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The Coordination Behaviour of Ferrocene-based Pyridylphosphine Ligands towards Ag^I and Au^I

Ulrich Siemeling,*[a] Thorsten Klemann,[a] Clemens Bruhn,[a] Jiří Schulz,[b] and Petr Štěpnička[b]

In Memory of Professor Kurt Dehnicke

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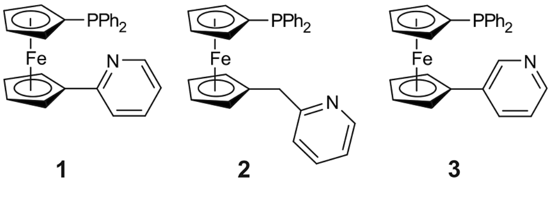
Abstract. The reaction of the *P*,*N*-ligands $[Fe(C_5H_4\text{-}PPh_2)(C_5H_4\text{-}2\text{-}py)]$ (**1**) (2-py = pyrid-2-yl), $[Fe(C_5H_4\text{-}PPh_2)(C_5H_4\text{-}CH_2\text{-}2\text{-}py)]$ (**2**) and $[Fe(C_5H_4\text{-}PPh_2)(C_5H_4\text{-}3\text{-}py)]$ (**3**) (3-py = pyrid-3-yl) with $Ag[BF_4]$ in a 1:1 stoichiometric ratio afforded complexes of the type $[Ag(L)][BF_4]$ (L = **1–3**), which were structurally characterised by X-ray diffraction. Two structure types were observed in the solid state, viz. coordination polymer (L = **1**, **2**) and cyclic dimer (L = **2**, **3**). The reaction of **1–3** with one equivalent of [AuCl(tht)] (tht = tetrahydrothiophene) afforded complexes of the type [AuCl(L-κ*P*)] (L = **1–3**), whose crystal structures were determined by X-ray diffraction. Their reactions with one equivalent of $Ag[BF_4]$ gave products of the general composition $[Au(L)][BF_4]$; of these the cyclic dimer $\{[Au(\mu\text{-}\mathbf{1})][BF_4]\}_2$ was structurally characterised by X-ray diffraction. The *P*,*N*,*P*-ligand $C_5H_3N\text{-}2,6\text{-}(fcPPh_2)_2$ (**4**, fc = 1,1′-ferrocenediyl) was synthesised by Negishi cross-coupling of $Ph_2PfcZnCl$ with 2,6-dibromopyridine. Its crystal structure was determined by X-ray diffraction. The reaction of **4** with two equivalents of [AuCl(tht)] afforded the dinuclear gold(I) complex $[(AuCl)_2(\mu\text{-}\mathbf{4}\text{-}\kappa^2P,P)]$. The mononuclear gold(I) complex $[Au(\mathbf{4}\text{-}\kappa^2P,P)][SbF_6]$ was obtained in a one-pot reaction of **4** with one equivalent of [AuCl(tht)] and subsequently with one equivalent of $Ag[SbF_6]$; it contains **4** in a *trans*-chelating binding mode, as revealed by a crystal structure determination.

