Gold(III) six-membered N^C^N pincer complexes: synthesis, structure, reactivity and theoretical calculations†

Giuseppe Alesso,*[a] Maria Agostina Cinellu,[a] Sergio Stoccoro,*[a] Antonio Zucca,[a] Giovanni Minghetti,[a] Carlo Manassero,[b] Silvia Rizzato,[b] Ole Swang[c] and Manik Kumer Ghosh[c]

Received 22nd June 2010, Accepted 9th August 2010
DOI: 10.1039/c0dt00705f

The first six-membered gold(III) N^C^N pincer complex was obtained in good yield, under very mild conditions, by transmetalation of [Hg(κ*C*-N^C^N)Cl] (N^CH^N = 1,3-bis(pyridin-2-ylmethyl)benzene, HL^1) with Na[AuCl$_4$]. The X-ray crystal structure of [Au(N^C^N)Cl][PF$_6$] showed that the fused six-membered metallacycles each exist in a strongly puckered boat conformation. As shown by the ^{1}H NMR spectra in various solvents, the same structure is also retained in solution: no inversion of the six-membered metallacycles is observed in DMSO up to 95 °C. This correlates well with a reaction barrier of 17.5 kcal/mole, as determined by quantum chemical calculations. The reactivity of the present pincer complex is compared to that of the analogous 1,3-bis(2-pyridyl)benzene, HL^2, derivative, which has five-membered fused metallacycles. Sharp differences are found in the reactions with phosphines, such as PPh$_3$ and dppe (1,2-bis-diphenylphosphino-ethane), and with silver salts. Theoretical calculations were carried out on the two pincer complexes in order to try to understand these differences, and we found that the gold–chlorine bond is significantly stronger in the case of the complex containing five-membered metallacyclic rings.

Introduction

E^C^E-pincer metal complexes (E = donor atoms, C = anionic or carbenic carbon atom) are a particular type of cyclometalate, the first examples of which, a series of phosphorus based (E = P) pincer derivatives, were reported in the late 1970s by Moulton and Shaw.[1] The great surge of interest stirred up by these organometallic compounds is witnessed by the huge number of publications.[2,3] Such an interest stems from the unusual physical and chemical properties of this variegated class of compounds, granted by the strong M–C σ bond, supported by two E–M dative bonds to the heteroatoms on the pendant arms of the central moiety, typically an anionic aryl ring. The ease with which steric and electronic properties of the complexed metal centres can be modulated, enables their use in a wide range of environments. Applications encompass different fields, such as catalysis and organic synthesis,[2a–i] bioorganometallic chemistry,[2j] and materials science.[2c,d,k]

Among the molecules potentially able to act as pincers, a number of N^C^N systems have been considered in the last few 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: the only examples reported so far are [Au{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$}Cl]$_2$[Hg$_2$Cl$_6$],[5] and the 1,3-bis(2-pyridyl)benzene derivative [Au{C$_6$H$_3$(C$_5$H$_4$N)$_2$}Cl][PF$_6$].[6] Both complexes, which feature five-membered metallacycles, have been structurally characterized.[5a,6] Aspects of the reactivity of the latter compound were also investigated.[6]

Following these previous reports, here we describe the synthesis of 1,3-bis(pyridin-2-ylmethyl)benzene, HL^1, (Fig. 1) and its reactions with gold(III) salts. Significant differences of chemical behaviour with respect to the previously studied analogous ligand 1,3-bis(2-pyridyl)benzene, HL^2, are pointed out.

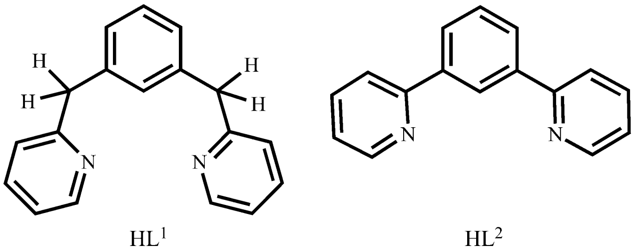


Fig. 1 N^CH^N pincer ligands HL^1 and HL^2.

The X-ray structures of the pincer complex [Au(η^3-N^C^N)Cl][PF$_6$], featuring six-membered fused metallacycles, and a salt of the ligand, [HN^CH^NH][AuCl$_4$]Cl, are reported and show a very interesting supramolecular organization, as well as that of the mercury(II) intermediate [Hg(κ*C*-N^C^N)Cl]. Reactivity studies of the new gold(III) pincer complex have been carried out, mainly with phosphines and silver salts, which indicated remarkable differences from the homologous HL^2 derivative, which has five-membered fused metallacycles. Theoretical calculations

---

[a]*Dipartimento di Chimica, Università degli Studi di Sassari, Via Vienna 2, I-07100, Sassari, Italy. E-mail: stoccoro@uniss.it*
[b]*Dipartimento di Chimica Strutturale e Stereochimica Inorganica e Facoltà di Farmacia, Università di Milano, I-20133, Milano, Italy*
[c]*SINTEF Materials and Chemistry, Department of Hydrocarbon Process Chemistry, P. O. Box 124 Blindern, N-0314, Oslo, Norway*

† Electronic supplementary information (ESI) available: Additional data. CCDC reference numbers 781488–781490. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00705f

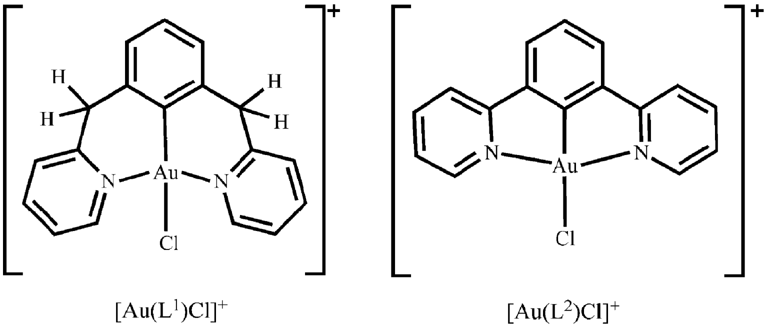


Fig. 2 Pincer complexes $[Au(N^\wedge C^\wedge N)Cl]^+$.

have been carried out on the two pincer complexes, in order to rationalize the observed differences.

Results and discussion

The new ligand, 1,3-bis(pyridin-2-ylmethyl)benzene, HL^1, was prepared by co-cyclotrimerization of 1,3-phenylenediacetonitrile with acetylene, in the presence of Bönnemann catalyst, according to literature procedures.[7] After purification, it was extensively characterized by ^1H NMR spectra, recorded in several solvents (see Experimental).

The main goal of the present study was to synthesize a six-membered pincer complex $[Au(N^\wedge C^\wedge N)Cl]^+$, and to compare its reactivity, especially towards common phosphinic ligands and silver salts, with that of the corresponding 1,3-bis(2-pyridyl)benzene (HL^2) derivative having five-membered fused metallacycles (Fig. 2).

Previous studies on palladium(II) pincer complexes $[Pd(N^\wedge C^\wedge N)Cl]$ ($N^\wedge CH^\wedge N$ = 1,3-bis(2-pyridyl)benzene (HL^2), 1,3-bis(2-pyridyloxy)benzene), have shown that insertion of an O spacer between the central benzenic ring and the pyridinic rings, while reducing the bond angle strain imposed by the presence of two five-membered fused metallacycles, had remarkably positive effects on the catalytic activity.[4h]

In the various methods developed for the preparation of metal pincer complexes, the direct cyclometalation protocol *via* C–H activation is particularly attractive, since it does not require prefunctionalization of the pincer ligands in order to achieve regioselective metalation. However, a survey of the literature shows that the direct cyclometalation of tridentate $N^\wedge CH^\wedge N$ ligands often fails to afford the expected pincer complexes (especially in the case of palladium).[8] The reduced tendency for direct C2 metalation with $N^\wedge CH^\wedge N$ ligands may be explained by the relatively low bond strength of the M–N bonds, with respect to that of both M–P and M–S bonds.[2c] Nevertheless, most $N^\wedge C^\wedge N$ pincer complexes, including gold(III) derivatives,[5,6] could be successfully synthesized through a transmetalation route.

As previously observed in the case of HL^2, the reaction of $H[AuCl_4]\cdot 3H_2O$ with HL^1 under mild conditions (diethyl ether, room temperature) affords, in almost quantitative yield, a salt of the protonated ligand, in the present case $[HN^\wedge CH^\wedge NH][AuCl_4]_2$ (**1**$[AuCl_4]_2$). This is a pale yellow solid that was characterized by CHN analysis and ^1H NMR spectroscopy. The ^1H NMR spectrum shows one set of resonances for the $H^{6'}$, $H^{6''}$ protons of the pyridine rings, with a significant downfield shift of *ca.* 0.6 ppm (acetone-d_6) with respect to the free ligand.

In the attempt to obtain crystals of X-ray quality by slow evaporation of an acetone solution, at room temperature, rearrangement occurred to give crystals of **1**$[AuCl_4]Cl$, resulting from formal loss of one equivalent of $AuCl_3$. An ORTEP view of the cation is shown in Fig. 3.[9]

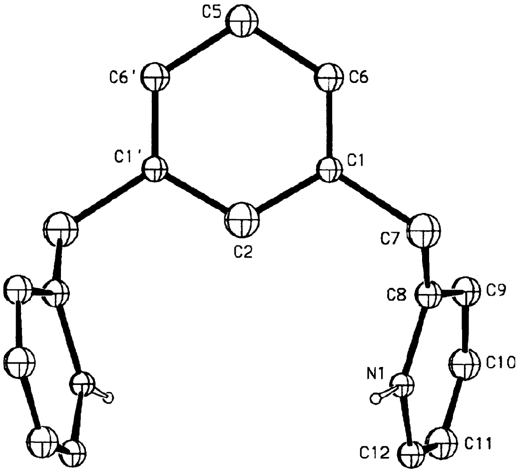
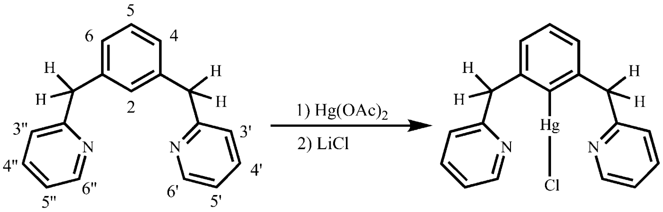


Fig. 3 ORTEP view of cation $\mathbf{1}^{2+}$ in compound **1**$[AuCl_4]Cl$. Ellipsoids are drawn at the 20% probability level. Cation $\mathbf{1}^{2+}$ lies on a crystallographic two-fold axis, passing through atoms C(2) and C(5).

