarity.

Scheme 3. Synthesis of the gold(I) complexes **2c-2e**.

Furthermore, we considered whether gold(I) complexes with stoichiometry $[Au_2Cl_2(NHCP)]$ could be also obtained directly from carbene precursors such as **d** and **e**, without the intermediacy of silver complexes. In doing this, we took advantage of the capability of simple potassium carbonate in acetonitrile or acetone to deprotonate carbene precursors [13]. Use of this synthetic strategy proved useful also in the case of NHCP ligand precursors and allowed to prepare in good yields complexes **2d** and **2e** (Scheme 3).

The products were fully characterized by elemental analysis, ^{1}H, ^{13}C, ^{31}P NMR and ESI mass spectra. The NMR spectroscopic data are consistent with the proposed structure; in particular, in the ^{1}H NMR spectra, the main feature that allows to distinguish between the dinuclear neutral complexes from the dicationic bis(NHCP) ones [7a] is the chemical shift of the *t*-butyl protons, which appear downfield shifted by ca. 0.3 ppm. This trend, as already observed and discussed for the tetrahydropyrimidin-2-ylidene NHCP derivatives, can be associated to the charge of the complexes and the different trans effect of chlorides compared to NHC ligands.

The molecular structure of compounds **2a** (Fig. 3) and **2c** (Fig. 4) are comparable and are discussed together in this Section. The most important bond distances and angles are collected in Table 2. Both complexes consist of a dinuclear species in which two gold atoms are bridged by a NHCP ligand through the carbene carbon and the phosphorous atoms. The coordination around each gold atom is completed by a chlorine atom in a nearly linear coordination mode. This type of molecular structure core is new. The $C_{carbene}$-Au and P-Au bond distances in both structures are comparable with other reported values [8b] and also the Cl-Au bond distances are in agreement with the values found in the Cambridge Crystallographic

Data Bank. The $C_{carbene}$-Au-Cl bond angle is nearly linear in both structures (174.4(2) and 176.76(15)° in **2a** and **2c** respectively), while the P-Au-Cl bond distance is more deviated from linearity (167.55(8) and 166.71(6)°). The Au···Au separation is 2.9282(4) and 3.0198(4) Å in **2a** and **2c** respectively, evidencing a closed shell d^{10}-d^{10} interaction [14]. Considering the Cl_2Au_2CNP molecular core of the compounds, this is almost planar in the case of **2c** while it is very twisted in the case of **2a**. The torsion angle for the connections of atoms Au-C···P-Au is 19.28° in **2a** while in **2c** is of 7.18°. Moreover an evident difference between the two structures is observed in the crystal packing of the compounds. In fact, both complexes tend to pack in a head to tail conformation, facing the chlorine atoms to the backside of the NHCP ligand; in doing this, they form pillars developing along a crystallographic axis, but in the case of **2c** the packing is tight while

Table 2
Selected bond distances (Å) and angles (°) for compounds **2a** and **2c**.

	2a	**2c**
Au1-C1	1.993(7)	1.985(5)
Au1-Cl1	2.286(2)	2.2788(15)
C1-N1	1.381(9)	1.374(6)
N1-P	1.730(6)	1.726(4)
Au2-P	2.2455(17)	2.2391(13)
Au2-Cl2	2.283(2)	2.2924(15)
Au1···Au2	2.9282(4)	3.0198(4)
C1-Au1-Cl1	174.4(2)	176.76(15)
P-Au2-Cl2	167.55(8)	166.71(6)
Au1-C1-N1	125.5(5)	129.3(4)
C1-N1-P	122.0(5)	124.2(3)
N1-P-Au2	114.6(2)	113.69(15)

in the case of **2a** it leaves some space between the pillars so that acetonitrile solvent molecules can cocrystallize. For this reason, while in **2a** the complexes themselves are well separated from one another, in the case of **2c** they lie closer and an interaction at 3.599 Å is observed between two gold atoms of two adjacent molecules.