Introduction

Pyridylphosphines are highly versatile *P*,*N*-ligands which are widely used in coordination chemistry. The combination of a soft *P*-donor site with a borderline to hard *N*-donor site has been utilised for applications in catalysis and supramolecular chemistry.[1] We have a long-standing interest in ferrocene-based bidentate ligands with a focus on symmetric *N*,*N*-ligands which contain a 1,1′-ferrocenediyl (fc) backbone.[2] We recently expanded our work to related heteroditopic *P*,*N*-systems, since to date the majority of ferrocene-based *P*,*N*-ligands does not contain the 1,1′-ferrocenediyl backbone but rather have the *P*- and *N*-donor groups attached to the same cyclopentadienyl ring.[3] Following our recent studies on phosphinoferrocene carboxamides with pyridine pendants,[4a,b] we have been addressing, inter alia, the pyridylphosphine ligands $[Fe(C_5H_4\text{-}PPh_2)(C_5H_4\text{-}2\text{-}py)]$ (**1**, 2-py = pyrid-2-yl), $[Fe(C_5H_4\text{-}PPh_2)(C_5H_4\text{-}CH_2\text{-}2\text{-}py)]$ (**2**) and $[Fe(C_5H_4\text{-}PPh_2)(C_5H_4\text{-}3\text{-}py)]$ (**3**, 3-py = pyrid-3-yl) (Scheme 1) in this context and recently reported results of a study focusing on their coordination behaviour toward a range of tetracoordinate metal atoms.[4c,d] The pseudotetrahedral, d^{10} configured Group 12 metal atoms Zn^{II}, Cd^{II}, and Hg^{II} were investigated particularly comprehensively.[4d] Saliently, we found three structure types in the solid state for the Group 12 metal dihalogenido complexes $[MX_2(L)]$ (L = **1–3**), viz. chelate, cyclic dimer and chain-like coordination polymer. Ligand **1** prefers the formation of chelates $[MX_2(\mathbf{1}\text{-}\kappa^2N,P)]$. **3** forms coordination polymers $[MX_2(\mu\text{-}\mathbf{3})]_n$. With the more flexible **2** all three structure types can occur. The P–*M*–N angle is much larger in the chelates (up to 125°) than in the ligand-bridged structures (≤ 109°).



Scheme 1. *P*,*N*-ligands investigated in this work.

We have now extended our study systematically to Ag^I and Au^I. Like the previously investigated Zn^{II}, Cd^{II}, and Hg^{II}, these monovalent Group 11 metal atoms are d^{10} configured. However, in contrast to the divalent Group 12 metals they frequently exhibit coordination numbers lower than four and hence particularly large coordination angles. Whereas the coordination chemistry

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* Prof. Dr. U. Siemeling
Fax: +49-561-804-4777
E-Mail: siemeling@uni-kassel.de
[a] Institut für Chemie
Universität Kassel
Heinrich-Plett-Str. 40
34132 Kassel, Germany
[b] Department of Inorganic Chemistry
Faculty of Science
Charles University in Prague
Hlavova 2030
12840 Prague 2, Czech Republic

of Au^I is clearly dominated by linear two-coordinate complexes, Ag^I is more flexible, typically giving rise to coordination numbers from two to four.[5] A moderate number of structurally characterised Ag^I pyridylphosphine complexes have been reported,[6] with PPh_2(2-py) being the most popular such ligand.[7] It is instructive to inspect representative silver(I) and gold(I) complexes of this iconic pyridylphosphine to illustrate pertinent differences between Ag^I and Au^I. The theoretically calculated strength of the M^+–L interaction (gas phase; M = Ag, Au; L = pyridine, PH_3) increases in the order Ag < Au, this increase being notably steeper for L = PH_3.[8] It is evident that pyridyl *N*-coordination is rather unattractive for these soft metal centres and occurs only if their coordination requirements cannot be satisfied otherwise.[9] For example, no *N*-coordination is observed for the chlorido complexes [MCl{PPh_2(2-py)}] (M = Ag,[10] Au[11]). Whereas the gold complex is monomeric (coordination number 2), the silver complex is tetrameric with a heterocubanoid Ag_4Cl_4 core (coordination number 4). Replacement of Cl^- by less strongly coordinating anions may result in pyridyl *N*-coordination, as is observed, for example, for the silver nitrito and nitrato analogues. These complexes crystallise as cyclic "head-to-tail" dimers, viz. [Ag(NO_2–κ^2O){μ-PPh_2(2-py)}$]_2$[12] and [Ag(NO_3–κ^1O){μ-PPh_2(2-py)}$]_2$,[13] exhibiting coordination numbers of 4 and 3, respectively. With the essentially non-coordinating tetrafluoroborate anion, NMR spectroscopic data ($CDCl_3$ solution) are in accord with the cyclic "head-to-tail" dimer [Ag{μ-PPh_2(2-py)}$]_2[BF_4]_2$[14] containing dicoordinate Ag^I. The gold analogue is known to exhibit such a structure in the solid state.[15] The "head-to-tail" dimer [Ag_2{μ-PPh_2(2-py)}$_2${PPh_2(2-py)-κP}]$(ClO_4)_2$, where an additional PPh_2(2-py) ligand is *P*-coordinated to one of the two silver atoms, has also been structurally characterised.[16] The structure of the heterobimetallic complex [Ag(ClO_4–κ^1O)$_2$-{μ-PPh_2(2-py)}$_2$Au$]_2$[14] demonstrates that the preference of Au^I for *P*-coordination is even stronger than that of Ag^I. The silver atom is in a distorted pseudotetrahedral environment, being coordinated by two nitrogen atoms and one oxygen atom each of the weakly coordinating perchlorate anions. The gold atom, on the other hand, is in an essentially linear *P,P*-dicoordinate environment. Finally, the *P*-philicty of Au^I is also reflected by the fact that [AuCl(SMe_2)] cleanly affords the tricoordinate complex [AuCl{PPh_2(2-py)}$_2$] with two equivalents of PPh_2(2-py).[17] In contrast, the analogous reaction of AgCl with two equivalents of the ligand results in the formation of the dinuclear complex [Ag_2(μ-Cl)$_2${μ-PPh_2(2-py)}{PPh_2(2-py)-κP}$_2$], which contains two tetracoordinate, chlorido-bridged Ag^I atoms, one being *P,P*- and the other one *P,N*-coordinated.[10]

