Reactivity of 1,3-bis(2-pyridyl)benzene, N^CH^N, with gold(III) chlorides: salts, adducts and cyclometalated pincer derivatives. Crystal and molecular structures of [HN^CH^N][$AuCl_4$], [Au(N^C^N)Cl][PF_6] and [Au(N^C^N)Cl(PPh_3)$_2$][PF_6]†

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The reaction of 1,3-bis(2-pyridyl)benzene, N^CH^N, with H[$AuCl_4$] has been studied under different conditions. Mono- ([N^CH^NH][$AuCl_4$]) and di-protonated salts ([HN^CH^NH][$AuCl_4$]$_2$), as well as an adduct, [(N^CH^N)($AuCl_3$)$_2$], have been isolated. Very rare cyclometalated pincer derivatives, [Au(N^C^N)Cl]$^+$ have been obtained as different salts, either by transmetallation from the corresponding mercury(II) derivative, [Hg(N^C^N)Cl], or by direct C–H activation. The structures in the solid state of [N^CH^NH][$AuCl_4$] and [Au(N^C^N)Cl][PF_6] have been solved by X-ray diffraction. Reaction of the pincer derivatives with PPh_3, dppm (bis(diphenylphosphino)methane) and dppe (1,2-bis(diphenylphosphino)ethane) occurs with displacement of the coordinated nitrogen atoms to afford [Au(N^C^N)(Cl)(PPh_3)$_2$]$^+$, [Au(N^C^N)(Cl)(dppm)$_2$]$^+$ and [Au(N^C^N)(Cl)(dppe)]$^+$, respectively. The X-ray structure of [Au(N^C^N)(Cl)(PPh_3)$_2$][PF_6] confirms that the ligand N^C^N is only σ-carbon bonded and the PPh_3 molecules are in a *trans*-arrangement. The pattern of the $^{31}P\{^1H\}$NMR spectrum of [Au(N^C^N)(Cl)(dppm)$_2$]$^+$, a pair of "triplets", deserves comments: the spectrum is not of the A_2X_2 type but a case of a deceptively simple AA'XX' spin system.

Introduction

Organometallic complexes with pincer ligands[1] are attracting much attention in catalysis[2] and material science.[1e,1f,3] In the aromatic pincer ligands containing two *meta*-positioned substituents bearing N, O, P, or S donors, coordination to a metal centre can enhance the reactivity of a C_{aryl}–H bond, favouring metalation. With ligands capable of *trans* coordination, the outcome of the reaction is a metallacycle, mostly with five or six-membered rings, where the metal ion is locked up by a tridentate monoanionic six-electron ligand. Most of the stable pincer complexes are square planar complexes of the d^8 metal ions: the coordination mode with *trans* positioned donors forces the aryl ring of the ligand into a conformation essentially coplanar with the coordination plane of the metal centre. Among the molecules potentially able to act as pincers, a number of N^C^N systems have been considered in the last years: many derivatives of the late transition metals, in particular of the nickel triad, Ni(II), Pd(II) and Pt(II), have been synthesized and their properties thoroughly investigated.[4] In spite of the widespread interest in these d^8 square planar complexes, studies relevant to the isoelectronic Au(III) ion are rare.[5] Noteworthy is the structurally characterized complex [Au{$C_6H_3(CH_2NMe_2\}$Cl]$_2$[Hg_2Cl_6].[5a]

We have previously reported on the reactivity of Pd(II) and Pt(II) with 1,3-bis(2-pyridyl)benzene, N^CH^N, and analogous ligands with substituted pyridines: the new pincer species have also been investigated for their catalytic activity in the Heck reaction and other C–C bond formations.[4f,6] Following these previous reports, here we describe the reactivity of 1,3-bis(2-pyridyl)benzene, N^CH^N, with gold(III), an ion for which we are not aware of any similar chemistry. Indeed in the course of the present study we have observed that the reaction of gold(III) chlorides with this molecule is complex and different species can form: salts, adducts and metalated pincer derivatives. As is the case for other late transition metals, the synthesis of the latter species is not straightforward. Nevertheless, under precise conditions, metalation by direct activation of a C–H bond of the ligand was achieved, albeit in moderate yields. As often reported, somewhat better yields were obtained by transmetalation of the corresponding mercury(II) derivative, [Hg(N^C^N)Cl].[4f] All the new species have been characterized analytically and by NMR spectroscopy. The X-ray structures of the pincer species [Au(N^C^N)Cl)][PF_6], of the outcome of its reaction with PPh_3, [Au(N^C^N)Cl)(PPh_3)$_2$][PF_6], as well as of the monoprotonated ligand, [HN^CH^N][$AuCl_4$], are also reported.

Results and discussion

The ligand, 1,3-bis(2-pyridyl)benzene, throughout this paper indicated as N^CH^N, was best prepared by co-cyclotrimerization of

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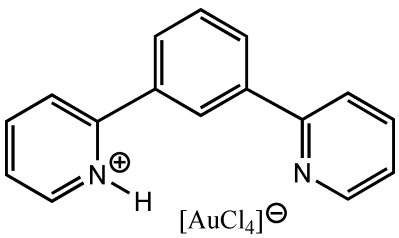
1,3-dicyanobenzene with acetylene, in the presence of Bönnemann catalyst, according to literature procedure.[7] After purification, it was extensively characterized by ^{1}H NMR spectra, registered in several solvents (see Experimental section).

The main goal of the present study was to synthesize pincer gold(III) derivatives [Au(N^C^N)X]$^+$[A]$^-$ (X = coordinating anion, [A]$^-$ = not coordinating anion) and to compare them with the corresponding, but neutral, palladium(II) and platinum(II) species, previously reported and found to be, at least in the case of palladium, catalysts of high activity in the Heck reaction.[4f,6]

To achieve direct C–H activation in this type of molecules by d^8 late transition metal ions is not an easy task; in addition, in gold(III) chemistry with nitrogen heterocycles, the pattern of the reaction is usually complex and strongly dependent on the exact experimental conditions. Several species are often formed, sometimes poorly soluble, and their separation and identification can be a tiresome matter.

In the present case we observed first that direct reaction of H[AuCl$_4$]·3H$_2$O with [N^CH^N], in mild conditions (diethyl ether, room temperature) affords, in almost quantitative yield, a salt of the diprotonated ligand, [HN^CH^NH][AuCl$_4$]$_2$, **1**. Compound **1** is a pale yellow solid that was characterized by CHN analysis and ^{1}H NMR spectroscopy. The NMR spectra show one set of resonances with a significant difference respect to the free ligand as for the H6′, H6″ protons of the pyridine rings that are *ca.* 0.5 ppm shifted downfield (acetone-d$_6$). The shift is comparable to that observed for 2-phenylpyridine, δ 8.68, *vs.* δ 9.15 upon protonation.[8]

The outcome of the same reaction, carried out in acetonitrile at reflux for five days is the monoprotonated salt, [HN^CH^N][AuCl$_4$], **2**, that was characterized, *inter alia*, by X-ray diffraction analysis.



2

The ^{1}H NMR spectrum shows also in this case one set of resonances indicating exchange of the hydrogen between the nitrogen atoms on the NMR time scale. The spectrum is similar but clearly distinct from that of the diprotonated species **1**: in particular the H6′, H6″ resonance is less deshielded than in **1**, *ca.* 0.3 ppm, with respect to the ligand.

Crystals of X-ray quality were obtained by slow evaporation of an acetone solution at room temperature. The structure of **2** consists of the packing of [HN^CH^N] cations and [AuCl$_4$]$^-$ anions in the molar ratio 1 : 1 in the monoclinic space group *Pc*. An ORTEP[9] view of the cation is shown in Fig. 1.

All bond lengths and angles in monomeric cations and anions are as usual. Instead, different cations are linked by very strong hydrogen bonds between nitrogen atoms of neighbouring moieties: so, if we mark as [a] the molecule generated by symmetry operation $x, -1 + y, \frac{1}{2} - z$, we find the following hydrogen bond parameters: N(2)–H(1) 0.970 Å, H(1)···N(1)^a 1.709 Å, N(2)–H(1)···N(1)^a 170.0°, N(2)···N(1)^a 2.670(4) Å, H(1)···N(1)^a–C(7)^a 128.6°, H(1)···N(1)^a–C(11)^a 111.1°. Obviously, each cation is hydrogen bonded to a neighbouring one, so that cations of **2** in the crystal can be seen as forming an infinite monodimensional chain. In the anion the shortest intermolecular Au–Au distance is 5.483(1) Å.