As in the case of the HL^2 derivative $[HN^\wedge CH^\wedge N][AuCl_4]$, attempts to convert the salt into the pincer derivative were unsuccessful: in CH_3CN, at reflux, the salt was quantitatively recovered. The same result was obtained in acetic acid, also in the presence of a base ($NaHCO_3$), while forcing the experimental conditions at reflux resulted in the formation of metallic gold. At variance with the pincer complex of HL^2, which could be also obtained from direct reaction of the ligand with $[AuCl_4]^-$, the only way to obtain the HL^1 gold pincer compound was a transmetalation reaction between the corresponding organomercury derivative and $[AuCl_4]^-$. This method of synthesis has been used previously to prepare other aryl gold(III) complexes.[10] The mercury derivative $[Hg(\kappa C\text{-}N^\wedge C^\wedge N)Cl]$, **2**, was obtained, as a colourless crystalline solid, following the classical procedure of synthesis (eqn (1)):



HL^1 **2** (1)

The ^{1}H NMR spectrum shows the lack of the H^2 proton. Furthermore it turns out that the resonances of the protons of the pyridine moieties are not very shifted in comparison with those of the free ligand: most likely this is due to the nitrogen atoms not being involved in the coordination of the metal ion. This is also supported by the resonance of the methylenic protons, that appears as a narrow singlet (this issue will be analyzed more deeply afterwards), and confirmed by X-ray diffraction of a single crystal of **2**. The molecular structure of **2** is depicted in Fig. 4, with principal bond parameters in the caption.[11]

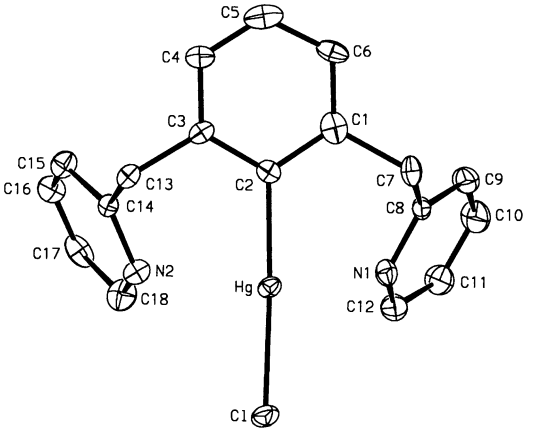


Fig. 4 ORTEP view of compound **2**. Ellipsoids as in Fig. 1. Principal bond and non-bond parameters are: Hg–Cl 2.308(2), Hg–C(2) 2.066(7), Hg···N(1) 2.730(7), Hg···N(2) 2.820(9) Å, Cl–Hg–C(2) 173.6(2), N(1)···Hg···N(2) 108.2(2)°.

Reaction of the mercury derivative **2**, with H[AuCl$_4$] in ethanol, in the presence of NaHCO$_3$, or directly with Na[AuCl$_4$], gives the gold pincer in excellent yield as a mercury salt, likely [Hg$_2$Cl$_6$]$^{2-}$ (eqn (2)):

$$\mathrm{H[AuCl_4]\cdot 3H_2O + \underset{\mathbf{2}}{[Hg(\kappa\mathit{C}\text{-}N\text{\^{}}C\text{\^{}}N)Cl]}} \xrightarrow[\text{-NaCl}]{\text{NaHCO}_3} \underset{(\mathbf{3})_2[\mathrm{Hg_2Cl_6}]}{1/2[\mathrm{Au(N\text{\^{}}C\text{\^{}}N)Cl}]_2[\mathrm{Hg_2Cl_6}]} \quad (2)$$

Compound (**3**)$_2$[Hg$_2$Cl$_6$] was characterized by elemental analysis and spectroscopic methods. The ^{1}H NMR spectrum, registered in DMSO-d_6, the only solvent in which the compound is soluble, shows in the aromatic region five resonances, not well resolved, which were completely assigned by comparison with those of the ligand, and by selective H–H decoupling. The strong deshielding of the H$^{6'}$, H$^{6''}$ protons (δ 9.21 *vs.* δ 8.46 in the free ligand), usually observed when a chlorine is in proximity of the pyridine ring, supports the N^C^N pincer-like coordination of the ligand.[12] The spectrum also suggests a boat conformation of the six-membered cyclometalated rings. No rapid inversion of the boats occurs on the NMR time-scale up to room temperature, as shown by the AB pattern displayed by the CH$_2$ resonances in the complex (δ_A 4.94; δ_B 4.46; J_{AB} = 15.2 Hz); in the free ligand, as well as in the C-bound Hg(II) derivative, the signals of the CH$_2$ protons appear as two singlets at δ 4.05 and δ 4.16, respectively. Exchange of Cl$^-$ or [PF$_6$]$^-$ for [Hg$_2$Cl$_6$]$^{2-}$, leading to a more soluble salt of **3**$^+$, allowed us to obtain a more complete characterization in solution.[13] A ^{1}H NOE difference experiment was performed in acetone, which showed contacts between H^B protons and H^4–H^6, H$^{3'}$–H$^{3''}$ and of course H^A protons, while H^A protons showed contacts only with H^B protons. Notably, in this solvent the H^4, H^5 and H^6 protons are casually isochronous, and give rise to a narrow singlet (see Experimental), while the CH$_2$ protons display an AB system again, with δ_A 4.96, δ_B 4.61, and J_{AB} = 15.7 Hz. On the whole, the ^{1}H NMR spectra suggest for cation **3**$^+$ the structure as shown in Fig. 5.

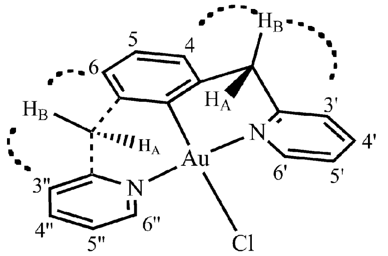
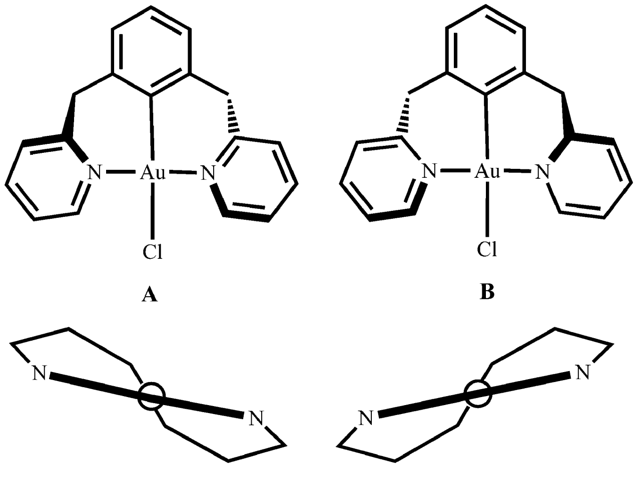


Fig. 5 Proposed structure for **3**$^+$ with numbering scheme and NOE contacts.

In fact, in the six-membered metallacycles having a boat conformation, the H^A protons occupy pseudo axial positions, lying respectively above and below the coordination plane, so that they can exhibit NOE effect only with the geminal proton H^B. On turn, the H^B protons, being in pseudo equatorial positions, can show NOE effects with neighbouring protons. Variable-temperature studies showed that these protons are not involved in a dynamic process: indeed, a sharp AB pattern is observed up to 95 °C in a DMSO-d_6 solution of **3**[PF$_6$], indicating that interconversion between the left- and right-handed twisted forms (**A**, **B** in Scheme 1) does not occur.



Scheme 1 Left- (A) and right-handed (B) twisted forms of **3**$^+$; bottom figures represent the Newman-projections along the Au–C bonds.

Using quantum chemical calculations, a transition state (TS) search was carried out for the interconversion reaction. The TS structure is shown in Fig. 6. This TS connects the two forms of **3**$^+$ as shown by Intrinsic Reaction Coordinate (IRC) calculations. We note that both methylene groups are on the same side of the Au–N–N–C plane in the TS. The computed activation energy for the transformation is 17.5 kcal mol^{-1}, which is in line with our failure to observe interconversion at 95 °C.

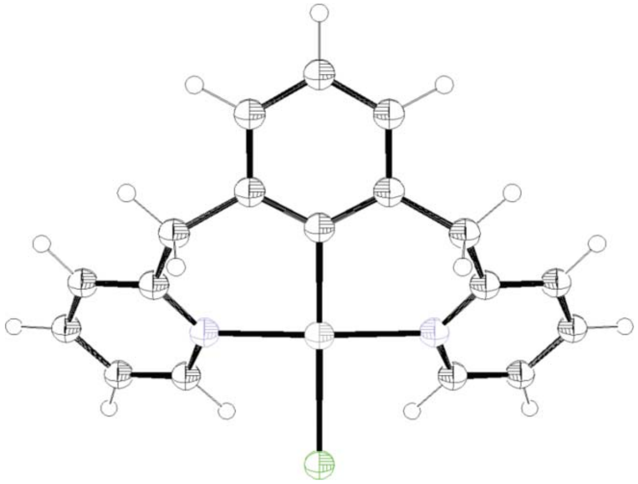


Fig. 6 ORTEP view of the calculated structure of the transition state of **3**$^+$.

A single crystal of **3**[PF$_6$] suitable for X-ray diffraction was grown by slow evaporation of an acetone solution at room temperature.

Gratifyingly, the calculated geometries are in excellent agreement with the experimental ones and with each other. [Au(L^1)Cl]$^+$ (**3**$^+$) and the corresponding five-membered ring pincer [Au(L^2)Cl]$^+$ (**3′**$^+$) are calculated to have C_2 and C_{2v} symmetries, respectively. In the following description, experimental values are used, unless otherwise mentioned. The structure consists of the packing of **3**$^+$ cations and [PF$_6$]$^-$ anions in the molar ratio 1 : 1, in the monoclinic space group $P2_1/n$, with no unusual van der Waals contacts. An ORTEP view of the cation is shown in Fig. 7, and its principal bond lengths and angles are listed in Table 1, together with corresponding bond parameters of the five membered pincer **3′**$^+$.[6] In **3**$^+$ the metal atom displays a square planar environment with a slight tetrahedral distortion, maximum displacements from the least-squares plane being +0.027(3) and –0.025(4) Å for atoms N(1) and C(2), respectively. The three aromatic rings are all strictly planar, and for the sake of simplicity we will call the ring of N(1) ring 1, that of C(2) ring 2, and that of N(2) ring 3. Thus, the dihedral angles formed by the metal best plane and these rings are 136.7(1), 40.7(2), and 43.0(1)° for rings 1, 2, and 3, respectively. Other important dihedral angles are: ring 2–ring 1 123.9(1)°, ring 2–ring 3 56.5(1)°, and ring 1–ring 3 93.7(1)°. It is peculiar of this cation that the moiety formed by ring 1 plus Au and C(7), and that formed by ring 2 plus C(13) (but not Au) show a high degree of planarity, maximum distances from the best plane, in the first case, being +0.011(4) and –0.010(4) Å for atoms C(8) and C(7), respectively. In the second case, maximum displacements are +0.023(3) and –0.025(4) Å for atoms N(2) and C(13), respectively. The metal atom is out of this second best plane by 0.144(1) Å, probably because of packing effects: the calculated gas-phase geometry gives a value of zero. Corresponding moieties in similar N^N^C cyclometalated derivatives are definitely non planar, as found, for example, in [Au(N^N^C)Cl]$^+$ (N^N^C = $N_2C_{10}H_7(CMe_2C_6H_4)$-6, *i.e.* deprotonated 6-(1,1-dimethylbenzyl)-2,2′-bipyridine).[14] Bond parameters of **3**$^+$ can be compared with those of the five-membered pincer **3′**$^+$ (see Table 1). At variance with **3**$^+$, this cation, which is totally planar, displays a certain degree of bond angle strain around the metal center. It follows that, with the only exception of the Cl–Au–C(2) angles, corresponding bond angles in the two cations are very different (see Table 1), whereas the main difference between the bond lengths of the two cations concerns the Au–C(2) distance, 2.014(4) Å here, and 1.950(5) Å in **3′**$^+$. This is not surprising, because a shortening of the metal–ligand central bond in planar bicyclo moieties is found as a rule. The other corresponding bond lengths are very similar in the two compounds. Analogous structural differences have been found between five- and six-membered N^C^N pincer complexes of palladium(II); notably, the reduced bond angle strain around the metal center, featured by the six-membered pincer complex, resulted in a higher catalytic activity of the complex compared to