Success of the described strategies for the synthesis of neutral gold(I) complexes prompted us to investigate on the preparation of copper(I) complexes with the same stoichiometry, by employing similar procedures with simple copper(I) salts such as CuCl or CuI as reagents. However, despite the efforts complexes of the type [Cu_2Cl_2(NHCP)] were invariably obtained in impure form, together with significant amounts of complexes with [Cu_2(NHCP)$_2$](X)$_2$ stoichiometry. The lower stability in solution of copper(I) complexes compared to the related gold(I) species made it also problematic to purify the compounds by e.g. recrystallization. For example, attempted crystallization of the product derived from the reaction with the silver complex **1e** resulted in the isolation of crystals which proved to actually consist in compound **4**, a polynuclear silver(I) complex with bridging triazole ligands of formula [Ag_4(4-ethyl-3-phenyl-4*H*-1,2,4-triazole)$_6$](OTf)$_4$ (Fig. 5) stemming from decomposition of the complex and hydrolysis of the NHCP ligand.

The structure of compound **4** is unusual and has no precedent in the Cambridge Crystallographic Data Bank. It is centrosymmetric. Four silver atoms are bridged by four triazole ligands through two sigma donor nitrogen atoms (namely N1, N2, N7 and N8 respectively on Ag1, Ag2, Ag2, and Ag1′); moreover, considering the quadrangle of silver atoms (Ag1,Ag2,Ag1′,Ag2′), which is planar, other two triazole ligands are connecting three silver atoms through two nitrogen atoms (N4 and N5 are sigma donor to Ag2 and Ag2′, respectively; the N5 atom is also involved in an asymmetric μ^2 bridging mode on Ag1′ and Ag2′). Each silver atom

presents a distorted tetrahedral environment and the coordination sphere of Ag1 and Ag1′ is completed by a long interaction with a triflate anion (metal to oxygen separation of 2.620 Å). The N-Ag bond distances span from 2.212(3) to 2.703(4) Å. The Ag⋯Ag separation is 3.3722(8). Finally, in the crystals of compound **4** water molecules are present, and they are involved in hydrogen bonds between themselves and the oxygen atoms of the triflate anions connecting the compounds, forming a ribbon developing along *b* axis.

3. Conclusions

A family of neutral dinuclear gold(I) complexes having general formula [Au_2Cl_2(NHCP)] (NHCP = *N*-phosphanyl *N*-heterocyclic carbene) has been disclosed. The complexes are accessible through two different synthetic routes upon careful choice of the reaction conditions. Moreover, the steric properties of the NHCP ligand also affect the ease of formation of complexes with the above-mentioned stoichiometry; in particular, ligands featuring a six-membered ring heterocycle with a bulky wingtip substituent at the nitrogen atom favour formation of these compounds. Extension of this synthetic strategy to the production of copper(I) complexes with analogous stoichiometry was attempted but resulted in the formation of product mixtures. The availability of gold(I) complexes with stoichiometry [Au_2Cl_2(NHCP)] paves the way to their application as e.g. dinuclear catalysts, which will be reported in due course.