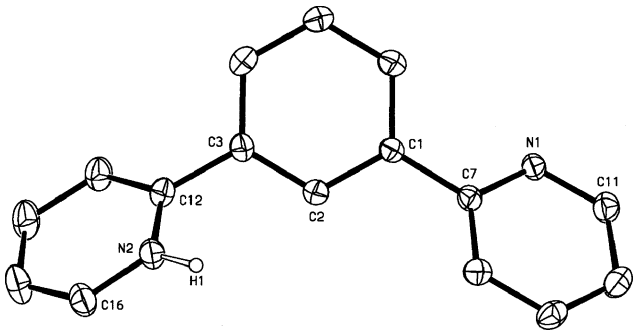
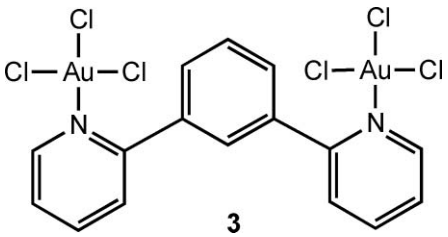


Fig. 1 ORTEP view of the cation in compound **2**. Ellipsoids are drawn at the 30% probability level.

In addition to the [AuCl$_4$]$^-$ salts of the mono and diprotonated ligand, **2** and **1**, also an adduct, [(N^CH^N)(AuCl$_3$)$_2$], **3**, can be isolated as a yellow solid. Compound **3** is frequently observed in solution when more species are simultaneously present. Compound **3** is best obtained on treating the diprotonated salt [HN^CH^NH][AuCl$_4$]$_2$, **1**, with the stoichiometric amount of NaHCO$_3$ in THF. The ^{1}H NMR spectrum, registered in acetone-d$_6$, gives evidence for a symmetric species. Complex **3** is soluble but unstable in DMSO.



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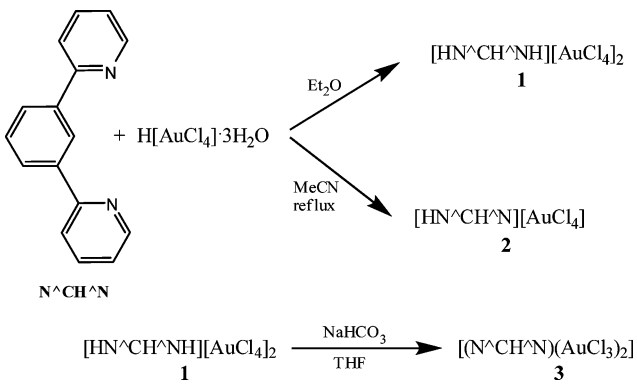
On the whole, the ^{1}H NMR spectra of compounds **1–3** give clear-cut evidence for all the protons of the aryl ring, ruling out metalation (see Scheme 1).



Scheme 1 Synthesis of compounds **1–3**.

As previously mentioned direct C–H activation is not easy and is usually accomplished under definite experimental conditions whose settlement often requires tiresome experiences. Many

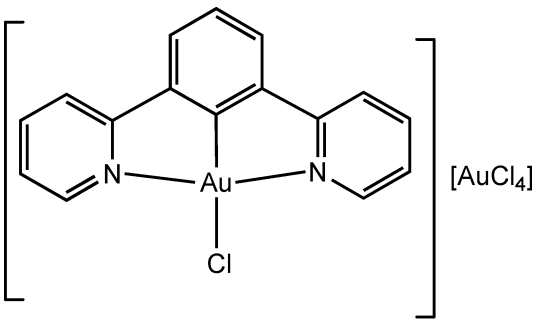
alternative strategies have been reported: among them transmetalation of the corresponding mercury(II) derivative is traditional in the synthesis of late-transition metal pincers.

The synthesis of the mercury derivative of 1,3-bis(2-pyridyl)benzene, [Hg(N^C^N)Cl], has been previously described.[4f] Reaction with $H[AuCl_4]$ in ethanol, in the presence of $NaHCO_3$, gives the gold pincer in excellent yield as a mercury salt, likely $[Hg_2Cl_6]^{2-}$, eqn (1):

$$H[AuCl_4]\cdot 3H_2O + [Hg(N^C^N)Cl] \xrightarrow[-NaCl]{NaHCO_3} 1/2[Au(N^C^N)Cl]_2[Hg_2Cl_6]\ (\mathbf{4a}) \quad (1)$$

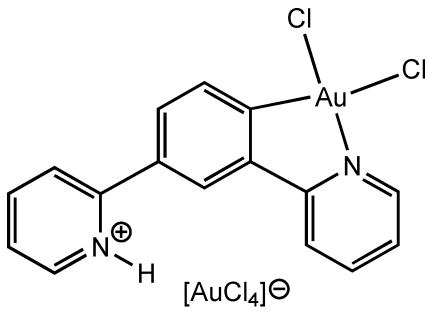
Attempts to achieve direct C–H activation by reaction of N^CH^N with $H[AuCl_4]$ (1 : 1) were carried out in acetic acid at reflux (*ca.* 120 °C) in the presence of a base. The reaction was partially successful: the pincer derivative, a yellow solid, was obtained as the $[AuCl_4]^-$ salt, [(Au(N^C^N)Cl][$AuCl_4$], **4b**, eqn (2); yields are moderate even using the correct ratio 1 : 2. Compound **4b** is soluble in DMSO, poorly soluble in most organic solvents.

$$H[AuCl_4]\cdot 3H_2O + N^CH^N \xrightarrow[reflux]{CH_3COOH,\ NaHCO_3} [Au(N^C^N)Cl][AuCl_4]\ (\mathbf{4b}) \quad (2)$$



4b

Complex **4b** was collected from the reaction medium after seven days at reflux: monitoring the reaction over this time by ^{1}H NMR, species such as $[HN^CH^NH][AuCl_4]_2$, **1**, and $[(N^CH^N)(AuCl_3)_2]$, **3**, were identified as by-products. Furthermore under this thermally promoted activation, C(2) metalation is not completely selective: in addition to complex **4b**, we isolated a minor product which on the basis of the analytical (CHN) values and ^{1}H NMR spectra we tentatively describe as compound **5**.



5

The NMR spectrum provides evidence for a non-symmetric species. In particular two resonances at δ 9.26 and δ 9.76 can be assigned to H6″ (protonated ring) and H6′ (coordinated ring) protons respectively. C(4) metalation has also been reported in platinum chemistry of analogous systems.[4c]

In the attempt to get simple and soluble salts of the pincer gold(III) complex the reaction between $H[AuCl_4]$ and the ligand was carried out in the presence of excess hexafluorophosphate or tetrafluoborate salts. Compound **4b** was still obtained: direct exchange of the anion, eqn (3), failed:

$$[Au(N^C^N)Cl][AuCl_4] + K[PF_6] \not\rightarrow [Au(N^C^N)Cl][PF_6]\ (\mathbf{4d}) + K[AuCl_4] \quad (3)$$

Nevertheless anion metathesis was achieved by a two step procedure: reaction of **4b** with $[NBu_4]Cl$ in dichloromethane gives [(Au(N^C^N)Cl][Cl], **4c**, and $[NBu_4][AuCl_4]$ (eqn (4)) which were isolated and characterized. Addition of an excess of $K[PF_6]$ to an acetone solution of **4c** allows the isolation of the soluble $[Au(N^C^N)Cl][PF_6]$, **4d** (eqn (5)).

$$[Au(N^C^N]Cl][AuCl_4]\ (\mathbf{4b}) + [NBu_4]Cl \rightarrow [Au(N^C^N)Cl][Cl]\ (\mathbf{4c}) + [NBu_4][AuCl_4] \quad (4)$$

$$[Au(N^C^N)Cl][Cl]\ (\mathbf{4c}) + K[PF_6] \rightarrow [Au(N^C^N)Cl][PF_6]\ (\mathbf{4d}) + KCl \quad (5)$$

Exchange of $[PF_6]^-$ for $[Hg_2Cl_6]^{2-}$ can also be accomplished in compound **4a**: yield is almost quantitative. On the whole the transmetalation path gives the best yields and reduces the reaction time.

All the complexes **4a–d** were characterized by elemental analysis (CHN) and ^{1}H NMR spectra (see Table 1). Most diagnostic is the lack of the H2 proton of the aryl ring. The other resonances were assigned by comparison with the spectrum of the ligand and by selective H–H decoupling. As shown in Table 1, at least in DMSO the chemical shifts are not affected by the counter ion.