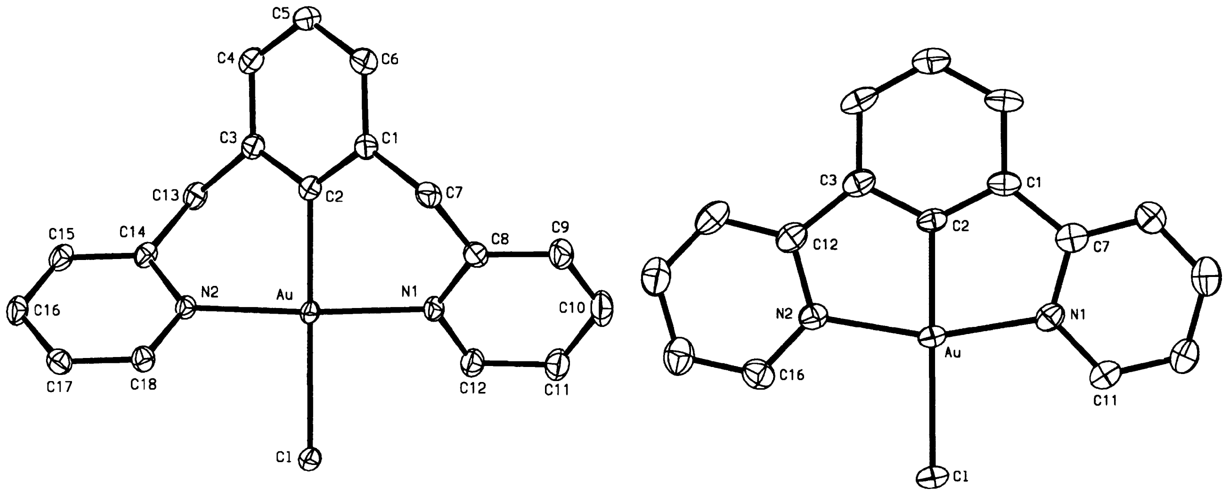


Fig. 7 ORTEP view of cations [Au(L^1)Cl]$^+$ (**3**$^+$) (left) and [Au(L^2)Cl]$^+$(**3′**$^+$) (right, ref. 6). Ellipsoids are drawn at the 30% probability level.

Table 1 Selected bond distances (Å) and angles (°) for $\mathbf{3}^{+}$ (this work) $\mathbf{3'}^{+}$ (ref. 6), and the TS for interconversion between the two isomers on $\mathbf{3}^{+}$ (this work). The first values in each column are experimental ones, with Estimated Standard Deviations (Esd's) on the last figure in parentheses, while the values in square brackets and in braces are calculated at the B3LYP/cc-pVTZ and MP2/cc-pVDZ level of theories, respectively

Parameter	$\mathbf{3}^{+}$	$\mathbf{3'}^{+}$	**TS**[a]
Au–Cl	2.386(1) [2.390]{2.343}	2.360(1) [2.367]{2.334}	[2.415]{2.367}
Au–N(1)	2.027(3) [2.066]{2.019}	2.019(5) [2.065]{2.029}	[2.102]{2.055}
Au–N(2)	2.031(3) [2.066]{2.019}	2.032(5) [2.065]{2.029}	[2.102]{2.055}
Au–C(2)	2.014(4) [2.044]{2.004}	1.950(5) [1.966]{1.944}	[2.080]{2.047}
N(1)–C(8)	1.350(6) [1.351]{1.363}		[1.346]{1.357}
N(1)–C(7)		1.385(8) [1.374]{1.384}	
N(1)–C(12)	1.340(6) [1.348]{1.360}		[1.354]{1.366}
N(1)–C(11)		1.345(8) [1.338]{1.353}	
N(2)–C(14)	1.362(4) [1.351]{1.363}		(1.346) [1.357]
N(2)–C(12)		1.377 (1.374) [1.384]	
N(2)–C(18)	1.349(5) [1.348]{1.360}		[1.354]{1.366}
N(2)–C(16)		1.346(8) [1.338]{1.353}	
Cl–Au–N(1)	91.7(1) [91.5]{92.1}	99.2(1) [99.7]{98.8}	[89.8]{90.0}
Cl–Au–N(2)	92.1(1) [91.5]{92.1}	99.6(1) [99.7]{98.8}	[89.8]{90.0}
Cl–Au–C(2)	179.2(1) [180.0]{180.0}	179.7(2) [180.0]{180.0}	[166.2]{166.0}
N(1)–Au–N(2)	175.8(1) [177.0]{175.8}	161.2(1) [160.7]{162.4}	[158.4]{157.2}
N(1)–Au–C(2)	88.2(1) [88.5]{87.9}	80.5(2) [80.3]{81.2}	[92.8]{92.8}
N(2)–Au–C(2)	88.1(1) [88.5]{87.9}	80.7(2) [80.3]{81.2}	[92.8]{92.8}
Au–N(1)–C(8)	121.2(3) [120.8]{120.2}		[125.4]{126.1}
Au–N(1)–C(7)		115.1(4) [114.0]{114.5}	
Au–N(1)–C(12)	117.5(3) [118.5]{118.3}		[114.4]{113.1}
Au–N(1)–C(11)		124.7(4) [124.7]{123.9}	
Au–N(2)–C(14)	120.9(3) [120.8]{120.2}		[125.4]{126.1}
Au–N(2)–C(12)		114.8(4) [114.0]{114.5}	
Au–N(2)–C(18)	118.8(2) [118.5]{118.3}		[114.4]{113.1}
Au–N(2)–C(16)		124.6(4) [124.7]{123.9}	

[a] Numbering scheme as in $\mathbf{3}^{+}$.

that of the corresponding five-membered analogue.[4h] We note that the computed distances corresponding to the coupling involving the H^B protons (see Fig. 5) are 2.38 and 2.32 Å for the central and pyridine rings, respectively.

At variance with $[Au(L^2)Cl]^+$, $\mathbf{3'}^{+}$, that can be obtained either by transmetalation from the corresponding mercury(II) derivative or by direct cycloauration, $[Au(L^1)Cl]^+$ could be obtained only by transmetallation. The opposite trend was instead observed in the C–H activation of phenyl rings of 6-substituted 2,2′-bipyridines to give N^N^C cycloaurated complexes. Indeed, the cyclometallation of 6-phenyl-2,2′-bipyridine, which affords a five-membered metallacycle, requires use of mercury(II) intermediates or silver salts and high temperature,[15] while formation of six-membered metallacycles can be easily accomplished by direct C–H activation, as shown by the cyclometalation of 6-benzyl-2,2′-bipyridines.[14] The high tendency of gold(III) to give six-membered metallacycles by direct C–H activation, was clearly demonstrated by Nonoyama and coworkers in the cycloauration of 3-phenyl-6-*p*-toluidinopyridazine, as this ligand can give both five- and six-membered metallacycles.[16]

Reactivity of [Au(N^C^N)Cl][PF$_6$], 3[PF$_6$]

As previously mentioned gold(III) N^C^N pincer derivatives are very few and their reactivity is almost completely unexplored. On the contrary the reactivity of gold(III) cyclometalated derivatives with bidendate C^N and tridentate C^N^N and C^N^C ligands has been reported by several groups: most reactions involve displacement of the nitrogen atoms or of halides by neutral ligands, typically PR_3, while complete removal of the cyclometalated ligands was never observed.[17] In the previous study concerning the five-membered pincer **3′**[PF$_6$] we showed that reaction with PPh_3 occurs with cleveage of the Au–N bonds to give the bis-phosphine derivative [Au(κ*C*-N^C^N)(PPh$_3$)$_2$Cl][PF$_6$], regardless of the stoichiometric ratio used.[6] Interestingly, a different behaviour was observed in reactions of the present pincer complex **3**[PF$_6$] with tertiary phosphines. Regardless of the stoichiometric ratio used, reaction with PPh_3 occurs without cleavage of the Au–N bonds to give [Au(N^C^N)(PPh$_3$)Cl][PF$_6$], **4**[PF$_6$], likely a pentacoordinated species (eqn (3)):

$$\underset{3[PF_6]}{[Au(N^\wedge C^\wedge N)Cl][PF_6]} \xrightleftharpoons[-PPh_3]{PPh_3} \underset{4[PF_6]}{[Au(N^\wedge C^\wedge N)(PPh_3)Cl][PF_6]} \qquad (3)$$

As suggested by the NMR data (see below), in complex **4**[PF$_6$] the donor atoms of the pincer system retain coordination to the metal centre. The reaction with PPh_3 in CD_3CN was monitored at room temperature by ^1H and ^{31}P NMR: after the addition of 1 equivalent of phosphine a mixture of $\mathbf{4}^{+}$ and $\mathbf{3}^{+}$ (*ca.* 6 : 1 molar ratio) and free PPh_3 (δ_P –4.12) was observed, whereas the presence of a bis-phosphine adduct, analogous to $[Au(\kappa C\text{-}L^2)(PPh_3)_2Cl]^+$, was definitely ruled out. Complete conversion of $\mathbf{3}^{+}$ to $\mathbf{4}^{+}$ was achieved on addition of an excess of PPh_3, while removal of excess PPh_3 from the mixture promoted the reverse reaction. Indeed, the ^1H and ^{31}P NMR spectra of isolated **4**[PF$_6$] (in CD_3CN) showed a 1 : 3 : 1 mixture of $\mathbf{3}^{+}$, $\mathbf{4}^{+}$ and free PPh_3. Any attempt to grow crystals of **4**[PF$_6$] suitable for X-ray analysis was unsuccessful; nevertheless, the structure of $\mathbf{4}^{+}$ was confidently inferred by its spectroscopic data. In the ^1H NMR spectrum only one resonance is observed for the $H^{6'}$, $H^{6''}$ protons of the pyridine rings, very slightly shifted to higher field (δ 9.07, CD_3CN) compared to δ 9.28 (same solvent) in **3**$^+$. Also shifted to higher field, in this case more significantly, are the resonances of the methylenic protons: δ 3.90 and 3.97 compared to δ 4.39 and 4.77 in **3**$^+$, becoming a very tight AB spin system.

As previously mentioned phosphines are also able to displace a bound halide from cycloaurated Au(III) halide complexes to the outer coordination sphere where it can be easily exchanged with another counter ion. Assuming this could be our case, complex **4**[PF_6] was treated with an excess of K[PF_6] in acetone. As no exchange was observed we suggest that cation **4**$^+$ retains its original arrangement with the chlorine *trans* to the carbon atom and the two pyridinic moieties coordinated to the metal centre, with the PPh_3 occupying a fifth coordination position. The large high field shift of the CH_2 protons strongly suggests a square based pyramidal geometry for this cation, with the phosphine in the apical position. The ^{31}P NMR spectrum of **4**[PF_6] showing only one resonance for the coordinated phosphine (δ 26.83) is a further evidence of this arrangement.[18] The reversibility of reaction 3 indicates that the phosphine ligand is not kinetically inert, likely due to steric hindrance of the methylenic groups and to the low stability of 5-coordinated species.