4. Experimental section

4.1. General remarks

All manipulations of air and moisture sensitive compounds
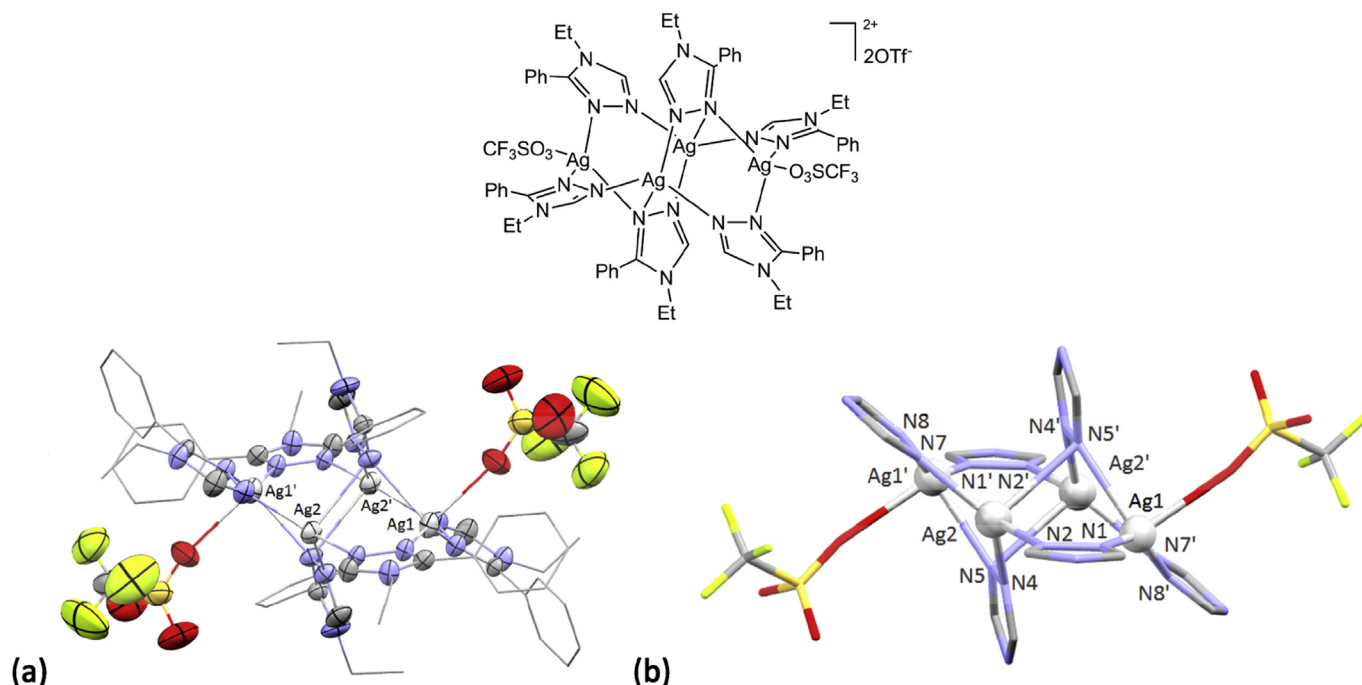
Fig. 5. Line structure and ORTEP view of compound **4**, with the atomic numbering scheme. (a) Water molecules and hydrogen atoms omitted for clarity; ellipsoids drawn at their 30% probability level; substituents on the triazole ring shown in wireframe. (b) Simplified view in capped stick mode with the silver atoms shown as balls; the substituents on the triazole rings are omitted for clarity. Bond distances (Å) and angles (°): Ag1-N1 2.212(3), Ag2-N2 2.225(4), Ag2-N7 2.228(4), Ag1′-N8 2.215(4), Ag1′-N5 2.525(4), Ag2′-N5 2.703(4), Ag2-N4 2.259(4), Ag1⋯Ag2 3.3722(8), N1-N2 1.384(5), N4-N5 1.386(5), N7-N8 1.385(5); N1-Ag1-N8′ 146.47(15), N1-Ag1-N5′ 91.48(13), N8′-Ag1-N5′ 115.05(13), N2-Ag2-N7 130.93(14), N2-Ag2-N4 112.30(14), N7-Ag2-N4 114.40(15). Symmetry transformation used to generate equivalent atoms, ' = −*x*, −*y*, −*z*'.