Table 1 ^{1}H NMR data of N^CH^N and [(Au(N^C^N)Cl][X] in DMSO-d_6

	H2	H5	H4, H6	H3′, H3″	H4′, H4″	H5′, H5″	H6′, H6″
N^CH^N	8.82	7.61	8.07	8.14	7.91	7.39	8.71
4a, X = $\frac{1}{2}[Hg_2Cl_6]$		7.70	7.99	8.47	8.52	7.86	9.13
4b, X = [$AuCl_4$]		7.72	8.01	8.49	8.52	7.87	9.16
4c, X = Cl		7.72	8.03	8.50	8.53	7.87	9.17
4d, X = [PF_6]		7.72	8.01	8.48	8.52	7.86	9.17

Table 2 Selected Distances (Å) and Angles (deg) in the cation of **4d** with Estimated Standard Deviations (Esd's) on the last figure in parentheses

Au–Cl	2.360(1)	Au–N(1)	2.019(5)
Au–N(2)	2.032(5)	Au–C(2)	1.950(5)
Cl–Au–N(1)	99.2(1)	Cl–Au–N(2)	99.6(1)
Cl–Au–C(2)	179.7(2)	N(1)–Au–N(2)	161.2(2)
N(1)–Au–C(2)	80.5(2)	N(2)–Au–C(2)	80.7(2)
Au–N(1)–C(7)	115.1(4)	Au–N(1)–C(11)	124.7(4)
Au–N(2)–C(12)	114.8(4)	Au–N(2)–C(16)	124.6(4)
C(2)–C(1)–C(7)	114.8(5)	C(2)–C(3)–C(12)	114.3(5)

A single crystal of **4d** suitable for X-ray diffraction was grown by slow evaporation of an acetone solution at room temperature. The structure of **4d** consists of the packing of $[Au(N^C^N)Cl]^+$ cations and $[PF_6]^-$ anions in the molar ratio 1 : 1 with no unusual van der Waals contacts. An ORTEP[9] view of the cation is shown in Fig. 2. Selected bond parameters of the cation are reported in Table 2.

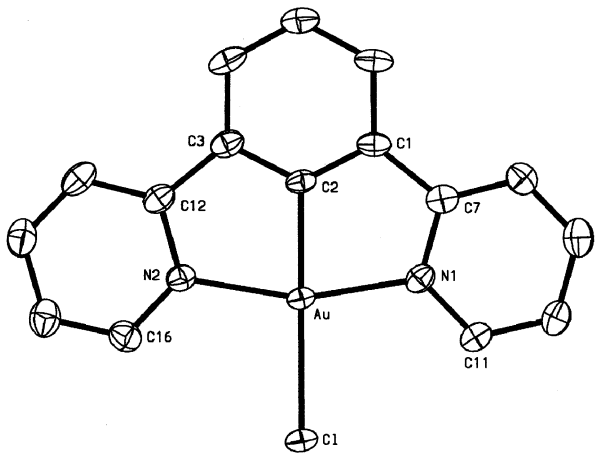


Fig. 2 ORTEP view of the cation in compound **4d**. Ellipsoids as in Fig. 1.

The Au atom displays a square-planar coordination with a very slight square-pyramidal distortion, maximum distances from the best plane being +0.004(1) and –0.001(5) Å for atoms Au and N(1), respectively. Bond lengths involving gold in the cation of **4d** can be compared with the corresponding Au–ligand distances found in the cation $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$,[5a] which is the only structurally characterized Au(III) N^C^N pincer compound. However in $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$, the N atoms are hybridized sp^3 and bear two methyl groups each. As a result, the Au–Cl and Au–C bond lengths are almost identical with those of the present cation (Au–Cl 2.360(1) and Au–C 1.950(5) Å here, 2.369(6) Å and 1.96(2) Å in $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$), whereas the two Au–N bond lengths in the two compounds are very different; thus, Au–N(1) 2.11(2) and Au–N(2) 2.12(1) Å in $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$ (note the high esd's), Au–N(1) 2.019(5) and Au–N(2) 2.032(5) Å here. The lengthening of the Au–N distances in $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$, can be attributed partly to the different hybridization of the nitrogen atoms, and partly to the steric hindrance of the bulky methyl groups.

We may compare also the present Au–ligand bond lengths with the Pd–ligand distances found in the neutral, strictly analogous pincer compound [Pd(N^C^N)Cl].[4f] In this complex Pd–Cl 2.427(1) Å, Pd–N(1) 2.065(1) Å, Pd–N(2) 2.063(1) Å, and Pd–C(2) 1.910(2) Å. A comparison with the Au–ligand distances reported in Table 2 shows that in three cases [Cl, N(1) and N(2)] the distances involving gold are shorter, whereas in one case [C(2)] the opposite occurs, so that no definite conclusion can be drawn on the relative length of the covalent radius of Au(III) with respect to that of Pd(II). The Pd–ligand bond lengths in [Pd(N^C^N)Cl] are very similar to those found in the analogous platinum pincer compound [Pt(N^C^N)Cl].[4c] The present Au–Cl distance is elongated by the *trans* influence of the C(2) carbon atom and is statistically identical with that found in $[AuCl_2(pop\text{-}C^1,N)]$[10] where Au–Cl (*trans*-C) = 2.369(5) Å. It is also very similar to that found in compound **6** (see later), Au–Cl(1) = 2.375(1) Å. In $[Au(PPh_3)Cl_3]$[11] the Au–Cl bond *trans* to phosphine is 2.347(2) Å long, the two Au–Cl bonds not *trans*-influenced show a length of 2.283 Å (mean value). The present Au–C(2) bond [1.950(5) Å] is shortened by the fact that it is the central bond of a bicyclic moiety formed by a tridentate ligand. In similar arrangements marked shortenings of the central bond are normal,[12] for instance Au–C = 1.96(2) Å in $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+$.[5a] Typical Au(III)–C bonds when the carbon atom is not confined in a cycle are much longer, as for instance Au–C(2) 2.052(2) Å in compound **6** (see later), Au–C(1) 2.06(1) Å in $[AuCl(pap\text{-}C^1,N)(PPh_3)][BF_4]$[10] and 2.033(5) Å in $[Au(C_6H_4N{=}NPh\text{-}2)Cl_2(PPh_3)]$.[13]

Reactivity of [Au(N^C^N)Cl][PF$_6$], 4d

Aspects of the reactivity of gold(III) cyclometalated derivatives with nitrogen donors have been reported for bidendate C^N[5a,10,14] and tridentate ligands with C^N^N[14b,14l,15] and C^N^C[16] sequence of atoms: reports mostly concern reactions not involving complete removal of the cyclometaled ligands but rather displacement of the nitrogen atoms or of halides by neutral ligands, typically PR_3. As previously mentioned, as yet gold(III) N^C^N pincer species are very few and their reactivity almost completely unexplored.

We first observed that attempts to obtain solvento species from the $[(Au(N^C^N)Cl]^+$ cations, *e.g.* **4d**, by displacement of the chloride were unsuccessful, despite it being *trans* to a carbon atom: with poorly coordinating solvents we were unable to isolate a definite species also in the presence of a silver salt. Even with acetonitrile, a coordinating solvent traditionally employed to trap unsaturated species, substitution of the chloride was not achieved: compound **4d** was recovered after treatment with Ag[PF_6] in acetonitrile at reflux.

Different behaviours were observed in reactions of (C^N)-cycloaurated gold(III) halide complexes with tertiary phosphines, a reaction often taken as indicative of the reactivity of these gold species: both replacement of the halide or cleavage of Au–N bonds can occur whereas the Au–C bond is usually unaffected. The hard nature of the nitrogen donors favours the gold(III) species towards reduction to gold(I), whereas easy substitution of the phosphine for the coordinated nitrogen(s) indicates relatively weak Au–N bonds.[17] In our case the reaction of complex **4d** with PPh_3 occurs with cleavage of the Au–N bonds to give the bis adduct $[Au(N^C^N)(PPh_3)_2Cl][PF_6]$, **6**, regardless of the stoichiometric ratio used, eqn (6):

Table 3 Selected distances (Å) and angles (°) in the cation of **6** with estimated standard deviations (esd's) on the last figure in parentheses

Au–Cl(1)	2.375(1)	Au–P(1)	2.363(1)
Au–P(2)	2.384(1)	Au–C(2)	2.052(2)
Cl(1)–Au–P(1)	90.5(1)	Cl(1)–Au–P(2)	90.4(1)
Cl(1)–Au–C(2)	176.3(1)	P(1)–Au–P(2)	176.3(1)
P(1)–Au–C(2)	87.8(1)	P(2)–Au–C(2)	91.5(1)

$$[Au(N\hat{}C\hat{}N)Cl][PF_6]\ (\mathbf{4d}) + 2PPh_3 \xrightarrow{\text{acetone}} [Au(N\hat{}C\hat{}N)(PPh_3)_2Cl][PF_6]\ (\mathbf{6}) \quad (6)$$

Formation of a mono adduct was never observed while monitoring the reaction at room temperature (^{31}P NMR). According to the ^{1}H NMR spectrum, compound **6** maintains its original arrangement with the chlorine opposite to the carbon atom. One resonance is observed for the H6′, H6″ protons of the pyridine rings, significantly shifted to higher field (δ 7.89) compared to δ 9.17 in **4d**. In the ^{31}P spectrum the only one resonance, δ 32.57, further supports the *trans* arrangement of the phosphines.

Crystals of compound **6** of X-ray quality were obtained by slow evaporation of a dichloromethane solution at room temperature. The X-ray structure confirms the cleavage of the Au–N bonds: the N^C^N ligand is now bonded only through the aromatic carbon atom.

The structure of **6**·CH_2Cl_2 consists of the packing of $[Au(N\hat{}C\hat{}N)(PPh_3)_2Cl]^+$ cations, $[PF_6]^-$ anions and CH_2Cl_2 molecules in the molar ratio 1 : 1 : 1 with no unusual van der Waals contacts.