Under the same experimental conditions reaction of **3**[PF_6] with $[Ph_2PCH_2]_2$, dppe, gave a complex that, on the basis of microanalytical data, was formulated as [Au(N^C^N)(dppe)][Cl][PF_6], **5**[Cl][PF_6] (eqn (4)):

$$\underset{3[PF_6]}{[Au(N^\wedge C^\wedge N)Cl][PF_6]} \xrightarrow{dppe} \underset{5[Cl][PF_6]}{[Au(N^\wedge C^\wedge N)(dppe)][Cl][PF_6]} \quad (4)$$

The presence of the chloride ligand as a counter ion, in the outer coordination sphere, is proven by the metathesis reaction with K[PF_6], which occurs quickly and quantitatively in acetone at room temperature to give compound **5**$[PF_6]_2$ (eqn (5)):

$$\underset{5[Cl][PF_6]}{[Au(N^\wedge C^\wedge N)(dppe)][Cl][PF_6]} \xrightarrow[-KCl]{K[PF_6]} \underset{5[PF_6]_2}{[Au(N^\wedge C^\wedge N)(dppe)][PF_6]_2} \quad (5)$$

The proposed structure for **5**$^{2+}$ rests on NMR spectroscopic evidence. In the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) two resonances at δ 55.26 and δ 56.54, indicative of a very similar chemical environment, are consistent with the classical chelating behaviour of dppe. In the ^1H NMR spectrum (CD_2Cl_2) two sets of multiplets at δ 2.84–3.06 and δ 3.36–3.60 have been assigned to the methylenic protons of the chelating diphosphine ligand. The presence in the spectrum of an AB system relative to the methylenic protons of the pincer ligand proves that the pyridinic moieties have not been displaced by the dppe. At variance with **4**$^+$, the $H^{6'}/H^{6''}$ resonances are now strongly shifted to high field (δ 8.00) compared to δ 9.36 in **3**$^+$, a common effect observed when a phosphine ligand is present in the coordination sphere of square planar complexes of d^8 late transition metals. We thus propose a trigonal bipyramidal geometry for cation **5**$^{2+}$ (Fig. 8) with the equatorial positions occupied by the metalated carbon and the phosphorus atoms and the nitrogen atoms in the axial ones.

In the attempt to obtain crystals of **5**$[PF_6]_2$ suitable for X-ray analysis we obtained instead the well known gold(I) derivative $[Au(dppe)_2][PF_6]$.[19]

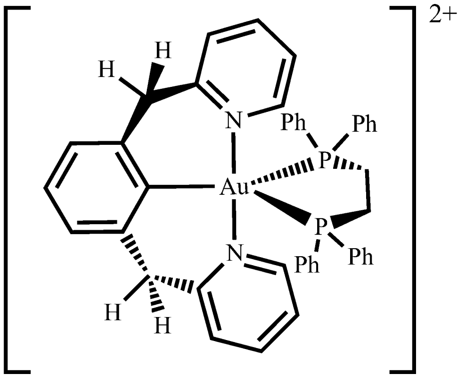


Fig. 8 Proposed structure for **5**$^{2+}$.

Displacement of the chloride ligand from **3**[PF_6] was easily accomplished by reaction with silver salts. Reaction with AgOTf in acetone or dichloromethane, at room temperature, led to formation of the aquo complex [Au(N^C^N)(H_2O)][PF_6][OTf]·nH_2O, **6**[PF_6][OTf]·nH_2O (n = 0, 1). In the ^1H NMR spectrum (CD_2Cl_2) a broad signal accounts for a coordinated water molecule in rapid exchange with the water molecules H-bonded to the solvent (n = 0) or to the crystallization water (n = 1). In the first case (n = 0), the chemical shift of the coordinated water is δ 6.65 while the peak of the water molecules H-bonded to CD_2Cl_2 (usually at 1.6) is not present. In the second case (n = 1), the chemical shift of the scrambling water molecules is δ 3.90; notably, in this case the resonances of the H^A and $H^{6'}$–$H^{6''}$ protons which face the coordinated H_2O molecule – respectively at δ 5.05 (4.74 in **3**$^+$) and δ 9.15 (9.36 in **3**$^+$) – are also broadened, while the signal of the H^B protons appears as a sharp "doublet". In the former case the resonance of H^A is only slightly broadened while $H^{6'}$–$H^{6''}$ are sharp signals. In both cases the other resonances are slightly shifted at low field with respect to **3**$^+$. The ^{19}F NMR spectrum confirms the presence of PF_6 and OTf as counterions (δ −50.65 d, J_{FP} = 710.9 Hz, δ −57.37 s, respectively).

Reaction of **3**[PF_6] with AcOAg afforded the acetato complex [Au(N^C^N)(OAc)][PF_6], **7**[PF_6], in good yield. It exhibits the ν_a(COO) and ν_s(COO) at 1620 and 1315 cm^{-1}, respectively, in accordance with an acetato group *trans* to a carbon atom.[20] The ^1H NMR spectrum in CD_3COCD_3 shows the resonance of the methyl protons at δ 1.95 with the correct integral ratio; also for this compound an AB pattern is displayed by the CH_2 protons (δ_A 4.84; δ_B 4.64; J_{AB} = 15.8 Hz). Complexes **6**[PF_6][OTf] and **7**[PF_6] could be both valuable starting materials for the obtainment of other gold(III) derivatives and catalytic precursors.

As shown by the reaction with dppe and with silver salts displacement of the chloride ligand from the present pincer complex [Au(L^1)Cl][PF_6] is easily accomplished contrary to what is observed for the pincer complex [Au(L^2)Cl][PF_6], whose chloride is neither displaced by phosphines nor by silver salts.[6] The latter behaviour being quite unexpected, considering that the chloride ion is *trans* to a carbon atom, we deemed it of interest to shed light on the nature of the Au–Cl bond in these pincer complexes by quantum chemical calculations. Reaction energies for the following reaction were computed:

$$[Au(L^x)Cl]^+ \rightarrow [Au(L^x)]^{2+} + Cl^-, x = 1,2$$

For obvious reasons of electrostatic origin, the reaction energies themselves were strongly endothermic (in the order of 200–250 kcal mol^{-1}) for these model reactions. The interesting aspect here is the difference between the two complexes: at the three employed levels of theory, the chlorine abstraction demanded from 12.5 to 13.1 kcal/mole less energy for **3**$^+$, containing six-membered rings, than for **3′**$^+$ with its five-membered rings. We infer that the difference in reactivity between the two complexes has its roots in different Au–Cl bond strengths.

Conclusion

A new N^C^N gold(III) pincer complex, featuring six-membered N^C metallacycles, was synthesized and structurally characterized. Its structural and reactivity features were compared to those of a previously studied pincer complex having five-membered N^C metallacycles. Profound differences were found between the two complexes in the reactions with phosphines and with silver salts. Contrary to what was observed with the five-membered pincer complex, reaction of the present complex with phosphines, both mono and bidentate, occurred without cleavage of the Au–N bonds leading to uncommon pentacoordinated phosphine adducts. An unprecedented dicationic aquo complex and an acetato complex were obtained by reaction with AgTOf and AgOAc, respectively, while no reaction with silver salts had been observed in the case of the five-membered pincer complex. Theoretical calculations shed some light into this unexpected behaviour, as heterolytic cleavage of the gold-chlorine bond in the six-membered ring complex demanded significantly less energy.

Experimental

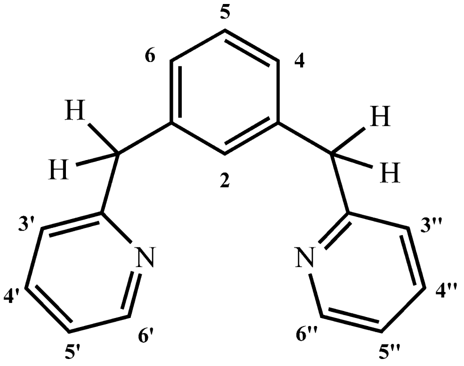
General

$H[AuCl_4]\cdot 3H_2O$ 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). Infrared spectra were recorded with a FT-IR Jasco 480P using Nujol mulls. ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature (20 °C) with a Varian VXR 300 spectrometer operating at 300.0, 282.2 and 121.4 MHz respectively. Chemical shifts are given in ppm relatively to internal TMS (^1H), external trifluoroacetic acid TFA (^{19}F) 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(pyridin-2-ylmethyl)benzene (N^CH^N), HL^1. A solution of 1,3-phenylenediacetonitrile (10.00 g, 0.063 mol) and [(η^5-cyclopentadienyl)cobalt-1,5-cyclooctadiene] (500 mg, 2.153 mmol) in degassed anhydrous toluene (100 mL) was introduced by suction, into a 0.2 L autoclave, evacuated from the air (0.133 mbar). The reaction vessel was pressurized to 13 bar with acetylene and then rocked and heated to 120 °C for 20 h. After cooling and release of residual gas, the solvent was evaporated and the brown residue treated with aqueous solutions of HCl (5%) and NaOH (5%), then extracted with Et_2O, and dried on Na_2SO_4 to give the ligand as a brown oil. Column chromatography on silica gel 60, using benzene/acetone (10 : 1) as eluent, gave 15.10 g (0.058 mol, 92%) of N^CH^N as light green oil.



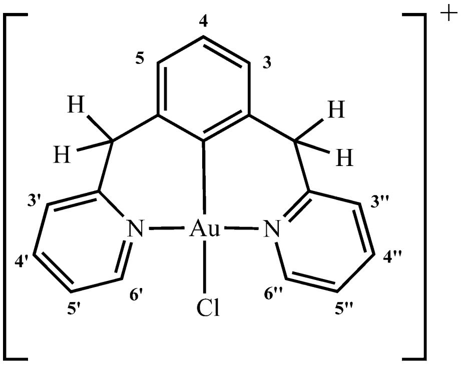
^1H NMR ($CDCl_3$): δ 4.12 (s, 4H, CH_2); 7.07–7.12 (m, 6H, H^4, H^6, $H^{3'}$, $H^{3''}$, $H^{5'}$, $H^{5''}$); 7.18 (s br, 1H, H^2); 7.20 (dd partially overlapped with $CHCl_3$, 1H, J_{HH} (av.) = 7.2 Hz, H^5); 7.56 (td, 2H, J_{HH} = 7.5 Hz, 1.8 Hz, $H^{4'}$, $H^{4''}$); 8.53 (ddd, 2H, J_{HH} = 4.5 Hz, 1.8 Hz, 0.9 Hz, $H^{6'}$, $H^{6''}$); (CD_2Cl_2): δ 4.11 (s, 4H, CH_2); 7.11–7.21 (m, 6H, H^4, H^6, $H^{3'}$, $H^{3''}$, $H^{5'}$, $H^{5''}$); 7.20 (s br, 1H, H^2); 7.24 (dd, 1H, J_{HH} = 6.7 Hz, H^5); 7.61 (td, 2H, J_{HH} = 7.6 Hz, 1.9 Hz, $H^{4'}$, $H^{4''}$); 8.52 (ddd, 2H, J_{HH} = 4.7 Hz, 1.6 Hz, 0.8 Hz, $H^{6'}$, $H^{6''}$); (acetone-d_6): δ 4.07 (s, 4H, CH_2); 7.11–7.17 (m, 6H, H^4, H^6, $H^{3'}$, $H^{3''}$, $H^{5'}$, $H^{5''}$); 7.20 (dd partially overlapped, 1H, J_{HH}(av) = 7.1 Hz, H^5); 7.27 (s br., 1H, H^2); 7.64 (td, 2H, J_{HH} = 7.8 Hz, 2.0 Hz, $H^{4'}$, $H^{4''}$); 8.47 (ddd, 2H, J_{HH} = 4.8 Hz, 1.8 Hz, 0.9 Hz, $H^{6'}$, $H^{6''}$); (DMSO-d_6): δ 4.05 (s, 4H, CH_2); 7.08 (d, 2H, J_{HH} = 8.4 Hz, H^4, H^6); 7.17–7.21 (m, 4H, H^2, H^5, $H^{5'}$, $H^{5''}$); 7.25 (d, 2H, J_{HH} = 7.8 Hz, $H^{3'}$, $H^{3''}$); 7.68 (td, 2H, J_{HH} = 7.8 Hz, 2.0 Hz, $H^{4'}$, $H^{4''}$); 8.46 (ddd, 2H, J_{HH} = 4.8 Hz, 1.8 Hz, 0.9 Hz, $H^{6'}$, $H^{6''}$); (CD_3CN): δ 4.06 (s, 4H, CH_2); 7.10 (d, 2H, J_{HH} = 8.1 Hz, H^4, H^6); 7.15 (ddd, 2H, J_{HH} = 8.1 Hz, $H^{5'}$, $H^{5''}$); 7.19–7.24 (m, 4H, H^2, H^5, $H^{3'}$, $H^{3''}$); 7.64 (td, 2H, J_{HH} = 7.6 Hz, 2.0 Hz, $H^{4'}$, $H^{4''}$); 8.47 (ddd, 2H, J_{HH} = 4.8 Hz, 1.8 Hz, 0.9 Hz, $H^{6'}$, $H^{6''}$).