Results and Discussion

Silver Complexes

The reaction of ligands **1**–**3** with one equivalent of silver tetrafluoroborate in methanol afforded products of the expected composition [Ag(L)][BF_4] (L = **1**–**3**) according to elemental analysis. Single-crystals were obtained in each case by recrystallisation from chloroform. The results of the X-ray diffraction studies are shown in Figure 1, Figure 2 and Figure 3. The crystalline compounds obtained with ligands **1** and **2** are coordination polymers, whereas a cyclic dimer was obtained with ligand **3**. Recrystallisation of [Ag(**2**)][BF_4] from dichloromethane gave single-crystals of the cyclic dimer {[Ag(μ-**2**)][BF_4]}$_2$ (Figure 4). This result underlines the structural flexibility of ligand **2**, which had already shown similar "ambiguous" coordination behaviour with zinc bromide, affording both the chelate [$ZnBr_2$(**2**-κ^2N,P)] and the cyclic dimer [$ZnBr_2$(μ-**2**)]$_2$.[4d] The silver atoms are *P,N*-coordinated in each case. Pertinent bond parameters are collected in Table 1.

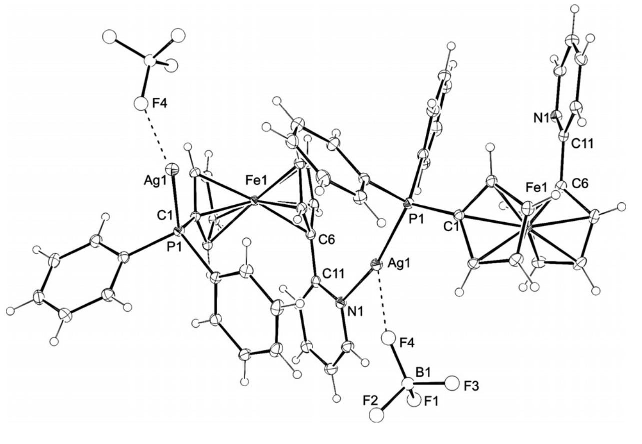

Figure 1. Section of the polymeric chain of {[Ag(μ-**1**)][BF_4]}$_n$ in the crystal.