An ORTEP[9] view of the cation is shown in Fig. 3. Selected bond lengths and angles of the cation are reported in Table 3.

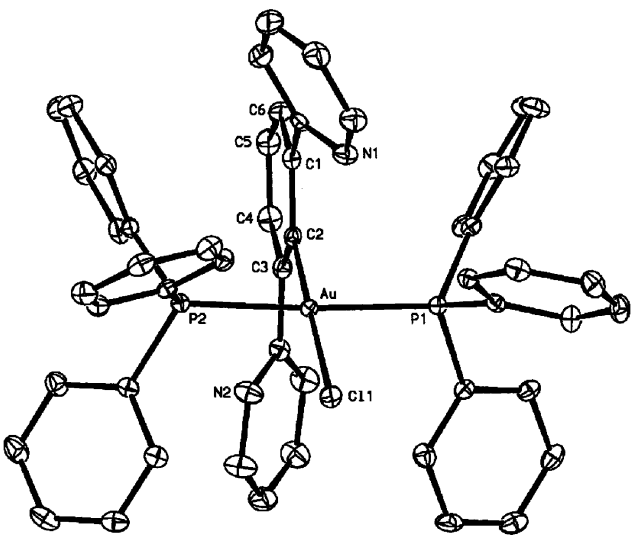


Fig. 3 ORTEP view of the cation in compound **6**·CH_2Cl_2. Ellipsoids as in Fig. 1.

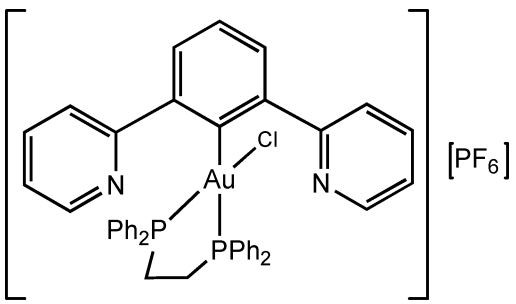
The Au atom displays a square-planar coordination with a tetrahedral distortion, maximum distances from the best plane being +0.072(2) and –0.071(1) Å for atoms C(2) and P(1), respectively. The C(1)–C(6) phenyl ring is strictly planar and forms a dihedral angle with the metal best plane of 85.9(1)°. The distance of Au from the C(1)–C(6) best plane is only of 0.027(1) Å. The non-bonding distances between Au and N(1) and Au and N(2) are 2.929(2) and 2.876(2) Å, respectively. The Au–P distances, Au–P(1) 2.363(1) and Au–P(2) 2.384(1) Å, are elongated by the mutual *trans* influence of the phosphorus atoms. Similar distances can be found in [AuCl(pap-C^1)(PEt_3)$_2$]Cl,[10] where the *trans* ligands are triethylphosphines: Au–P(1) 2.365(3), Au–P(2) 2.361(3) Å. When the phosphine is not *trans* to a *trans* influencing atom, typical Au(III)–P distances are shorter, see for instance Au–P 2.329(2) Å in $[Au(PPh_3)Cl_3]$[11] and Au–P 2.314(6) Å in $[Au(PPh_3)Br_2Cl]$.[18] The present Au–Cl(1) bond length, 2.375(1) Å, is very similar to the one found in compound **4d** (see above) (both are elongated by the *trans* C atom), and the Au–C(2) distance, 2.052(2) Å, has already been discussed above in comparison to that found in **4d**, 1.950(5) Å.

Reaction of **4d** with $[Ph_2PCH_2]_2$, dppe, gives complex **7**, eqn (7):

$$[Au(N\hat{}C\hat{}N)Cl][PF_6]\ (\mathbf{4d}) + \text{dppe} \xrightarrow{\text{acetone}} [Au(N\hat{}C\hat{}N)(\text{dppe})Cl][PF_6]\ (\mathbf{7}) \quad (7)$$

In the ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2) two resonances, δ 46.47 (d, $^3J_{PP}$ = 11.8 Hz) and δ 55.86 (d, $^3J_{PP}$ = 11.8 Hz), are consistent with a chelating behaviour of the phosphine ligand. In the ^{1}H NMR spectrum the methylenic protons are observed as two sets of multiplets (δ 2.62–2.84, m + m overlapping; δ 3.04–3.26, m + m overlapping) each integrating for two protons. In the aromatic region, four systems at δ 6.83 (d, $^3J_{HH}$ = 7.5 Hz, 2H) δ 6.88 (d, $^3J_{HH}$ = 7.5 Hz, 2H), δ 8.07 (d, $^3J_{HH}$ = 7.5 Hz, 2H) and δ 8.12 (d, $^3J_{HH}$ = 7.5 Hz, 2H) can be assigned to the *ortho* protons of the phenyl rings of dppe. ^{1}H–^{1}H NOESY experiments indicate contacts between the resonances at δ 8.07, δ 8.12 and multiplets at δ 2.62–2.84 and between those at δ 6.83, δ 6.88 and multiplets at δ 3.04–3.26.

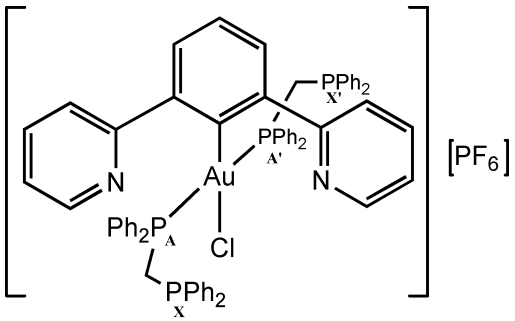
Though in the absence of a X-ray structure of compound **7**, the experimental evidence supports displacement of the nitrogen atoms from the coordination sphere of the metal. It is noteworthy that the chelating behaviour displayed by the bidentate dppe entails isomerization from a *trans* to a *cis* C–Au–Cl arrangement.



7

The reaction between **4d** and $[Ph_2PCH_2PPh_2]$, dppm, was initially monitored by NMR spectroscopy that provides evidence for a symmetric species: an adduct was isolated as a white solid, soluble in most organic solvents (dichloromethane, acetone, acetonitrile) but thermally rather unstable: gentle heating causes decomposition and free ligand, N^CH^N, is released. The behaviour of dppm is reminiscent of that of PPh_3: elemental

analyses (CHN), support a bis adduct, [Au(N^C^N)(Cl)(dppm)$_2$]-[PF$_6$], **8**.



8

The $^{31}P\{^1H\}$ NMR spectrum of the complex consists of two equally intense sets of resonances, both "triplets", at δ 28.15 and δ –25.83 (Fig. 4) corresponding to coordinated and non-coordinated phosphorus atoms, respectively, in line with two η^1-dppm coordinated in a *trans* disposition. The pair of "triplets" may be interpreted as a "deceptively simple" example of an AA'XX' spin system[15d,19] corresponding to the static structure of complex **8** shown above, and are due to (i) the *trans* ^2J(P–P) (usually >300 Hz in d^8 square planar systems[20]) >> $^6J(P_X–P_{X'})$, (ii) the inner lines of the AB subspectra are very close so that they cannot be resolved, and (iii) the outer lines lie below the limit of detection. In our case $^2J(P_A–P_{A'})$ should be very large (*ca.* 400–500 Hz)[20] whereas $^6J(P_X–P_{X'})$ should be approximately zero.

The *trans* arrangement of the two η^1-dppm implies that the two pairs of chemically equivalent phosphorus centres are magnetically not equivalent. In this case several of the twelve lines of the AA'XX' system collapse or have low intensity.[21] Simulation of this AA'XX' system is possible but does not give a unique solution.[22] In our case, the distance of the outer lines in the "triplet" is $N = |J_{AX} + J_{AX'}| = 50.3$ Hz, unfortunately not all the other coupling constants can be obtained from the spectrum as not enough lines are available.

Conclusion

In conclusion we have obtained very rare cyclometalated pincer derivatives, [Au(N^C^N)Cl]$^+$, of 1,3-bis(2-pyridyl)benzene, N^CH^N, as different salts, either by transmetallation from the corresponding mercury(II) derivative, [Hg(N^C^N)Cl], or by direct C–H activation with H[AuCl$_4$] as the metal source. The structure in the solid state of [Au(N^C^N)Cl][PF$_6$] has been solved by X-ray diffraction. Reactions of this pincer compound with phosphines in acetone at room temperature produced compounds in which the pincer ligand N^C^N behaves as a C monodentate ligand and the square-planar coordination of gold(III) is completed by the phosphines and a chloride ligand. The X-ray structure of the complex with two PPh$_3$ confirms the cleavage of the Au–N bonds and the N^C^N ligand bonded only through the aromatic carbon atom. Attempts to remove the halide were unexpectedly unsuccessful even in the presence of silver salts.

The syntheses and reactivity studies of other pincer N^C^N gold(III) complexes are in progress. Application of the various species to some catalytic reactions is under investigation.