Synthesis of [NH^CH^NH][AuCl$_4$]$_2$, 1[AuCl$_4$]$_2$. A solution of N^CH^N (260.3 mg; 1.00 mmol) in 30 mL 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 mL) 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**[AuCl$_4$]$_2$ as a pale yellow solid. Yield 892.9 mg, 95%; m.p. 155 °C (dec.); (Found: C 23.44; H 1.82; N 2.85%. Calc. for $C_{18}H_{18}Au_2Cl_8N_2$: C 23.00; H 1.93; N 2.98%). ^1H NMR (DMSO-d_6): δ 4.16 (s, 4H, CH_2); 7.15 (d, 2H, J_{HH} = 7.8 Hz, H^4, H^6); 7.25 (s, 1H, H^2); 7.26 (t, 1H, J_{HH} = 7.5 Hz, H^5); 7.47 (t, 2H, J_{HH} = 7.8 Hz, $H^{5'}$, $H^{5''}$); 7.49 (d, 2H, J_{HH} = 7.5 Hz, $H^{3'}$, $H^{3''}$); 8.00 (td, 2H, J_{HH} = 7.8 Hz, 1.8 Hz, $H^{4'}$, $H^{4''}$); 8.60 (d, 2H, J_{HH} = 4.8 Hz, $H^{6'}$, $H^{6''}$); (acetone-d_6): δ 4.72 (s, 4H, CH_2); 7.43–7.52 (m, 3H, H^4, H^6, H^5); 7.64 (s, 1H, H^2); 8.11 (d, 2H, J_{HH} = 8.1 Hz, $H^{3'}$, $H^{3''}$); 8.17 (tm, 2H, J_{HH}(av) = 6.9 Hz, $H^{5'}$, $H^{5''}$); 8.76 (td, 2H, J_{HH} = 7.8 Hz, 1.5 Hz, $H^{4'}$, $H^{4''}$); 9.04 (dd, 2H, J_{HH} = 6.1 Hz, 0.9 Hz, $H^{6'}$, $H^{6''}$).

By slow evaporation, at room temperature, of an acetone solution of compound **1**[AuCl$_4$]$_2$, crystals suitable for X-ray diffraction were grown. The resolved structure showed that one of the two [AuCl$_4$]$^-$ anions had been replaced by Cl$^-$ leading to **1**[AuCl$_4$]Cl.

Synthesis of [Hg(κ*C*-N^C^N)Cl], 2. A mixture of N^CH^N (260.3 mg, 1.00 mmol) and mercury(II) acetate (318.5 mg, 1.00 mmol) in absolute ethanol (20 mL) was heated for 24 h at reflux, under stirring. Afterwards a solution of lithium chloride (94 mg, 2.22 mmol) in methanol (15 mL) was added and the mixture gently heated for 15 min. The solution was poured into distilled water (100 mL): the white precipitate which formed was filtered off, washed with water, ice-cold methanol and dried under vacuum to give compound **2**. Yield 381.4 mg, 77%; m.p. 132 °C. (Found: C, 43.60; H, 2.91; N, 5.53%. Anal. Calc. for $C_{18}H_{15}HgClN_2$: C 43.64; H 3.05; N 5.66%). ^{1}H NMR ($CDCl_3$): δ 4.10 (s, 4H, CH_2); 7.12–7.25 (m, 7H, H^{3}, H^{4}, H^{5}, H$^{3'}$, H$^{3''}$, H$^{5'}$, H$^{5''}$); 7.54 (td, 2H, J_{HH} = 7.8 Hz, 1.8 Hz, H$^{4'}$, H$^{4''}$); 8.53 (d, 2H, J_{HH} = 4.2 Hz, H$^{6'}$, H$^{6''}$); (DMSO-d_6): δ 4.10 (s, 4H, CH_2); 7.11 (m, 2H, H$^{5'}$, H$^{5''}$); 7.24–7.27 (m, 3H, H^{4}, H^{5}, H^{6}); 7.38 (d, 2H, J_{HH} = 7.5 Hz, H$^{3'}$, H$^{3''}$); 7.71 (td, 2H, J_{HH} = 7.5 Hz, 1.5 Hz, H$^{4'}$, H$^{4''}$); 8.43 (d, 2H, J_{HH} = 4.3 Hz, H$^{6'}$, H$^{6''}$); (acetone-d_6): δ 4.16 (s, 4H, CH_2); 7.12 (t, 1H, J_{HH} = 7.5 Hz, H^{5}), 7.25 (ddd, 2H, J_{HH} = 7.5 Hz, 4.8 Hz, 0.9 Hz, H$^{5'}$, H$^{5''}$); 7.34 (d, 2H J_{HH} = 7.5 Hz, J_{HgH} ~ 60 Hz, H^{4}, H^{6}); 7.40 (d br, 2H, J_{HH} = 7.5 Hz, H$^{3'}$, H$^{3''}$); 7.68 (td, 2H, J_{HH} = 7.5 Hz, 1.9 Hz, H$^{4'}$, H$^{4''}$); 8.49 (dm, 2H, J_{HH} = 5.1 Hz, H$^{6'}$, H$^{6''}$). Crystals of X-ray quality were obtained by slow evaporation of an acetone solution at room temperature.

Synthesis of [Au(N^C^N)Cl]$_2$[Hg$_2$Cl$_6$], (3)$_2$[Hg$_2$Cl$_6$]. A mixture of [Hg(κ*C*-N^C^N)Cl], **2**, (495.4 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 mL) was left for 5 h to react under stirring. The formation of a white precipitate could be observed. Afterwards, the precipitate was filtered off, washed with diethyl ether and dried in vacuum to give compound (**3**)$_2$[Hg$_2$Cl$_6$]. Yield 685.2 mg, 86%; m.p. 135–136 °C (dec.); (Found: C, 27.14; H, 1.57; N, 3.43%. Anal. Calcd. for $C_{18}H_{15}AuCl_4HgN_2$: C, 27.07; H, 1.89; N, 3.51%).



^{1}H NMR (DMSO-d_6): δ 4.46 (2H, J_{HH} = 15.2 Hz, CH^{A}H^{B}, AB system); 4.94 (2H, J_{HH} = 15.2 Hz, CH^{A}H^{B}, AB system); 7.22–7.32 (m, 3H, H^{4}, H^{5}, H^{6}), 7.81 (t, 2H, J_{HH} = 7.5 Hz, H$^{5'}$, H$^{5''}$); 8.10 (d, 2H, J_{HH} = 7.5 Hz, H$^{3'}$, H$^{3''}$); 8.37 (t, 2H, J_{HH} = 7.5 Hz, H$^{4'}$, H$^{4''}$); 9.21 (d, 2H, J_{HH} = 6.3 Hz, H$^{6'}$, H$^{6''}$).

Synthesis of [Au(N^C^N)Cl]Cl, 3[Cl]. Tetra(*n*-butyl)-ammonium chloride (833.7 mg, 3.00 mmol) was added under stirring to a suspension of (**3**)$_2$[Hg$_2$Cl$_6$], (798.7 mg, 1.00 mmol) in 50 mL of dichloromethane. The suspension was left under stirring at room temperature for two hours. The colour of the solution turned pale green and the solid gray. This was collected and dried under vacuum to give compound **3**[Cl], as a white solid. Yield 495.6 mg, 94%; m.p. 188–190 °C (dec.); (Found: C 40.41; H 2.75; N 5.14%. Anal. Calcd. for $C_{18}H_{15}AuCl_2N_2$: C 41.01; H 2.87; N 5.31%). ^{1}H NMR (DMSO-d_6): δ 4.46 (2H, J_{HH} = 15.2 Hz, CH^{A}H^{B}, AB system); 5.09 (2H, J_{HH} = 15.2 Hz, CH^{A}H^{B}, AB system); 7.23–7.27 (m, 3H, H^{4}, H^{5}, H^{6}), 7.78 (t, 2H, J_{HH} = 7.5 Hz, H$^{5'}$, H$^{5''}$); 8.09 (d, 2H, J_{HH} = 7.5 Hz, H$^{3'}$, H$^{3''}$); 8.35 (t, 2H, J_{HH} = 7.5 Hz, H$^{4'}$, H$^{4''}$); 9.28 (d, 2H, J_{HH} = 6.0 Hz, H$^{6'}$, H$^{6''}$).

Synthesis of [Au(N^C^N)Cl][PF$_6$], 3[PF$_6$].

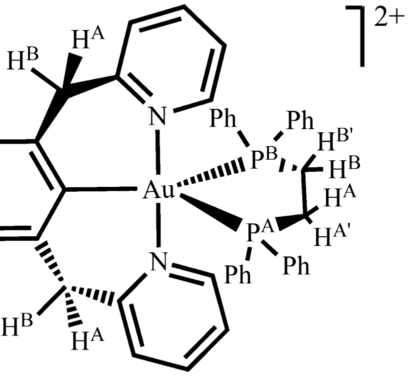
Method a. K[PF$_6$] (220.8 mg, 1.2 mmol) was added to a suspension of **3**[Cl] (527.2 mg, 1.00 mmol) in 100 mL of acetone. The suspension was left under stirring at room temperature overnight. After filtration the solution was evaporated to dryness and 15 mL of water were added to the residue. The white solid was filtered off, washed with diethyl ether and dried in vacuum to give compound **3**[PF$_6$]. Yield 452.1 mg, 71%; m.p. 208–210 °C (dec.); (Found: C 33.72; H 2.18; N 4.51%. Anal. Calcd. for $C_{16}H_{11}AuClF_6N_2P$: C 33.95; H 2.37; N 4.40%.