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were carried out using standard Schlenk techniques under an atmosphere of argon or dinitrogen. The reagents were purchased from Aldrich as high-purity products and generally used as received; all solvents were purified and dried by standard methods. The tetrahydropyrimidinium salts **a** and **b** [11], the azolium salts **c-e** [9a,10,15] and the silver complex **1c** [10] were prepared according to literature procedures. NMR spectra were recorded on a Bruker Avance spectrometers working at 500 MHz (500.13 MHz for ^{1}H, 125.75 MHz for ^{13}C, 202.43 MHz for ^{31}P), 300 MHz (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, 282.2 MHz for ^{19}F and 121.5 MHz for ^{31}P) and 200 MHz (80.89 MHz for ^{31}P); chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals and to external 85% H_3PO_4 (for ^{31}P). FT-IR spectra were recorded using a Bruker Tensor27 spectrophotometer with a resolution of 2 cm^{-1}. ESI-MS analyses were performed using a LCQ-Duo (Thermo-Finnigan) operating in positive ion mode. Instrumental parameters: capillary voltage 10 V, spray voltage 4.5 kV; capillary temperature 200 °C; mass scan range from 150 to 2000 amu; N_2 was used as sheath gas; the He pressure inside the trap was kept constant. The pressure directly read by an ion gauge (in the absence of the N_2 stream) was 1.33×10^{-5} Torr. Sample solutions were prepared by dissolving the compounds in acetonitrile. Sample solutions were directly infused into the ESI source by a syringe pump at 8 µL/min flow rate. Elemental analyses were carried out by the microanalytical laboratory of Chemical Sciences Department (University of Padova) with a Fisons EA 1108 CHNS-O apparatus.

4.2. Synthesis of the silver complex *1a*

Ag$_2$O (1.06 mmol) was added to a stirred solution of compound **a** (2 mmol) in dichloromethane (20 mL). The reaction mixture was kept stirring for 15 h at 18 °C. Excess Ag$_2$O was filtered off and washed with methylene chloride (2 × 5 mL). The filtrate was evaporated to dryness; the residue was dissolved in acetonitrile (10 mL) and filtered through activated charcoal, and the filtrate was concentrated to 2 mL. Addition of pentane caused the formation of crystals of the desired product **1a**, which were filtered and dried under vacuo. Yield 1.08 g (89%); mp 245 °C. Anal. Calcd for C$_{44}$H$_{70}$Ag$_2$F$_6$N$_4$O$_6$P$_2$S$_2$ ($MM = 1206.88$): C, 43.80; H, 5.85; N, 4.64; P, 5.13; S, 5.30%. Found: C, 43.73; H, 5.93; N, 4,58; P, 5.57; S, 5.46%. ^{1}H NMR (500 MHz, CD$_3$CN) δ 1.19 (d, J_{PH} = 16.5 Hz, 18H, CH$_3$ of ^{t}Bu), 1.94 (m, 2H, CH$_2$), 2.21 (s, 6H, CH$_3$), 2.28 (s, 3H, CH$_3$), 3.42 (m, 2H, NCH$_2$), 3.74 (bs, 2H, NCH$_2$), 7.03 (s, 2H, CH Ar). ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN) δ 16.3 (s, CH$_3$), 19.7 (s, CH$_3$), 19.9 (s, CH$_2$), 28.6 (d, J_{CP} = 12.6 Hz, CH$_3$), 37.3 (t, J_{CP} = 3 Hz, C of ^{t}Bu), 44.4 (d, J_{CP} = 4 Hz, CH$_2$), 45.6 (d, J_{CP} = 4 Hz, CH$_2$), 120.8 (q, J_{CF} = 322 Hz, CF$_3$), 130.1 (s, CH Ar), 134.3 (s, C Ar), 139.5 (s, C Ar), 142.1 (s, C Ar), 213.4 (md, J_{CAg} = 14 Hz, NCN) and 215.0 (md, J_{CAg} = 15 Hz, NCN). ^{31}P{^{1}H} NMR (202 MHz, CD$_3$CN) δ 137.6 (two set doublets, J_{PAg} = 535 and 38 Hz).