Experimental section

General

The ligand N^CH^N[7] and the corresponding mercury(II) derivative, [Hg(N^C^N)Cl],[4f] were prepared as previously described. H[AuCl$_4$]·3H$_2$O was obtained from Johnson Matthey. All the solvents were purified before use according to standard procedures. All the reactions were performed in air.

Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B by Mr Antonello Canu (Dipartimento di Chimica, Università degli Studi di Sassari, Italy). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature (20 °C) with a Varian VXR 300 spectrometer operating at 300.0 and 121.4 MHz respectively. Chemical shifts are given in ppm relatively to internal TMS (^1H) and external H_3PO_4 (^{31}P). 2D-COSY and NOESY spectra were performed by means of standard pulse sequences.

Syntheses

The ligand 1,3-bis(2-pyridyl)benzene (N^CH^N). The ligand 1,3-bis(2-pyridyl)benzene (N^CH^N) was prepared from 1,3-dicyanobenzene and acetylene, in the presence of a cobalt catalyst according to a literature procedure (see ref. 7).

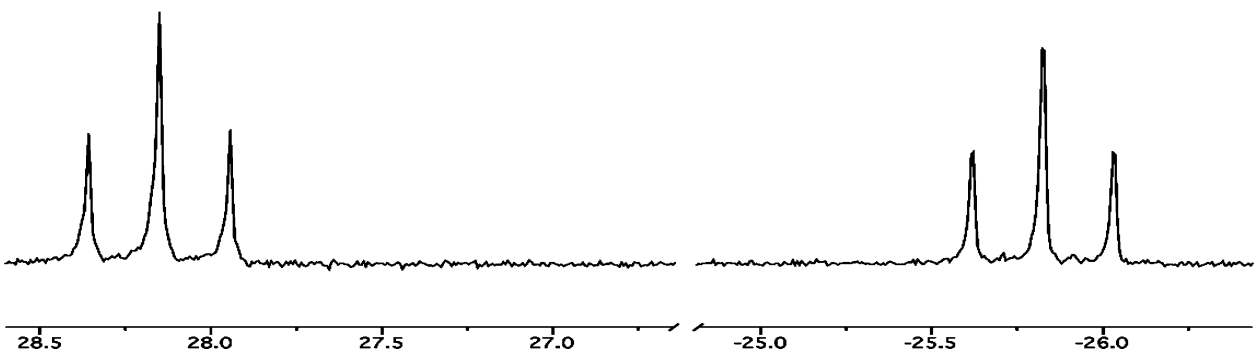
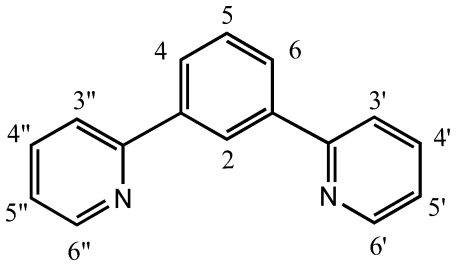


Fig. 4 Region of $^{31}P\{^1H\}$NMR spectrum (121.4 MHz) of complex **8** in deuterated acetone showing the 'deceptively simple' triplets of the AA'XX' spin system with $N = |J_{AX} + J_{AX'}| = 50.3$ Hz.



^{1}H NMR (300 MHz, CD_2Cl_2, 296 K): δ 7.30 (ddd, 2H, J_{HH} = 7.4 Hz, 4.8 Hz, 1.1 Hz, *H5′*, *H5″*); 7.62 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.81 (ddd, 2H, J_{HH} = 8.0 Hz, 7.4 Hz, 1.9 Hz, *H4′*, *H4″*); 7.90 (ddd, 2H, J_{HH} = 8.0 Hz, 1.1 Hz, 0.9 Hz *H3′*, *H3″*); 8.12 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, *H4*, *H6*); 8.75 (ddd, 2H, J_{HH} = 4.8 Hz, 1.9 Hz, 0.9 Hz, *H6′*, *H6″*); 8.78 (t, 1H, $^4J_{HH}$ = 1.7 Hz, *H2*).

^{1}H NMR (300 MHz, $CDCl_3$, 296 K): δ 7.25 (ddd, 2H, J_{HH} = 7.4 Hz, 4.8 Hz, 1.1 Hz, *H5′*, *H5″*); 7.60 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.77 (ddd, 2H, J_{HH} = 8.0 Hz, 7.4 Hz, 1.8 Hz, *H4′*, *H4″*); 7.85 (ddd, 2H, J_{HH} = 8.0 Hz, 1.1 Hz, 0.9 Hz, *H3′*, *H3″*); 8.07 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.9 Hz, *H4*, *H6*); 8.63 (t, 1H, $^4J_{HH}$ = 1.9 Hz, *H2*); 8.72 (ddd, 2H, J_{HH} = 4.8 Hz, 1.8 Hz, 0.9 Hz, *H6′*, *H6″*).

^{1}H NMR (300 MHz, acetone-d_6, 296 K): δ 7.35 (ddd, 2H, J_{HH} = 7.5 Hz, 4.8 Hz, 1.1 Hz, *H5′*, *H5″*); 7.60 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.90 (ddd, 2H, J_{HH} = 8.0 Hz, 7.5 Hz, 1.7 Hz, *H4′*, *H4″*); 8.04 (ddd, 2H, J_{HH} = 8.0 Hz, 1.1 Hz, 0.9 Hz, *H3′*, *H3″*); 8.19 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.9 Hz, *H4*, *H6*); 8.71 (ddd, 2H, J_{HH} = 4.8 Hz, 1.7 Hz, 1.1 Hz, *H6′*, *H6″*); 8.91 (t, 1H, $^4J_{HH}$ = 1.9 Hz, *H2*).

^{1}H NMR (300 MHz, DMSO-d_6, 296 K): δ 7.39 (ddd, 2H, J_{HH} = 7.4 Hz, 4.8 Hz, 1.1 Hz, *H5′*, *H5″*); 7.61 (td, 1H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, *H5*); 7.91 (ddd, 2H, J_{HH} = 7.8 Hz, J_{HH} = 7.4 Hz, J_{HH} = 1.7 Hz, *H4′*, *H4″*); 8.07 (dm, 2H, $^3J_{HH}$ = 7.7 Hz, *H4*, *H6*); 8.14 (ddd, 2H, J_{HH} = 7.8 Hz, 1.1 Hz, 0.9 Hz, *H3′*, *H3″*); 8.71 (ddd, 2H, J_{HH} = 4.8 Hz, 1.7 Hz, 0.9 Hz, *H6′*, *H6″*); 8.82 (t, 1H, $^4J_{HH}$ = 1.8 Hz, *H2*).

^{1}H NMR (300 MHz, CD_3CN, 296 K): δ 7.34 (ddd, 2H, J_{HH} = 7.4 Hz, 4.7 Hz, 1.1 Hz, *H5′*, *H5″*); 7.62 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *H5*); 7.87 (ddd, 2H, J_{HH} = 8.1 Hz, 7.4 Hz, 1.9 Hz, *H4′*, *H4″*); 7.97 (ddd, 2H, $^3J_{HH}$ = 8.1 Hz, 1.1 Hz, 0.9 Hz, *H3′*, *H3″*); 8.12 (dd, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, *H4*, *H6*); 8.71 (dm, 2H, $^3J_{HH}$ = 4.7 Hz, *H6′*, *H6″*); 8.91 (t, 1H, $^4J_{HH}$ = 1.8 Hz, *H2*).

Synthesis of [NH^CH^NH][$AuCl_4$]$_2$ (1). A solution of 232.3 mg (1.00 mmol) of N^CH^N in 30 cm^3 of diethyl ether was added under vigorous stirring to a solution of $HAuCl_4 \cdot 3H_2O$ (787.7 mg, 2.00 mmol) in the same solvent (50 cm^3) and let to react for 30 min. The precipitate which formed was filtered off, washed with diethyl ether and dried under vacuum to give compound **1** as a pale yellow solid. Yield 884.5 mg, 97%; mp 201–204 °C; (Found: C 20.91; H 1.26; N 2.94%. Calc. for $C_{16}H_{14}Au_2Cl_8N_2$: C 21.07; H 1.55; N 3.07%).

^{1}H NMR (300.0 MHz, DMSO-d_6, 296 K): δ 7.71 (tm, 2H, $^3J_{HH}$ = 6.1 Hz, *H5′*, *H5″*); 7.79 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 8.23 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H4*, *H6*); 8.31 (m, 4H, *H4′*, *H4″*, *H3′*, *H3″*); 8.73 (s, 1H, *H2*); 8.84 (dd, 2H, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 0.9 Hz *H6′*, *H6″*).