Method b. K[PF$_6$] (920.3 mg, 5.0 mmol) was added to a suspension of (**3**)$_2$[Hg$_2$Cl$_6$] (798.7 mg, 1.00 mmol) in 100 mL of acetone. The suspension was left under stirring at room temperature overnight. After filtration the solution was evaporated to dryness and 15 mL of water were added to the residue. The white solid was filtered off, washed with diethyl ether and dried in vacuum to give **3**[PF$_6$]. Yield 346.1 mg, 54%; m.p. 208–210 °C (dec.). (Found: C 33.65; H 2.41; N 4.44%. Anal. Calcd. for $C_{16}H_{11}AuClF_6N_2P$: C 33.95; H 2.37; N 4.40%). ^{1}H NMR (acetone-d_6): δ 4.61 (2H, J_{HH} = 15.6 Hz, AB system, CH^{A}H^{B}); 4.96 (2H, J_{HH} = 15.6 Hz, AB system, CH^{A}H^{B}); 7.34 (s, 3H, H^{4}, H^{5}, H^{6}), 7.84 (t, 2H, J_{HH}(av) = 7.0 Hz, H$^{5'}$, H$^{5''}$); 8.19 (d, 2H, J_{HH} = 7.8 Hz, H$^{3'}$, H$^{3''}$); 8.44 (td, 2H, J_{HH} = 7.8 Hz, 1,2 Hz, H$^{4'}$, H$^{4''}$); 9.33 (d, 2H, J_{HH} = 6.0 Hz, H$^{6'}$, H$^{6''}$); (CD_3CN): δ 4.39 (2H, J_{HH} = 15.9 Hz, CH^{A}H^{B}, AB system); 4.77 (2H, J_{HH} = 15.9 Hz, CH^{A}H^{B}, AB system); 7.24–7.33 (m, 3H, H^{4}, H^{5}, H^{6}); 7.66 (tm, 2H, J_{HH}(av) = 6.8 Hz, H$^{5'}$, H$^{5''}$); 7.94 (d, 2H, J_{HH} = 4.5 Hz, H$^{3'}$, H$^{3''}$); 8.25 (td, 2H, J_{HH} = 7.7 Hz, 1,5 Hz, H$^{4'}$, H$^{4''}$); 9.28 (dd, 2H, J_{HH} = 6.0 Hz, 0.9 Hz, H$^{6'}$, H$^{6''}$); (CD_2Cl_2): δ 4.35 (2H, J_{HH} = 15.9 Hz, CH^{A}H^{B}, AB system); 4.74 (2H, J_{HH} = 15.9 Hz, CH^{A}H^{B}, AB system); 7.29 (d, 2H, J_{HH} = 6.3 Hz, H^{4}, H^{6}); 7.36 (dd, 1H, J_{HH}(av) = 6.3 Hz, H^{5}), 7.66 (t, 2H, J_{HH} = 6.3 Hz, H$^{5'}$, H$^{5''}$); 7.96 (d, 2H, J_{HH} = 7.2 Hz, H$^{3'}$, H$^{3''}$); 8.24 (td, 2H, J_{HH} = 7.8 Hz, 1,5 Hz, H$^{4'}$, H$^{4''}$); 9.36 (d, 2H, J_{HH} = 5.7 Hz, H$^{6'}$, H$^{6''}$); (DMSO-d_6): δ 4.45 (d, 2H, J_{HH} = 15.3 Hz, CH^{A}H^{B}, AB system); 4.95 (d, 2H, J_{HH} = 15.3 Hz, CH^{A}H^{B}, AB system); 7.20–7.32 (m, 3H, H^{4}, H^{5}, H^{6}), 7.81 (t, 2H, J_{HH} = 7.0 Hz, H$^{5'}$, H$^{5''}$); 8.10 (d, 2H, J_{HH} = 7.2 Hz, H$^{3'}$, H$^{3''}$); 8.37 (td, 2H, J_{HH} = 7.5 Hz, 1.2 Hz, H$^{4'}$, H$^{4''}$); 9.21 (d, 2H, J_{HH} = 6.0 Hz, H$^{6'}$, H$^{6''}$). ^{31}P NMR (acetone-d_6): δ –143.3 (sept, J_{PF} = 707.0 PF_6^-); (CD_3CN): δ –143.4 (sept, J_{PF} = 707.0 PF_6^-). ^{19}F NMR (acetone-d_6): δ –56.01 (d, J_{PF} = 707.7 PF_6^-); (CD_3CN): δ –45.55 (d, J_{PF} = 704.9 PF_6^-). Crystals of X-ray quality were obtained by slow evaporation of an acetone solution at room temperature.

Synthesis of [Au(N^C^N)(PPh$_3$)Cl][PF$_6$], 4[PF$_6$]. An excess of PPh_3 (65.6 mg, 0.25 mmol) was added to a solution of **3**[PF$_6$] (63.6 mg, 0.10 mmol) in 20 mL of acetone and left under stirring for 15 min. Afterwards, the solvent was evaporated to dryness and diethyl ether (15 mL) added. The solid was filtered off, washed with diethyl ether and dried under vacuum to give **4**[PF$_6$] as a white solid. Yield 82.4 mg, 93%; m.p. 175–177 °C (dec.); (Found: C 47.85; H 3.15; N 2.98%. Anal. Calcd. for $C_{36}H_{30}AuClF_6N_2P_2$:

C 48.10; H 3.36; N 3.12%. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.82 (2H, J_{HH} = 14.2 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 3.97 (2H, J_{HH} = 14.4 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 6.92 (d, 2H, J_{HH} = 7.2 Hz. H^{4}, H^{6}); 7.08 (t, 1H, J_{HH} = 7.4 Hz, H^{5}); 7.50 (t, 2H, J_{HH} = 7.4 Hz, H$^{5'}$, H$^{5''}$); 7.64 (d, 2H, J_{HH} = 7.4 Hz, H$^{3'}$, H$^{3''}$); 7.38–7.68 (m, 15H, P*Ph*$_{3}$), 7.87 (td, 2H, J_{HH} = 7.4 Hz, 1,5 Hz, H$^{4'}$, H$^{4''}$); 9.06 (dm, 2H, J_{HH} = 5.1 Hz, H$^{6'}$, H$^{6''}$); (acetone-d_{6}): δ 4.07 (2H, J_{HH} = 14.3 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 4.10 (2H, J_{HH} = 14.3 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 6.98–7.08 (m, 3H, H^{4}, H^{5}, H^{6}); 7.48–7.72 (m, 19H, H$^{3'}$, H$^{3''}$, H$^{5'}$, H$^{5''}$ + P*Ph*$_{3}$), 7.98 (td, 2H, J_{HH} = 7.5 Hz, 1,5 Hz, H$^{4'}$, H$^{4''}$); 9.24 (d, 2H, J_{HH} = 5.1 Hz, H$^{6'}$, H$^{6''}$); ($\mathrm{CD_3CN}$): δ 3.90 (2H, J_{HH} = 14.6 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 3.97 (2H, J_{HH} = 14.6 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 6.89 (d, 2H, J_{HH} = 7.2 Hz, H^{4}, H^{6}); 7.10 (ddd, 1H, J_{HH}(av) = 7.2 Hz, H^{5}); 7.36–7.66 (m, 19H, H$^{3'}$, H$^{3''}$, H$^{5'}$, H$^{5''}$ + P*Ph*$_{3}$); 7.89 (td, 2H, J_{HH} = 7.5 Hz, 1,5 Hz, H$^{4'}$, H$^{4''}$); 9.07 (d, 2H, J_{HH} = 5.4 Hz, H$^{6'}$, H$^{6''}$). ^{31}P NMR ($\mathrm{CD_2Cl_2}$): δ −143.34 (sept, *P*F$_{6}^{-}$); 26.34 (*P*Ph$_{3}$); (acetone-d_{6}): δ −143.13 (sept, *P*F$_{6}^{-}$); 26.84 (*P*Ph$_{3}$); ($\mathrm{CD_3CN}$): δ −143.52 (sept, *P*F$_{6}^{-}$); 26.83 (*P*Ph$_{3}$).

Synthesis of [Au(N^C^N)(dppe)][Cl][PF$_{6}$], 5[Cl][PF$_{6}$]. An excess of [Ph$_{2}$PCH$_{2}$]$_{2}$, (dppe), (99.6 mg, 0.25 mmol) was added to a solution of **3**[PF$_{6}$] (63.6 mg, 0.10 mmol) in 20 mL of acetone and left under stirring for 15 min. Afterwards, the solvent was evaporated to dryness and diethyl ether (15 mL) added. The solid was collected, washed with diethyl ether and dried under vacuum to give **5**[Cl][PF$_{6}$] as a white solid. Yield 90.2 mg, 87%; m.p. 143–145 °C; (Found: C 51.39; H 3.16; N 2.57%. Anal. Calcd. for $\mathrm{C_{44}H_{41}AuClF_6N_2P_3}$: C 50.95; H 3.98; N 2.70%.



^{1}H NMR (acetone-d_{6}): δ 3.15–3.33 (m+m, overlapping, 1H+1H, $\mathrm{P^{A}\text{-}C}H^{A}\mathrm{H^{A'}\text{-}C}H^{B}\mathrm{H^{B'}\text{-}P^{B}}$); 3.79 (2H, J_{HH} = 14.9 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 3.83–4.05 (m+m, overlapping 1H+1H, $\mathrm{P^{A}\text{-}CH^{A}}H^{A'}\mathrm{\text{-}CH^{B}}H^{B'}\mathrm{\text{-}P^{B}}$); 4.09 (2H, J_{HH} = 14.9 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 6.80 (d, 1H, overlapping, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, H^{4}); 6.82 (d, overlapping, 1H, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, H^{6}); 6.98 (t, 1H, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, H^{5}); 7.02–7.08 (m, 4H, H$^{3'}$, H$^{3''}$, H$^{5'}$, H$^{5''}$); 7.43–7.49 (m, 2H+2H, H^{p} Ph dppe); 7.55 (td, 2H, J = 7.5 Hz, 1.5 Hz, H$^{4'}$, H$^{4''}$); 7.66–7.70 (m, 4H+4H+2H+2H, H^{m} + H^{o} Ph dppe); 8.03 (d, 2H, $^{3}J_{\mathrm{HH}}$ = 5.4 Hz, H$^{6'}$, H$^{6''}$); 8.08–8.16 (m, 2H + 2H, H° Ph dppe); ($\mathrm{CD_2Cl_2}$): δ 2.84–3.06 (m+m, overlapping, 1H+1H, $\mathrm{P^{A}\text{-}C}H^{A}\mathrm{H^{A'}\text{-}C}H^{B}\mathrm{H^{B'}\text{-}P^{B}}$); 3.36–3.60 (m+m, overlapping 1H+1H, $\mathrm{P^{A}\text{-}CH^{A}}H^{A'}\mathrm{\text{-}CH^{B}}H^{B'}\mathrm{\text{-}P^{B}}$); 3.75 (2H, J_{HH} = 14.9 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 4.04 (2H, J_{HH} = 14.9 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 6.87 (d, 1H, overlapping, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, H^{4}); 6.88 (d, overlapping, 1H, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, H^{6}); 7.00–7.09 (m, 1H+2H+2H, H^{5}, H$^{3'}$, H3$''$, H$^{5'}$, H$^{5''}$); 7.33–7.40 (m, 2H+2H, H^{p} Ph dppe); 7.49–7.70 (m, 4H+4H+2H+2H+2H, H^{m} + H^{o} Ph dppe, H$^{4'}$, H$^{4''}$); 7.93–7.97 (m, 2H+2H, H^{o} Ph dppe); 8.00 (d, 2H, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, H$^{6'}$, H$^{6''}$); ($\mathrm{CD_3CN}$): δ 2.82–3.02 (m+m, overlapping, 1H+1H, $\mathrm{P^{A}\text{-}C}H^{A}\mathrm{H^{A'}\text{-}C}H^{B}\mathrm{H^{B'}\text{-}P^{B}}$); 3.36–3.60 (m+m, overlapping 1H+1H, $\mathrm{P^{A}\text{-}CH^{A}}H^{A'}\mathrm{\text{-}CH^{B}}H^{B'}\mathrm{\text{-}P^{B}}$); 3.73 (2H, J_{HH} = 14.7 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 4.05 (2H, J_{HH} = 14.7 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 6.76 (d, 1H, overlapping, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, H^{4}); 6.78 (d, overlapping, 1H, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, H^{6}); 6.94–7.10 (m, 1H+2H+2H, H^{5}, H$^{3'}$, H$^{3''}$, H$^{5'}$, H$^{5''}$); 7.34–7.41 (m, 2H+2H, H^{p} Ph dppe); 7.53–7.67 (m, 4H+4H+2H+2H, H^{m} dppeP^{A}, H^{m} dppeP^{B}, H^{o} dppeP^{A}, H^{o} dppeP^{B}); 7.74 (td, 2H, J = 7.5 Hz, 1.5 Hz, H$^{4'}$, H$^{4''}$); 7.92–8.02 (m, 2H+2H+2H, H$^{6'}$, H$^{6''}$, H^{o} dppeP^{A}, H^{o} dppeP^{B}). ^{31}P NMR (acetone-d_{6}): δ −143.39 (sept, 1P, *P*F$_{6}^{-}$); 53.63 (d, 1P, J_{PP} = 7.0 Hz, P_{A}); 54.20 (d, 1P, J_{PP} = 7.0 Hz, P_{B}); ($\mathrm{CD_2Cl_2}$): δ −143.16 (sept, 1P, *P*F$_{6}^{-}$); 55.26 (d, 1P, J_{PP} = 7.0 Hz, P_{A}); 56.54 (d, 1P, J_{PP} = 7.0 Hz, P_{B}); ($\mathrm{CD_3CN}$): δ −143.51 (sept, 1P, *P*F$_{6}^{-}$); 55.85 (d, 1P, J_{PP} = 7.0 Hz, P_{A}); 56.54 (d, 1P, J_{PP} = 7.0 Hz, P_{B}).