4.3. Synthesis of the silver complex *1b*

Silver triflate (1.50 g, 5.8 mmol) in THF (10 mL) was added at −70 °C to a stirred solution of carbene (prepared from the salt **b** (1.20 g, 26.4 mmol) and LiHMDS (572 mg, 3.42 mmol) in THF (25 mL) at −90 to −70 °C for 2 h); the reaction mixture was kept under stirring for 1 h until the temperature had risen to −40 °C. Then it was allowed to warm to room temperature (18 °C). The precipitated solid was filtered, washed with THF (2 × 5 mL), dried and recrystallized at −18 °C from a mixture of acetonitrile and THF (1:2). Yield 1.15 g (78%), mp 250 °C (decomp.). Anal Calcd for C$_{38}$H$_{58}$Ag$_2$F$_6$N$_4$O$_6$P$_2$S$_2$ ($MM = 1122.72$): C, 40.66; H, 5.21; N, 4.99; P, 5.52; S, 5.70%. Found: C, 40.84; H, 5.55; N, 4.94, P 5.67; S, 5.69%. ^{1}H NMR (500 MHz, CD$_3$CN) δ 1.19 (d, J_{PH} = 16.0 Hz, 18H, CH$_3$ of ^{t}Bu), 2.20 (m, 2H, CH$_2$), 3.63−3.67 (m, 4H, NCH$_2$), 7.44−7.52 (m, 5H, Ph).

^{13}C{^{1}H} NMR (125.7 MHz, CD$_3$CN) δ 20.1 (CH$_2$), 28.6 (d, J_{CP} = 11 Hz, CH$_3$ of ^{t}Bu), 37.5 (d, J_{CP} = 4 Hz, C of ^{t}Bu), 44.1 (m, CH$_2$), 48.4 (s, CH$_2$), 120.8 (q, J_{CF} = 322 Hz, CF$_3$), 126.5 (s, CH Ph), 129.0 (s, CH Ph), 130.4 (s, CH Ph), 148.5 (s, C Ph), carbene carbon not detected. ^{31}P{^{1}H} NMR (202 MHz, CD$_3$CN) δ 137.5 (two set doublets, J_{PAg} = 536 and 39 Hz) and 137.4 (d, J_{PAg} = 536 Hz).

4.4. Synthesis of the gold complex *2a*

A solution of [AuCl(SMe$_2$)] (81 mg, 0.28 mmol) in acetonitrile (15 mL) was added to a stirred solution of complex **1a** (80 mg, 0.067 mmol) in acetonitrile (5 mL). The reaction mixture was stirred overnight at room temperature. The small quantity of off-white precipitate was filtered and the clear filtrate was concentrated under vacuum; addition of diethyl ether (15 mL) afforded the precipitation of an off-white solid, which was collected by filtration and dried in vacuum. Yield 76%. Anal. Calcd for C$_{21}$H$_{35}$Au$_2$Cl$_2$N$_2$P ($MM = 811.32$): C, 31.09; H, 4.35; N, 3.45%. Found: C, 31.18; H, 3.75; N, 3.04%. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.58 (d, J_{PH} = 17 Hz, 18H, CH$_3$ of ^{t}Bu), 2.15 (m, 2H, CH$_2$), 2.20 (s, 6H, CH$_3$), 2.28 (s, 3H, CH$_3$), 3.53 (m, 2H, NCH$_2$), 3.91 (m, 2H, NCH$_2$), 7.06 (s, 2H, CH Ar). ^{13}C NMR{^{1}H} (75 MHz, CD$_3$CN) δ 16.8 (s, CH$_3$), 20.0 (bs, CH$_3$ + CH$_2$), 29.5 (s, CH$_3$ of ^{t}Bu), 40.8 (d, $^1J_{PC}$ = 18 Hz, C of ^{t}Bu), 46.1 (s, CH$_2$), 47.6 (s, CH$_2$), 129.9 (CH Ar), 134.7 (C Ar), 139.5 (C Ar), 141.5 (C Ar), 191.0 (NCN). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN) δ 140.4 (s). ESI−MS, m/z: 815.8 [Au$_2$LCl(CH$_3$CN)]$^+$. Crystals were obtained by slow diffusion of ether into an acetonitrile solution of the complex.