^{1}H-NMR (300.0 MHz, acetone-d_6, 296 K): 8.11 (td, 1H, $^3J_{HH}$ = 8.0 Hz, $^5J_{HH}$ = 0.6 Hz, *H5*); 8.32 (ddd, 2H, J_{HH} = 7.7 Hz, 5.9 Hz; 1.2 Hz, *H5′*, *H5″*); 8.47 (dd, 2H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz, *H4*, *H6*); 8.74 (dt, 2H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, *H3′*, *H3″*); 8.91 (td, 1H, $^4J_{HH}$ = 1.7 Hz, *H2*); 8.95 (td, 2H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, *H4′*, *H4″*); 9.24 (ddd, 2H, $^3J_{HH}$ = 5.9 Hz, 1.7 Hz, 0.7 Hz *H6′*, *H6″*).

Synthesis of [N^CH^NH][$AuCl_4$] (2). A solution of N^CH^N (232.1 mg, 1.00 mmol) in 30 cm^3 of acetonitrile was added under vigorous stirring to 393.8 mg (1.00 mmol) of $H[AuCl_4] \cdot 3H_2O$ and heated for 5 days at reflux. The solution was evaporated under vacuum to give a yellow solid. After treatment with 5 cm^3 of diethyl ether the solid was filtered off, washed with diethyl ether and dried under vacuum to give compound **2**. Yield 429.0 mg, 75%; mp 177–179 °C; (Found: C 33.48; H 2.45; N 4.85%. Calc. for $C_{16}H_{13}AuCl_4N_2$: C 33.59; H 2.29; N 4.90%).

^{1}H NMR (300.0 MHz, DMSO-d_6, 296 K): δ 7.66 (m, 2H, *H5′*, *H5″*); 7.76 (t, 1H, $^3J_{HH}$ = 8.1 Hz, *H5*); 8.21(dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, *H4*, *H6*); 8.27 (m, 4H, *H4′*, *H4″*, *H3′*, *H3″*); 8.74 (s, 1H, *H2*); 8.81 (dm, 2H, $^3J_{HH}$ = 5.1 Hz, *H6′*, *H6″*).

^{1}H NMR (300.0 MHz, acetone-d_6, 296 K): δ 7.90 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.95 (t, 2H, $^3J_{HH}$ = 6.0 Hz, *H5′*, *H5″*); 8.35 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, *H4*, *H6*); 8.49 (d, 2H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz *H3′*, *H3″*); 8.55 (td, 2H, $^3J_{HH}$ = 7.2 Hz, *H4′*, *H4″*); 8.86 (s, 1H, *H2*); 9.02 (d, 2H, $^3J_{HH}$ = 5.1 Hz, *H6′*, *H6″*).

Synthesis of [($AuCl_3$)$_2$(N^CH^N)] (3). 168.0 mg (2.00 mmol) of $NaHCO_3$ were added under vigorous stirring to a suspension of 911.8 mg (1.00 mmol) of compound **1** in 30 cm^3 of THF and left 24 h to react at room temperature. The corresponding solution was evaporated and the crude solid was recrystallized from acetone/diethyl ether to give a yellow solid that was filtered off and dried under vacuum: compound **3**. Yield 486.6 mg, 58%; mp 208–210 °C; (Found: C 23.16; H 1.18; N 3.02%. Calc. for $C_{16}H_{12}Au_2Cl_6N_2$: C 22.91; H 1.44; N 3.34%).

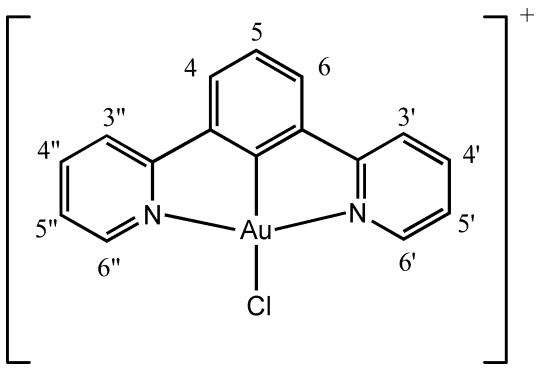
^{1}H NMR (300.0 MHz, DMSO-d_6, 296 K): δ 7.50 (tm, 2H, $^3J_{HH}$ = 6.1 Hz, *H5′*, *H5″*); 7.68 (t, 1H, $^3J_{HH}$ = 7.9 Hz, *H5*); 8.04 (tm, 2H, $^3J_{HH}$ = 7.7 Hz, *H4′*, *H4″*); 8.16 (dm, 2H, $^3J_{HH}$ = 7.8 Hz, *H3′*, *H3″*); 8.17 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, *H4*, *H6*); 8.75 (dm, 2H, $^3J_{HH}$ = 4.8 Hz, *H6′*, *H6″*); 8.78 (t, 1H, $^4J_{HH}$ = 1.8 Hz, *H2*).

^{1}H NMR (300.0 MHz, acetone-d_6, 296 K): δ 7.78 (m, 2H, *H5′*, *H5″*); 7.81 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 8.29 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, *H4*, *H6*); 8.35 (d, broad, 4H, J_{HH} = 3.9 Hz, *H4*, *H4″*, H3′, H3″); 8.83 (t, 1H, $^3J_{HH}$ = 1.8 Hz, *H2*); 8.93 (dm, 2H, $^3J_{HH}$ = 5.1 Hz, *H6′*, *H6″*).

Synthesis of [Au(N^C^N)Cl]$_2$[Hg_2Cl_6] (4a). A mixture of [Hg(N^C^N)Cl] (467.3 mg, 1.00 mmol), $H[AuCl_4] \cdot 3H_2O$ (393.8 mg, 1.00 mmol) and $NaHCO_3$ (84.01 mg, 1.00 mmol) in absolute ethanol (100 cm^3) was let under stirring for 5 h. The formation of abundant white precipitate could be observed. Afterwards, the precipitate was filtered off, washed with diethyl ether and dried in vacuum to give **4a**.

Yield 703.6 mg, 91%; mp >250 °C; (Found: C, 24.62; H, 1.39; N, 3.41%. Calc. for $C_{16}H_{11}AuCl_4HgN_2$: C, 24.94; H, 1.44; N, 3.64%).

^{1}H-NMR (300.0 MHz, DMSO-d_6, 296 K): δ 7.70 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *H5*); 7.86 (t, broad, 2H, $^3J_{HH}$ = 6.3 Hz, *H5′*, *H5″*); 7.99 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *H4*, *H6*); 8.47 (d, broad, $^3J_{HH}$ = 7.4 Hz 4H, *H3′*, *H3″*); 8.52 (dd, 2H, $^3J_{HH}$ = 7.9 Hz, 7.4 Hz, *H4′*, *H4″*); 9.13 (d, 2H, $^3J_{HH}$ = 5.6 Hz, *H6′*, *H6″*).



Synthesis of [Au(N^C^N)Cl][AuCl$_4$] (4b).

Method a. To a solution of H[AuCl$_4$]·3H$_2$O (808.2 mg, 2.05 mmol) in 30 cm^3 of freshly distilled acetic acid were added 238.3 mg (1.03 mmol) of N^CH^N and an excess of NaHCO$_3$ (428.3 mg, 5.10 mmol) under stirring. Immediately a yellow precipitate was formed which dissolved as soon as the reflux started. The precipitate obtained after 7 days of reaction was filtered off, washed with acetone, diethyl ether and dried under vacuum to give **4b**, as a yellow solid. Yield 350,2 mg, 41%; mp > 250 °C (Found: C 24.35; H 1.49; N 3.52%. Calc. for C$_{16}$H$_{11}$Au$_2$Cl$_5$N$_2$: C 23.95; H 1.38; N 3.49%).

Method b. To a suspension of **2**, [NH^CH^NH][AuCl$_4$]$_2$ (911.8 mg, 1.00 mmol) in 30 cm^3 of freshly distilled acetic acid was added NaHCO$_3$ (206.3 mg, 3.1 mmol). The suspension was kept one week under stirring at 120 °C. The hot suspension was quickly filtered, and the solid washed with acetone and dried under vacuum to give **4b** as a yellow solid. Yield 453.5 mg, 57%; mp > 250 °C (Found: C 24.23; H 1.48; N 3.58%; Calc. for C$_{16}$H$_{11}$Au$_2$Cl$_5$N$_2$: C 23.95; H 1.38; N 3.49%).

^{1}H NMR (300.0 MHz, DMSO-d$_6$, 296 K): δ 7.72 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.87 (td, 2H, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.1 Hz, *H5′*, *H5″*); 8.01 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H4*, *H6*); 8.49 (d, broad, 2H, $^3J_{HH}$ = 7.8 Hz, *H3′*, *H3″*); 8.52 (dd, 2H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, *H4′*, *H4″*); 9.16 (d, 2H, $^3J_{HH}$ = 5.8 Hz, *H6′*, *H6″*).

Synthesis of [Au(N^C^N)Cl]Cl (4c). Tetra(n-butyl)ammonium chloride (833.7 mg, 3.00 mmol) was added under stirring to a suspension of **4b**, (802.5 mg, 1.00 mmol) in 50 cm^3 of dichloromethane. The suspension was left two hours under stirring at room temperature. The colour of the solution turns yellow and the solid white. The solid was collected and dried to give **4c**, white. Yield 486.2 mg, 97%; mp >250 °C.