Synthesis of [Au(N^C^N)(dppe)][PF$_{6}$]$_{2}$, 5[PF$_{6}$]$_{2}$. K[PF$_{6}$] (18.4 mg, 0.1 mmol) was added to a suspension of compound **5**[Cl][PF$_{6}$] (103.5 mg, 0.1 mmol) in 30 mL of acetone. The suspension was left under stirring at room temperature for 4 h. The solution was concentrated to small volume and 15 mL of water were added. The white precipitate obtained was filtered off, washed with ice-cold methanol and diethyl ether, then dried *in vacuo* to give compound **5**[PF$_{6}$]$_{2}$. Yield 99.2 mg, 87%; m.p. 185–186 °C. (Found: C 46.27; H 3.03; N 2.48%. Anal. Calcd. for $\mathrm{C_{44}H_{39}AuF_{12}N_2P_4}$: C 46.17; H 3.43 N 2.45%). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 2.86–3.03 (m + m, overlapping, 1H + 1H, $\mathrm{P^{A}\text{-}C}H^{A}\mathrm{H^{A'}\text{-}C}H^{B}\mathrm{H^{B'}\text{-}P^{B}}$); 3.52–3.70 (m + m, overlapping 1H + 1H, $\mathrm{P^{A}\text{-}CH^{A}}H^{A}\mathrm{\text{-}CH^{B}}H^{B'}\mathrm{\text{-}P^{B}}$); 3.89 (2H, J_{HH} = 14.6 Hz, $\mathrm{C}H^{A}\mathrm{H}^{B}$, AB system); 3.96 (2H, J_{HH} = 14.6 Hz, $\mathrm{CH}^{A}H^{B}$, AB system); 6.97–6.98 (m, 3H, H^{4}, H^{5}, H^{6}); 7.29 (t, 2H, J_{HH} = 6.9 Hz, H$^{5'}$, H$^{5''}$); 7.43–7.57 (m, overlapping, 2H + 2H + 2H, H$^{3'}$, H$^{3''}$, H^{p} dppeP^{A}, H^{p} dppeP^{B}); 7.58–7.82 (m, 4H+4H+4H+4H+2H, H^{m} dppeP^{A}, H^{m} dppeP^{B}, H° dppeP^{A}, H° dppeP^{B}, H$^{4'}$, H$^{4''}$); 8.60 (d, 2H, $^{3}J_{\mathrm{HH}}$ = 5.4 Hz, H$^{6'}$, H$^{6''}$). ^{31}P NMR ($\mathrm{CD_3CN}$): δ −143.51 (sept, 1P, *P*F$_{6}^{-}$); 48.22 (d, 1P, J_{PP} = 4.0 Hz, P_{A}) and 55.07 (d, 1P, $^{2}J_{\mathrm{PP}}$ = 4.0 Hz, P_{B}).

Synthesis of [Au(N^C^N)(H$_{2}$O)][OTf][PF$_{6}$], 6[OTf][PF$_{6}$]·*n*H$_{2}$O. (a) *n* = 0: solid Ag(OTf) (38.5 mg, 0.15 mmol) was added to a solution of **3**[PF$_{6}$] (63.6 mg, 0.10 mmol) in dichloromethane (20 mL). The mixture was stirred in the dark for 1 h at room temperature; then the silver chloride was removed by filtration and the solution evaporated to dryness. The crude product was recrystallized from dichloromethane/*n*-pentane to give **6**[OTf][PF$_{6}$] as a white solid. Yield 50.0 mg, 65%; (Found: C 29.45; H 2.21; N 3.50%. Anal. Calcd. for $\mathrm{C_{19}H_{17}AuF_9N_2O_4PS}$: C 29.70; H 2.23; N 3.65%. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 4.31 (2H, J_{HH} = 15.9 Hz, AB system, $\mathrm{CH}^{A}H^{B}$); 5.04 (br, J_{HH} = 16.2 Hz, 2H, AB system, $\mathrm{C}H^{A}\mathrm{H}^{B}$); 6.67 (br, 2H, *H*$_{2}$O); 7.21 (d, 1H, J_{HH} = 7.2 Hz, H^{4}, H^{6}); 7.33 (dd, 1H, J_{HH}(av) = 7.4 Hz, H^{5}); 7.70 (t, 2H, J_{HH} = 6.6 Hz, H$^{5'}$, H$^{5''}$); 7.93 (d, 2H, J_{HH} = 7.8 Hz, H$^{3'}$, H$^{3''}$); 8.23 (td, 2H, J_{HH} = 7.5 Hz, 1.2 Hz, H$^{4'}$, H$^{4''}$); 9.15 (d, 2H, J_{HH} = 5.7 Hz, H$^{6'}$, H$^{6''}$); ^{19}F NMR (acetone-d_{6}): δ −50.65 (d, J_{PF} = 710.9 P*F*$_{6}^{-}$); −57.37 (s, $\mathrm{CF_3SO_3^{-}}$).

(b) *n* = 1: The same reaction carried out in acetone afforded **6**[OTf][PF$_{6}$]·H$_{2}$O. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.90 (br, 4H, *H*$_{2}$O); 4.30 (2H, J_{HH} = 15.9 Hz, AB system, $\mathrm{CH}^{A}H^{B}$); 5.05 (br, 2H, AB system, $\mathrm{C}H^{A}\mathrm{H}^{B}$); 7.21 (d, 1H, J_{HH} = 7.5 Hz, H^{4}, H^{6}); 7.33 (dd, 1H, J_{HH}(av) = 7.4 Hz, H^{5}); 7.70 (t, 2H, J_{HH} = 6.4 Hz, H$^{5'}$, H$^{5''}$); 7.94 (d, 2H, J_{HH} = 7.5 Hz, H$^{3'}$, H$^{3''}$); 8.23 (td, 2H, J_{HH} = 7.5 Hz, 1.2 Hz, H$^{4'}$, H$^{4''}$); 9.15

(br, 2H, $H^{6'}$, $H^{6''}$). ^{19}F NMR (acetone-d_6): δ –50.63 (d, J_{PF} = 711.1 PF_6^-); –57.44 (s, $CF_3SO_3^-$, OTf).

Synthesis of [Au(N^C^N)(OAc)][PF$_6$], 7[PF$_6$]. Solid Ag(OAc) (25.0 mg, 0.15 mmol) was added to a solution of **3**[PF$_6$] (63.6 mg, 0.10 mmol) in 20 mL of acetone. The mixture was stirred in the dark for 24 h at room temperature; then the silver chloride was removed by filtration and the solution concentrated to small volume. Addition of diethyl ether (15 mL) afforded a white precipitate which was filtered off, washed with diethyl ether and dried *in vacuo* to give **7**[PF$_6$] as a white solid. Yield 38.2 mg, 58%; m.p. 160–162 °C (dec.); (Found: C 36.15; H 2.21; N 4.23%. Anal. Calcd. for $C_{20}H_{18}AuClF_6N_2O_2P$: C 36.38; H 2.75; N 4.24%. IR(ν_{max} (Nujol)/cm^{-1}): 1620m; 1610m; 1315m. ^{1}H NMR (acetone-d_6): δ 1.95 (s, 3H, CH_3COO); δ 4.64 (2H, J_{HH} = 15.8 Hz, AB system, CH^AH^B); 4.84 (2H, J_{HH} = 15.8 Hz, AB system, CH^AH^B); 7.33 (s, 3H, H^4, H^5, H^6), 7.89 (t, 2H, J_{HH}(av) = 6.5 Hz, $H^{5'}$, $H^{5''}$); 8.22 (d, 2H, J_{HH} = 7.8 Hz, $H^{3'}$, $H^{3''}$); 8.46 (td, 2H, J_{HH} = 7.8 Hz, 1.6 Hz, $H^{4'}$, $H^{4''}$); 9.00 (dd, 2H, J_{HH} = 6.0 Hz, 0.9 Hz, $H^{6'}$, $H^{6''}$). ^{31}P NMR (acetone-d_6): δ –143.16 (sept, PF_6^-).

X-Ray data collection and structure determination†

Crystal data are summarised in Table 2. The diffraction experiments were carried out on a Bruker APEX II CCD area-detector diffractometer, at 296 K for **1**[AuCl$_4$]Cl and **2**, and at 150 K for **3**[PF$_6$], using Mo-Kα radiation (λ = 0.71073) with a graphite crystal monochromator in the incident beam. The crystal of **3**[PF$_6$] gave an excellent diffraction, whereas for the other two crystals the diffraction was poor (actually bad for **1**[AuCl$_4$]Cl). No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[21] and an empirical absorption correction was applied (SADABS)[22] to the collected reflections. The calculations were performed using the Personal Structure Determination Package[23] and the physical constants tabulated therein.[24] The structures were solved by direct methods (SHELXS)[25] 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 **1**[AuCl$_4$]Cl, cation $\mathbf{1}^{2+}$ lies on a crystallographic two-fold axis, with atoms C(2) and C(5) lying on the axis. The non hydrogen atoms of this cation (C and N atoms) had to be refined with isotropic thermal factors. Hydrogen atoms H(9), bonded to C(2), and H(10), bonded to C(5), were detected in the final Fourier maps, and not refined. The overall crystallographic results for **1**[AuCl$_4$]Cl are very poor, but they are nevertheless sufficient to show that in its packing an extremely interesting supramolecular structure is present, that deserves to be described. This is done exhaustively, by means of both verbal descriptions and relevant drawings, in the ESI.†

Table 2 Crystallographic data

Compound	**1**[AuCl$_4$]Cl	**2**	**3**[PF$_6$]
Formula	$C_{18}H_{18}AuCl_5N_2$	$C_{18}H_{15}ClHgN_2$	$C_{18}H_{15}AuClF_6N_2P$
M	636.59	495.38	636.72
Colour	Yellow	Colourless	Pale yellow
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Abm2$	$C2/c$	$P2_1/n$
a/Å	4.5498(4)	15.1595(12)	9.5120(4)
b/Å	26.3130(26)	15.3382(12)	11.9014(4)
c/Å	18.0718(18)	15.9166(13)	17.2639(7)
α/°	90	90	90
β/°	90	116.039(1)	101.343(2)
γ/°	90	90	90
U/Å^3	2163.5(19)	3325.2(5)	1916.2(1)
Z	4	8	4
F(000)	1216	1872	1208
D_c/g cm^{-3}	1.954	1.979	2.207
T/K	296	296	150
λ (Mo-Kα)	0.71073	0.71073	0.71073
Crystal dimensions/mm	0.05 × 0.15 × 0.22	0.14 × 0.27 × 0.41	0.21 × 0.23 × 0.45
μ(Mo-Kα)/cm^{-1}	74.17	94.15	79.49
Min. and max. transmiss. factors	0.366–1.000	0.461–1.000	0.391–1.000
Scan mode	ω	ω	ω
Frame width/°	0.45	0.50	0.40
Time per frame/s	25	20	10
No. of frames	2760	3240	750
Detector-sample distance/cm	6.00	6.00	6.00
θ-range/°	3.00–25.00	3.00–28.00	3.00–27.00
Reciprocal space explored	Full sphere	Full sphere	Full sphere
No. of reflections (total; independent)	16 357; 2344	46 165; 4637	10 043; 4289
R_{int}	0.0673	0.0442	0.0215
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.095, 0.132	0.081, 0.128	0.042, 0.060
Conventional R_1 index [$I > 2\sigma(I)$]	0.056	0.043	0.026
Reflections with $I > 2\sigma(I)$	1377	2230	3658
No. of variables	68	199	262
Goodness of fit[b]	0.962	1.016	1.014

[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 = 0.02 for **3′**[PF$_6$], = 0.03 for **1**[AuCl$_4$]Cl, and = 0.04 for **2**.