4.5. Synthesis of the gold complex *2b*

A solution of [AuCl(SMe$_2$)] (76 mg, 0.26 mmol) in dichloromethane (10 mL) was added to a stirred mixture of complex **1b** (70 mg, 0.063 mmol) and KCl (22 mg, 0.29 mmol) in dichloromethane (20 mL). The reaction mixture was stirred overnight at room temperature. The small quantity of off-white precipitate was filtered and the clear filtrate was concentrated under vacuum; addition of hexane (20 mL) afforded the precipitation of an off-white solid, which was collected by filtration and dried in vacuum. Yield 67%. Anal. Calcd for C$_{18}$H$_{29}$Au$_2$Cl$_2$N$_2$P ($MM = 769.24$): C, 28.11; H, 3.80; N, 3.64%. Found: C, 25.81; H, 3.76; N, 2.39%. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.58 (d, $^3J_{PH}$ = 17 Hz, 18H, CH$_3$ of ^{t}Bu), 2.73 (m, 2H, CH$_2$), 3.76 (m, 2H, NCH$_2$), 3.85 (m, 2H, NCH$_2$), 7.19 (m, 5H, CH Ph). ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN) δ 21.4 (CH$_2$), 30.5 (d, $^2J_{PC}$ = 10 Hz, CH$_3$ of ^{t}Bu), 42.0 (d, $^1J_{PC}$ = 14 Hz, C of ^{t}Bu), 47.0 (s, CH$_2$), 51.6 (s, CH$_2$), 128.3 (CH Ar), 130.4 (C Ar), 131.3 (C Ar), 148.8 (C Ar), 203.4 (NCN). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN) δ 140.2 (s). ESI−MS, m/z: 773.89 [Au$_2$LCl(CH$_3$CN)]$^+$.

4.6. Synthesis of the gold complexes *2c*

The dinuclear silver complex **1c** (50 mg, 0.05 mmol) and KCl (17 mg, 0.20 mmol) were placed in a 50 mL two-necked round-bottomed flask equipped with a magnetic stirring bar under inert atmosphere. Acetonitrile (10 mL) was subsequently added, followed by a solution of [AuCl(SMe$_2$)] (64 mg, 0.20 mmol) in the same solvent (5 mL). The reaction mixture was maintained at room temperature whilst stirring for 12 h and then filtered. The filtrate was concentrated to about 1−2 mL under reduced pressure; treatment with diethyl ether (15 mL) afforded an off-white solid, which was filtered off, washed with diethyl ether (3 mL) and dried under reduced pressure. Yield 79%. Anal. Calcd for C$_{12}$H$_{23}$Au$_2$Cl$_2$N$_2$P ($MM = 691.13$): C, 20.85; H, 3.35; N, 4.05. Found: C, 22.14; H, 3.54; N, 4.13%. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.45 (d, $^3J_{PH}$ = 17 Hz, 18H, CH$_3$ of ^{t}Bu), 3.89 (s, 2H, CH$_3$), 7.47 (d, $^3J_{HH}$ = 2 Hz, 1H, CH), 7.52 (d, $^3J_{HH}$ = 2 Hz, 1H, CH). ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN) δ 39.8 (d, $^1J_{PC}$ = 11 Hz, C of ^{t}Bu),

Table 3
Main crystallographic parameters of compounds.