^{1}H NMR (300.0 MHz, DMSO-d$_6$, 296 K): δ 7.72 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.87 (ddd, 2H, J_{HH} = 8.7 Hz, 6.2 Hz, 2.7 Hz, *H5′*, *H5″*); 8.03 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H4*, *H6*); 8.50 (d, 2H, $^3J_{HH}$ = 6.9 Hz, *H3′*, *H3″*); 8.53 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, *H4′*, *H4″*); 9.17 (d, 2H, $^3J_{HH}$ = 6.2 Hz, *H6′*, *H6″*).

Synthesis of [Au(N^C^N)Cl][PF$_6$] (4d). K[PF$_6$] (220.8 mg, 1.2 mmol) was added to a suspension of **4c** (499 mg, 1.00 mmol) in 100 cm^3 of acetone. The suspension was left under stirring at room temperature overnight. After filtration the solution was evaporated to dryness and 15 cm^3 of water were added to the residue. The white solid was filtered off, washed with diethyl ether and dried in vacuum to give **4d**. Yield 264.8 mg, 44%; mp >250 °C (Found: C 31.79; H 1.37; N 4.61%, Calc. for C$_{16}$H$_{11}$AuClF$_6$N$_2$P: C 31.57; H 1.82; N 4.60%).

^{1}H NMR (300.0 MHz, DMSO-d$_6$, 296 K): δ 7.72 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.86 (t, 2H, $^3J_{HH}$ = 6.3 Hz, *H5′*, *H5″*); 8.01 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H4*, *H6*); 8.48 (m, 2H, *H3′*, *H3″*); 8.52 (m, 2H, *H4′*, *H4″*); 9.17 (d, 2H, $^3J_{HH}$ = 5.5 Hz, *H6′*, *H6″*). ^{31}P NMR (121.4 MHz, DMSO-d$_6$, 296 K): δ -143.13 (sept, *P*F$_6^-$).

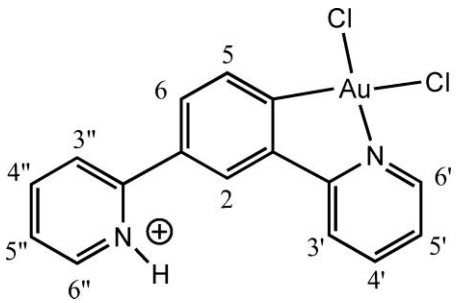
^{1}H NMR (300.0 MHz, acetone-d$_6$, 296 K): δ 7.81 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *H5*); 7.99 (ddd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 6.0 Hz, *H5′*, *H5″*); 8.06 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H4*, *H6*); 8.51(dd, 2H, $^3J_{HH}$ = 7.5 Hz, *H3′*, *H3″*); 8.62 (td, 2H, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5 Hz, *H4′*, *H4″*); 9.34 (d, 2H, J_{HH} = 6.0 Hz, *H6′*, *H6″*). ^{31}P NMR (121.4 MHz, acetone-d$_6$, 296 K): δ -143.43 (sept, *P*F$_6^-$).

^{1}H NMR (300.0 MHz, CD$_3$CN, 296 K): δ 7.63–7.77 (m, 5H, *H5*, *H5′*, *H5″*, *H4*, *H6*); 8.15 (dd, 2H, $^3J_{HH}$ = 8.1 Hz, J_{HH} = 0.9 Hz, *H3′*, *H3″*); 8.38 (td, 2H, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.6 Hz, *H4′*, *H4″*); 9.18 (dd, 2H, $^3J_{HH}$ = 5.9 Hz, J_{HH} = 1.0 Hz *H6′*, *H6″*). ^{31}P NMR (121.4 MHz, CD$_3$CN, 296 K): δ -143.33 (sept, *P*F$_6^-$).

Synthesis of [Au(NH^C4^N)Cl$_2$][AuCl$_4$] (5). Compound **5** was isolated from the mother liquor of the synthesis of **4b** (method b). The solution was evaporated to dryness and 15 cm^3 of acetone were added to residue. After filtration, the yellow solution was evaporated to small volume and diethyl ether was added. The precipitate obtained was filtered off, washed with diethyl ether and dried in vacuum to give **5** as a yellow solid.

Yield 35.4 mg; mp 230–231 °C (dec.) (Found: C 22.91; H 1.44; N 3.34%. Calc. for C$_{16}$H$_{12}$Au$_2$Cl$_6$N$_2$: C 22.95; H 1.31; N 2.89%).

^{1}H NMR (300.0 MHz, acetone-d$_6$, 296 K): δ 7.94 (m, 1H, *H5′*); 8.11 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.4 Hz, *H6*); 8.26 (d, 1H, $^3J_{HH}$ = 8.4 Hz, *H5*); 8.34 (ddd, 1H, J_{HH} = 7.4 Hz, 1.2 Hz, *H5″*); 8.57 (m, 2H, *H3′*+*H4′*); 8.75 (d, 1H, $^4J_{HH}$ = 2.4 Hz, *H2*); 8.79 (dm, 1H, $^3J_{HH}$ = 8.1 Hz, *H3″*); 8.98 (td, 1H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.8 Hz, *H4″*); 9.26 (dm, 1H, $^3J_{HH}$ = 5.7 Hz, *H6″*); 9.76 (dd, 1H, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.1 Hz, *H6′*).



Synthesis of [Au(N^C^N)(PPh$_3$)$_2$Cl][PF$_6$] (6). An excess of PPh$_3$ (65.6 mg, 0.25 mmol) was added to a suspension of **4d** (60.9 mg, 0.10 mmol) in 20 cm^3 of acetone and let under stirring for 15 min. Afterwards, the solvent was evaporated and diethyl ether (15 cm^3) was added. The solid was filtered off, washed with diethyl ether and dried to give **6** as a white solid. Yield 110.3 mg, 97%; mp 180 °C (dec.) (Found: C 55.13; H 3.47; N 2.51%, Calc. for C$_{52}$H$_{41}$AuClF$_6$N$_2$P$_3$: C 55.11; H 3.65; N 2.47%).

^{1}H NMR (300.0 MHz, CD$_2$Cl$_2$, 296 K): δ 6.88 (dm, 2H, $^3J_{HH}$ = 7.8 Hz, *H3′*, *H3″*); 6.96–7.48 (m, 24H + 5H, H$_o$, H$_m$ PPh$_3$, *H4*, *H5*, *H6*, *H5′*, *H5″*); 7.53 (t, broad, 6H, *H$_p$* P*Ph$_3$*); 7.68 (td, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, *H4′*, *H4″*); 7.89 (dm, 2H, $^3J_{HH}$ = 4.5 Hz, *H6′*, *H6″*). ^{31}P NMR (121.4 MHz, CD$_2$Cl$_2$, 296 K): δ -143.31 (sept, *P*F$_6^-$); 32.57 (s, 2P, *P*Ph$_3$). Crystals of X-ray quality

were obtained by slow evaporation of a dichloromethane solution at room temperature.

Synthesis of [Au(N^C^N)(dppe)Cl][PF$_6$] (7). An excess of [Ph$_2$PCH$_2$]$_2$, (dppe), (99.6 mg, 0.25 mmol) was added to a suspension of **4d**, (60.9 mg, 0.10 mmol) in 20 cm^3 of acetone and let under stirring for 15 min. Afterwards the solvent was evaporated and diethyl ether (15 cm^3) was added. The solid was collected, washed with diethyl ether and dried to give **7** as a white solid. Yield 74,1 mg, 74%; mp 183 °C (Found: C 50.07; H 3.45; N 2.53%, Calc. for $C_{42}H_{35}AuClF_6N_2P_3$: C 50.09; H 3.50; N 2.78%).

^{1}H NMR (300.0 MHz, CD_2Cl_2, 296 K): δ 2.62–2.84 (m + dm, overlapping, 1H + 1H, P$_1$–C*H*$_1$*H*$_{1'}$-CH$_2$H$_{2'}$–P$_2$); 3.04–3.26 (m + m, overlapping 1H + 1H, P$_1$–CH$_1$H$_{1'}$–C *H*$_2$H$_{2'}$-P$_2$); 6.83 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *ortho-H*dppe$_{(P1)}$); 6.88 (d, 2H, $^3J_{HH}$ = 7.5 Hz *ortho-H*dppe$_{(P1)}$); 7.07 and 7.09 (t, 2H, ^3J = 7.8 Hz, *meta–H*dppe$_{(P1)}$ + t, 2H, ^3J = 7.8 Hz, *meta–H*dppe$_{(P1)}$, overlapping); 7.21 (tm, 2H, $^3J_{HH}$ = 7.2 Hz, *H5′*, *H5″*); 7.35 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *H5*); 7.44 (tm, broad, 2H, $^3J_{HH}$ = 7.5, *para–H*dppe$_{(P1)}$); 7.56 (d + d, overlapping, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.2 Hz, *H4*, *H6*); 7.66–7.84 (m, 10H, *H4′*, *H4″*, *H6*, *H6′*, *para–H*dppe$_{(P2)}$, *meta-H*dppe$_{(P2)}$); 7.92 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *H6*, *H6′*); 8.07 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *ortho-H*dppe$_{(P2)}$); 8.12 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *ortho-H*dppe$_{(P2)}$). ^{31}P NMR (121.4 MHz, CD_2Cl_2, 296 K): δ -143.31 (sept, 1P, *P*F$_6^-$); 46.47 (d, 1P, $^2J_{PP}$ = 11.8 Hz, *P$_1$* dppe-*cis* C); 55.86 (d, 1P, $^2J_{PP}$ = 11.8 Hz, *P$_2$* dppe-*cis* Cl).