In the three compounds, all the other non-hydrogen atoms were refined with anisotropic thermal parameters, and all the other hydrogen atoms were placed in their ideal positions (C–H or N–H = 0.97 Å), with the thermal parameter U being 1.10 times that of the atom to which they are attached, and not refined. For non-centrosymmetric **1**[AuCl$_4$]Cl, both the inverted structure models were fully refined: final R_2 and R_{2w} indices were 0.095 and 0.132 for the correct one, and 0.109 and 0.151 for the other. In the final Fourier maps the maximum residuals were 3.57(1.34) e Å^{-3} at 0.97 Å from Au, 2.19(1.01) e Å^{-3} at 0.28 Å from Hg, and 1.48(26) e Å^{-3} at 0.53 Å from Au, for **1**[AuCl$_4$]Cl, **2**, and **3**[PF$_6$], respectively. Minimum peaks (holes), in the same order, were −2.27(1.34), −2.19(1.01), and −1.14(26) e Å^{-3}.

Computational details

All quantum chemical calculations were carried out using the Gaussian03 program system.[26] The equilibrium and transition structures were computed using gradient-corrected density functional theory (DFT) with the Becke three-parameter exchange functional[27] and the Lee–Yang–Parr correlation functional (B3LYP).[28] For gold, a multielectron adjusted quasirelativistic effective core potential covering 60 electrons ([Kr]4d^{10}4f^{14}) and an (8s7p6d/[6s5p3d]-GTO valence basis set (31111, 22111, 411, 21) were used.[29] To further improve the quality of basis set, f-type polarization functions in a (21) contraction were added.[30] All non-metal atoms (C, H, Cl, and N) were described with the Dunning correlation consistent cc-pVDZ and cc-pVTZ basis sets.[31] Geometries of all stationary points were calculated at the B3LYP/cc-pVTZ and MP2/cc-pVDZ[32] levels.

The transition state for the inversion between the left- and right-handed twisted forms of **3**$^+$ was scrutinized by performing Intrinsic Reaction Coordinate (IRC) calculations using the Gonzalez-Schlegel second-order method.[33] The reaction path leading down from the transition structure in both directions on the potential energy surface (PES) was thus studied to ensure that the transition states connected the desired reactant and product. Further, the normal modes corresponding to the imaginary frequencies of the transition state structures were examined with molecular visualization to verify that the nuclear motion tends to deform the transition state structure along the pertinent reaction coordinate. To characterize all stationary points, the Hessian (matrix of energy second derivatives) was calculated and diagonalized at each stationary point which also yielded zero-point energy (ZPE) corrections.

Acknowledgements

We are grateful to the Ministero dell'Istruzione, Università e della Ricerca (MIUR) and the Università degli Studi di Sassari for financial support of this research (PRIN Project). G. A. gratefully acknowledges the Regione Autonoma della Sardegna (RAS) for a Master & Back fellowship. We also thank Johnson Matthey for a generous loan of H[AuCl$_4$]·3H$_2$O, while M. K. G. is similarly grateful for a postdoctoral scholarship from the Research Council of Norway under the GASSMAKS program, project no. 185513/I30. Finally, thanks are due to the NOTUR project (http://www.notur.com, project No. NN2147K) for a generous grant of computing time.

References

1 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020–1024.

2 (*a*) Selected Reviews: R. A. Gossage, L. A. van de Kuil and G. van Koten, *Acc. Chem. Res.*, 1998, **31**, 423–431; (*b*) B. Rybtchinski and D. Milstein, *Angew. Chem. Int. Ed.*, 1999, **38**, 870–883; (*c*) M. Albrecht and G. van Koten, *Angew. Chem. Int. Ed.*, 2001, **40**, 3750–3781; (*d*) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792; (*e*) J. T. Singleton, *Tetrahedron*, 2003, **59**, 1837–1857; (*f*) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239–2246; (*g*) D. Morales-Morales, *Rev. Soc. Quím. Méx.*, 2004, **48**, 338–346; (*h*) J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527–2571; (*i*) D. Pugh and A. A. Danopoulos, *Coord. Chem. Rev*, 2007, **251**, 610–641; (*j*) B. Wieczorek, H. P. Dijkstra, M. R. Egmond, R. J. M. Klein Gebbink and G. van Koten, *J. Organomet. Chem.*, 2009, **694**, 812–822; (*k*) J. A. G. Williams, *Chem. Soc. Rev.*, 2009, **38**, 1783–1801.

3 *The Chemistry of Pincer Compounds*, D. Morales-Morales and C. M. Jensen, ed.; Elsevier: Amsterdam, 2007.

4 (*a*) Some recent papers: K. Takenaka, M. Minakawa and Y. Uozumi, *J. Am. Chem. Soc.*, 2005, **127**, 12273–12281; (*b*) J. Kjellgren, H. Sundén and K. J. Szabó, *J. Am. Chem. Soc.*, 2005, **127**, 1787–1796; (*c*) H. Jude, J. A. Krause Bauer and W. B. Connick, *Inorg. Chem.*, 2005, **44**, 1211–1220; (*d*) S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard and J. A. G. Williams, *Inorg. Chem.*, 2005, **44**, 9690–9703; (*e*) B. Soro, S. Stoccoro, G. Minghetti, A. Zucca, M. A. Cinellu, S. Gladiali, M. Manassero and M. Sansoni, *Organometallics*, 2005, **24**, 53–61; (*f*) C. H. M. Amijs, A. W. Kleij, G. P. M. van Klink, A. L. Spek and G. van Koten, *Organometallics*, 2005, **24**, 2773–2779; (*g*) A. J. Canty, T. Rodemann, B. W. Skelton and A. H. White, *Inorg. Chem. Commun.*, 2005, **8**, 55–57; (*h*) M. S. Yoon, D. Ryu, J. Kim and K. H. Ahn, *Organometallics*, 2006, **25**, 2409–2411; (*i*) B. Soro, S. Stoccoro, G. Minghetti, A. Zucca, M. A. Cinellu, M. Manassero and S. Gladiali, *Inorg. Chim. Acta*, 2006, **359**, 1879–1888; (*j*) S. Yamaguchi, T. Katoh, H. Shinokubo and A. Asuka, *J. Am. Chem. Soc.*, 2007, **129**, 6392–6393; (*k*) S. W. Botchway, M. Charnley, J. W. Haycock, A. W. Parker, D. L. Rochester, J. A. Weinstein and J. A. G. Williams, *Proc. Natl. Acad. Sci. USA*, 2008, **105**, 16071–16076; (*l*) L.-Y. Wu, X.-Q. Hao, Y.-X. Xu, M.-Q. Ja, Y.-N. Wang, J.-F. Gong and M.-P. Song, *Organometallics*, 2009, **28**, 3369–3380; (*m*) X.-Q. Hao, Y.-N. Wang, J.-R. Liu, K.-L. Wang, J.-F. Gong and M.-P. Song, *J. Organomet. Chem.*, 2010, **695**, 82–89; (*n*) H. Nishiyama and J.-I. Ito, *Chem. Commun.*, 2010, **46**, 203–212; (*o*) K. L. Garner, L. F. Parkers, J. D. Piper and J. A. G. Williams, *Inorg. Chem.*, 2010, **49**, 476–487.

5 (*a*) P. A. Bonnardel, R. V. Parish and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1996, 3185–3193; (*b*) M. Contel, M. Stol, M. A. Casado, G. P. M. van Klink, D. D. Ellis, A. L. Spek and van G. Koten, *Organometallics*, 2002, **21**, 4556–4559.

6 S. Stoccoro, G. Alesso, M. A. Cinellu, G. Minghetti, A. Zucca, M. Manassero and C. Manassero, *Dalton Trans.*, 2009, 3467–3477.

7 H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 505–515.

8 See for example: D. J. Cárdenas, A. M. Echavarren and M. C. Ramírez de Arellano, *Organometallics*, 1999, **18**, 3337–3341; D. J. de Geest, B. J. O'Keefe and P. J. Steel, *J. Organomet. Chem.*, 1999, **579**, 97–105.

9 For information on the interesting packing of **1**[AuCl$_4$]Cl, see the Experimental Section and ESI.

10 (*a*) J. Vicente, M. T. Chicote, M. D. Bermudez, M. J. Sanchez-Santano, P. G. Jones, C. Fittschen and G. M. Sheldrick, *J. Organomet. Chem.*, 1986, **310**, 401–409; (*b*) J. Vicente, M. T. Chicote, A. Arcas, M. Artigao and R. Jimenez, *J. Organomet. Chem.*, 1983, **247**, 123–129.

11 More parameters are given in Table S2 in the ESI.

12 P. K. Byers and A. J. Canty, *Organometallics*, 1990, **9**, 210.

13 Notably, the chemical shifts of the pincer complexes **3**[X] are not affected by the counter-ion: see Table S3 in the ESI.

14 M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1996, 4217–4225.

15 E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443–449.

16 M. Nonoyama, K. Nakajima and K. Nonoyama, *Polyhedron*, 2001, **20**, 3019–3025.

17 The syntheses and reactivity studies of these gold(III) cyclometallated complexes have been recently reviewed: W. Henderson, *Adv. Organomet. Chem*, 2006, **54**, 207–265.

18 See for example: J. Vicente, M.-D. Bermúdez, M. T. Chicote and M.-J. Sánchez-Santano, *J. Organomet. Chem.*, 1990, **381**, 285–292.

19 S. J. Berners-Price, M. A. Mazid and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1984, 969–974.

20 See for example: J. Vicente, M. T. Chicote, M. D. Bermudez and M. Garcia-Garcia, *J. Organomet. Chem.*, 1985, **295**, 125–130.

21 *SAINT Reference manual*, Siemens Energy and Automation, Madison, W1, 1994–1996.

22 G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Gottingen, 1997 Gottingen, 1997.

23 B. A. Frenz, *Comput. Phys.*, 1988, **2**, 42.

24 *Crystallographic Computing 5*, Oxford University Press: Oxford, U.K., 1991, Chapter 11, p. 126.

25 G. M. Sheldrick, (1985) *SHELXS 86*. Program for the solution of crystal structures. University of Gottingen, Germany.

26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople,*Gaussian 03, Rev. C.02*Gaussian Inc.: Wallingford, CT, 2004.

27 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

28 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785–9.

29 D. Andrae, U. Haussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123–141.

30 M. K. Ghosh, M. Tilset, A. Venugopal, R. H. Heyn and O. Swang, *J. Phys. Chem. A* Submitted.

31 (*a*) T. H. Dunning, Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023; (*b*) R. A. Kendall, T. H. Dunning, Jr. and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806; (*c*) D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, 1993, **98**, 1358–1371.

32 C. Moller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618–622.

33 C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523–5527.