Compound	1a	1b	2a	2c	4
Formula	$C_{42}H_{70}Ag_2N_4P_2$ x $2(CF_3SO_3)$	$C_{36}H_{58}Ag_2N_4P_2$ x $2(CF_3SO_3)$ x $2(CH_3CN)$	$C_{21}H_{35}Au_2Cl_2N_2P$ x $\frac{1}{4}(CH_3CN)$	$C_{12}H_{23}Au_2Cl_2N_2P$	$C_{62}H_{66}Ag_4F_6N_{18}O_6S_2$ x $2(CF_3SO_3)$ x $2(H_2O)$
Molecular Weight	1206.87	1204.81	821.57	691.13	2103.10
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P b c a$	$C 2/c$	$C 2/c$	$P c n b$	$P\text{-}1$
a[Å]	17.3500(4)	22.8217(8)	19.2277(9)	9.7739(9)	11.577(3)
b[Å]	13.4021(3)	9.3222(3)	9.7146(3)	13.3459(12)	13.874(3)
c[Å]	22.7933(5)	25.7686(13)	30.4555(14)	27.875(2)	14.509(3)
α[°]	90	90	90	90	99.582(4)
β[°]	90	113.0610(10)	105.235(5)	90	112.165(4)
γ[°]	90	90	90	90	99.911(4)
V[Å^3]	5300.0(2)	5044.1(4)	5488.8(4)	3636.1(6)	2056.6(8)
T [K]	173	173	293	293	293
Z	4	4	8	8	1
D_{calc}[g cm^{-3}]	1.512	1.586	1.988	2.525	1.698
μ[cm^{-1}]	0.946	0.995	1.0943	1.6492	11.36
F(000)	2480	2464	3094	2528	1052
θ_{max} [°]	26.4	26.4	29.8	30.7	30.7
Reflections collected	38982	26246	20743	54286	25482
Independent reflections	5432	5200	6994	5648	12544
Reflections in refinement	4324	3974	5086	4495	5512
R(int)	0.032	0.045	0.0462	0.048	0.0536
Refined parameters	298	298	268	180	526
$R_1(F)$	0.0285 ($I \geq 3\sigma$)	0.0263 ($I \geq 3\sigma$)	0.0405($I \geq 2\sigma$)	0.0321($I \geq 2\sigma$)	0.0595($I \geq 2\sigma$)
$R_w(F)$	0.0235	0.0231	0.0934	0.0758	0.1778
GOF	1.1073	1.1205	1.029	1.037	0.986
Largest peak/hole [e cm^{-3}]	0.53/−0.37	0.78/−0.50	1.851/−0.934	2.412/−0.923	1.641/−0.862
CCDC dep. num.	1500921	1500922	1503137	1503138	1503139

29.2 (CH$_3$), 43.2 (CH$_3$ of ^{t}Bu), 123.9 (CH), 126.6 (CH), 195.5 (NCN).

4.7. Synthesis of the gold complexes 2d and 2e

Complex **2d**. The azolium salt **d** (60 mg, 0.14 mmol), [AuCl(SMe$_2$)] (80 g, 0.28 mmol), K$_2$CO$_3$ (20 mg, 0.14 mmol) and KCl (40 mg, 0.56 mmol) were placed in a 50 mL two-necked round-bottomed flask equipped with a magnetic stirring bar under inert atmosphere. Acetonitrile (ca. 3 mL) was subsequently added and the reaction mixture was maintained at room temperature whilst stirring for 12 h, then filtered. The filtrate was concentrated to about 1 mL under reduced pressure; treatment with diethyl ether (15 mL) afforded an off-white solid, which was filtered off, washed with diethyl ether (3 mL) and dried under reduced pressure. The product was recrystallized by slow diffusion of ether into an acetonitrile solution of the crude isolated solid. Yield 43%. Anal. Calcd for $C_{20}H_{31}Au_2Cl_2N_2P$ ($MM = 795.30$): C, 30.21; H, 3.93; N, 3.52. Found: C, 29.60; H, 3.58; N, 3.46%. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.53 (d, $^3J_{PH}$ = 17 Hz, 18H, CH$_3$ of ^{t}Bu), 2.02 (s, 6H, CH$_3$), 2.36 (s, 3H, CH$_3$), 7.10 (s, 1H, CH), 7.81 (s, 1H, CH). ^{13}C NMR{^{1}H} (75 MHz, CD$_3$CN) δ 17.9 (s, CH$_3$), 21.2 (s, CH$_3$), 29.3 (d, $^2J_{PC}$ = 7 Hz, CH$_3$ of ^{t}Bu), 40.1 (d, $^1J_{PC}$ = 19 Hz, C of ^{t}Bu), 124.8 (s, CH Im), 126.8 (s, CH Im), 130.0 (C Ar), 130.2 (CH Ar), 135.8 (C Ar), 141.3 (C Ar), 190.0 (NCN). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN) δ 125.4.