^{1}H NMR (300.0 MHz, CD_3CN, 296 K, δ 2.67–2.80 (m + m, overlapping, 1H + 1H, P$_1$–C*H*$_1$*H*$_{1'}$-CH$_2$H$_{2'}$–P$_2$); 3.08–3.26 (m + m, overlapping 1H + 1H, P$_1$-CH$_1$H$_{1'}$–C *H*$_2$H$_{2'}$-P$_2$); 6.82 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *ortho-H*dppe$_{(P1)}$); 6.86 (d, 2H, $^3J_{HH}$ = 7.5 Hz *ortho-H*dppe$_{(P1)}$); 7.06 and 7.07 (t, 2H, ^3J = 7.8 Hz, *meta–H*dppe$_{(P1)}$ + t, 2H, ^3J = 7.8 Hz, *meta-H*dppe$_{(P1)}$, overlapping); 7.23 (tm, 2H, $^3J_{HH}$ = 7.2 Hz, *H5′*, *H5″*); 7.31 (t, 1H, J_{HH} = 7.5 Hz, *H5*); 7.43 (tm, 2H, *para-H*dppe$_{(P1)}$); 7.53 (d +d, overlapping, 1H + 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.5 Hz, *H4*, *H6*); 7.68–7.82 (m, 8H, *H4′*, *H4″*, *para-H*dppe$_{(P2)}$, *meta-H*dppe$_{(P2)}$); 7.86–7.90 (m, 4H, *H3′*, *H3″*,*H6′*, *H6″*); 8.03 and 8.08 (d + d, 2H + 2H, J_{HH} = 7.5 Hz, *ortho-H*dppe$_{(P2)}$). ^{31}P NMR (121.4 MHz, CD_3CN, 296 K): δ -143.49 (sept, 1P, *P*F$_6^-$); 48.25 (d, 1P, $^2J_{PP}$ = 11.4 Hz, P$_1$dppe-*cis* C); 57.15 (d, 1P, $^2J_{PP}$ = 11.4 Hz, P$_2$dppe-*cis* Cl).

Synthesis of [Au(N^C^N)(η^1-dppm)$_2$Cl][PF$_6$] (8). An excess of [Ph$_2$P]$_2$CH$_2$ (dppm) (96.1 mg, 0.25 mmol) was added to a suspension of **4d** (60.9 mg, 0.10 mmol) in 20 cm^3 of acetone and let under stirring for 15 min. Afterwards the solvent was evaporated and diethyl ether (15 cm^3) was added. The solid was collected, washed with diethyl ether and dried to give **8** as a white solid. Yield 115,7 mg, 84%; mp 130–131 °C (Found: C 57.30; H 3.88; N 2.19%, Calc. for $C_{66}H_{55}AuClF_6N_2P_5$: C 57.55; H 4.02; N 2.03%).

Table 4 Crystallographic data

Compound	**2**	**4d**	**6**·CH$_2$Cl$_2$
Formula	$C_{16}H_{13}AuCl_4N_2$	$C_{16}H_{11}AuClF_6N_2P$	$C_{53}H_{43}AuCl_3F_6N_2P_3$
M	572.05	608.66	1218.19
Colour	Yellow	Yellow	Colourless
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*Pc*	$P2_1/c$	$P2_12_12_1$
a/Å	9.3686(6)	5.8260(5)	14.8738(9)
b/Å	12.3340(8)	13.4747(12)	16.5750(10)
c/Å	7.6777(5)	21.3305(19)	19.6092(12)
α/°	90	90	90
β/°	96.130(1)	93.960(1)	90
γ/°	90	90	90
U/Å^3	882.10(10)	1670.5(3)	4834.3(5)
Z	2	4	4
F(000)	540	1144	2416
D_c/g cm^{-3}	2.154	2.420	1.674
T/K	150	150	115
Crystal dimensions/mm	0.33 × 0.45 × 0.51	0.02 × 0.02 × 0.31	0.41 × 0.43 × 0.50
μ(Mo-Kα)/cm^{-1}	89.43	91.12	33.63
Min. and max. transmiss. factors	0.593–1.000	0.320–1.000	0.668–1.000
Scan mode	ω	ω	ω
Frame width/°	0.30	0.50	0.50
Time per frame/s	10	10	10
No. of frames	5400	1260	1440
Detector–sample distance/cm	6.00	6.00	6.00
θ range/°	3–28	3–27	3–27
Reciprocal space explored	Full sphere	Full sphere	Full sphere
No. of reflections (total, independent)	24432, 4630	17779, 4319	58803, 12496
R_{int}	0.0192	0.0558	0.0346
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.031, 0.045	0.070, 0.077	0.034, 0.043
Conventional R_1 index [$I > 2\sigma(I)$]	0.018	0.040	0.021
Reflections with $I > 2\sigma(I)$	4554	3099	11393
No. of variables	206	260	613
Goodness of fit[b]	1.036	0.960	0.949

[a] $R_2 = [\sum(|F_o^2 - kF_c^2|/\sum F_o^2]$, $R_{2w} = [\sum w(F_o^2 - kF_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $[\sum w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and p = 0.03 for **2** and 0.02 for **4d** and for **6**. CH$_2$Cl$_2$.

^{1}H NMR (300.0 MHz, CD_2Cl_2, 296 K, δ 3.43 (t, 4H, P – CH_2P, $^2J_{PH}$ = 5.0 Hz); 7.00–7.38 (m, 47H) 7.59 (td, 2H, *H4′*, *H4″*); 8.29 (m + m, 2H, *H6′*, *H6″*);

^{31}P NMR (121.4 MHz, CD_2Cl_2, 296 K): δ -143.39 (sept, 1P, PF_6^-); AA'XX' spin system δ_A 28.15; δ_X –26.51, $N = |J_{AX} + J_{AX'}| = 50.3$ Hz.

X-Ray data collections and structure determinations

Suitable crystals were grown by slow evaporation of an acetone solution for [N^CH^NH][$AuCl_4$], **2** and [Au(N^C^N)Cl][PF_6], **4d**, whereas by slow evaporation of a dichloromethane solution for [Au(N^C^N)(PPh_3)$_2$Cl][PF_6], **6**.

Crystal data are summarised in Table 4. The diffraction experiments were carried out on a Bruker APEX II CCD area-detector diffractometer, at 150 K for **2** and **4d**, and at 115 K for **6**·CH_2Cl_2, using Mo-Kα radiation (λ = 0.71073) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[23] and an empirical absorption correction was applied (SADABS)[24] to the collected reflections. The calculations were performed using the Personal Structure Determination Package[25] and the physical constants tabulated therein.[26] The structures were solved by direct methods (SHELXS)[27] and refined by full-matrix least-squares using all reflections and minimising the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on F^2). In **4d** the PF_6^- anion is partially disordered, with atoms P, F1 and F2 (in *trans* position) ordered, and the other four F atoms split into pairs having occupancy factors (refined) of 0.80 and 0.20, respectively. The F atoms with occupancy 0.20 were refined with isotropic thermal parameters, whereas all the other non-hydrogen atoms were refined with anisotropic thermal factors. All the hydrogen atoms were placed in their ideal positions (C–H or N–H = 0.97 Å), with the thermal parameter U 1.10 times that of the atom to which they are attached, and not refined. For noncentrosymmetric compound **2** full refinement of the correct structure model led to R_2 = 0.031 and R_{2w}= 0.045, full refinement of the inverted structure led to R_2 = 0.089 and R_{2w}= 0.169. For chiral **6**·CH_2Cl_2 full refinement of the correct structure enantiomorph led to R_2 = 0.034 and R_{2w}= 0.043, full refinement of the wrong one led to R_2 = 0.107 and R_{2w}= 0.180. In the final Fourier maps the maximum residuals were 1.34(15) e Å^{-3} at 0.79 Å from Au, 4.29(68) e Å^{-3} at 0.96 Å from Au, and 2.10(25) e Å^{-3} at 1.01 Å from Au, for **2**, **4d**, and **6**·CH_2Cl_2, respectively.

CCDC reference numbers 713741–713743. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b822842f

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