Complex **2e**. The triazolium salt **e** (100 mg, 0.20 mmol), [AuCl(SMe$_2$)] (120 g, 0.40 mmol), K$_2$CO$_3$ (30 mg, 0.20 mmol) and KCl (60 mg, 0.80 mmol) were placed in a 50 mL two-necked round-bottomed flask equipped with a magnetic stirring bar under inert atmosphere. Acetonitrile (ca. 3 mL) was subsequently added and the reaction mixture was maintained at room temperature whilst stirring for 12 h, then filtered. The filtrate was concentrated to about 1 mL under reduced pressure; treatment with diethyl ether (15 mL) afforded an off-white solid, which was filtered off, washed with diethyl ether (3 mL) and dried under reduced pressure. Yield 51%. Anal. Calcd for $C_{18}H_{28}Au_2Cl_2N_3P$ ($MM = 782.26$): C, 27.64; H,

3.61; N, 5.37. Found: C, 27.33; H, 3.35; N, 4.64%. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.46 (t, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$), 1.51 (d, $^3J_{PH}$ = 17 Hz, 18H, CH$_3$ of ^{t}Bu), 4.32 (q, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$), 7.66 (m, 5H, Ph). ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN) δ 16.4 (CH$_3$), 29.0 (CH$_3$ of ^{t}Bu), 40.6 (C of ^{t}Bu), 45.8 (CH$_2$), 119.9, 124.2, 125.1 and 130.2 (CH Ph), 130.3 and 132.8 (C Ar), carbene carbon not detected. ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN) δ 130.3.

4.8. X-ray crystal structure determination of compounds 1a,b, 2a, 2c and 4

The crystallographic measurements of compounds **1a,b** were performed at 173 K on a Bruker Smart Apex II diffractometer (MoKα) (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation using the SHELXS97 and SHELXL97 programs [16,17] and CRYSTALS program package [18]. In the refinement the Chebychev weighting scheme [19] was used. All hydrogen atoms were located in the difference Fourier maps and refined with fixed positional and thermal parameters. X-ray diffraction data for complex **2a** were collected at room temperature on a prototype instrumentation Rigaku-Oxford Diffraction Supernova equipped with a X-ray micro-source (spot size at the crystal of about 120 μm) and a Pilatus 200 K Dectris detector using Mo-K$_\alpha$ radiation (λ = 0.71073 Å; working conditions = 50 kV and 0.8 mA) [20]. A full sphere of reciprocal space was sampled by 1° steps in ω collecting 491 frames over 9 runs. The exposure time for each frame was 15 s. The software CrysAlis Pro (Rigaku-Oxford Diffraction) was used for data collection, unit cell determination, data reduction; the absorption correction was applied by the interframe scaling procedure. X-ray diffraction data for complexes **2c** and **4** were collected at room temperature on a Bruker APEX II single-crystal diffractometer, working with Mo-Kα graphite monochromatic radiator (λ = 0.71073 Å) and equipped with an

area detector. The raw frame data (20 s per frame scan time for a sphere of diffraction data) were processed using SAINT software [21]; a correction for absorption was made using SCALE program implemented in the SAINT package [22] to yield the reflection data file. The structures of compounds **2a**, **2c** and **4** were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-2014/7 [23] using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in the ideal geometrical positions. Details for the X-ray data collections are reported in Table 3. Crystallographic data for all the compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC numbers in Table 3). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

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