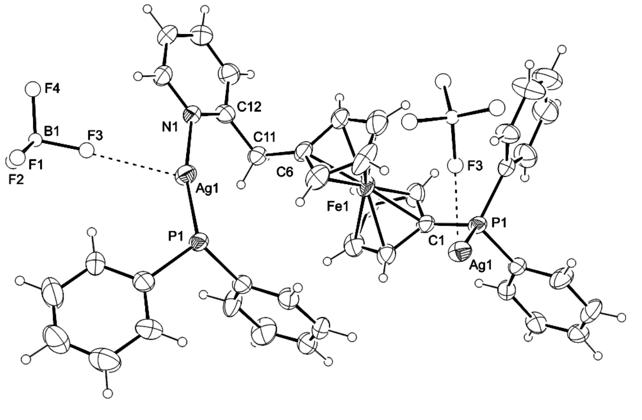

Figure 2. Section of the polymeric chain of {[Ag(μ-**2**)][BF_4]}$_n$ in the crystal.

The Ag–N and Ag–P bond lengths are each almost identical for these complexes, their average values being ca. 2.17 Å and 2.36 Å, respectively. These values compare well to those of closely related compounds. For example, Ag–N and Ag–P bond lengths of 2.181(5) Å and 2.376(2) Å, respectively, were reported for [{Ag(PPh_3)}$_2$(μ-4,4′-bipy)]$(ClO_4)_2$, which exhibits a P–Ag–N angle of 158.4(1)°.[18] A very similar situation has also been found for the *P,N*-coordinated Ag^I atom in the dinuclear [Ag_2{μ-PPh_2(2-py)}$_2${PPh_2(2-py)-κP}]$(ClO_4)_2$ already mentioned above [Ag–N 2.227(6) Å, Ag–P 2.368(2) Å, P–Ag–N 162.8(2)°].[16] Note that for both these compounds the P–Ag–N angle deviates from the ideal value of 180° ex-

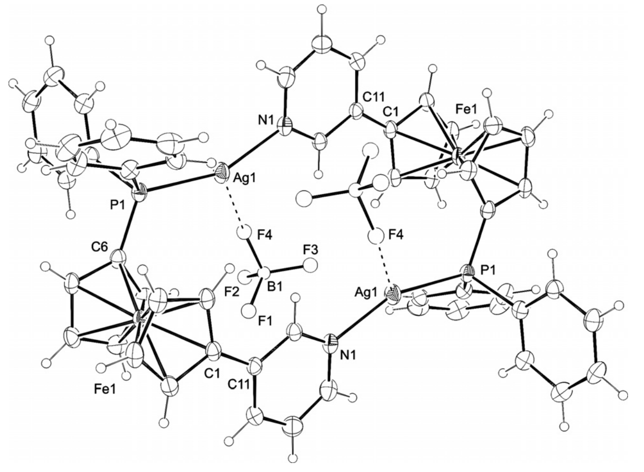

Figure 3. Molecular structure of the cyclic dimer $\{[Ag(\mu\text{-}\mathbf{3})][BF_4]\}_2$ in the crystal.

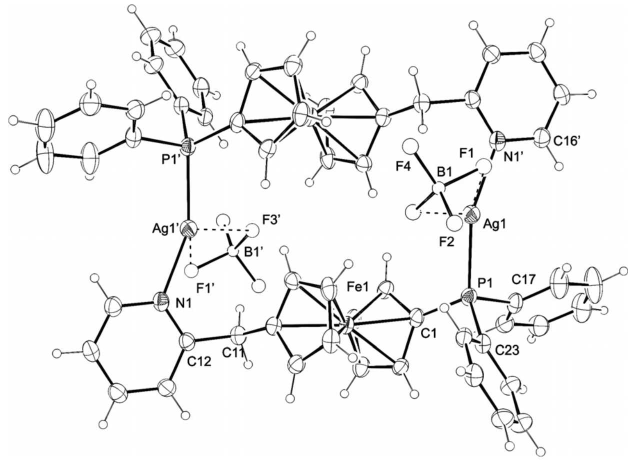

Figure 4. Molecular structure of the cyclic dimer $\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_2$ in the crystal.

pected for a strictly dicoordinate Ag^I environment. This can be attributed to weak interactions of the Ag^I atom with the perchlorate anion, giving rise to the 2+1 coordination motif frequently observed with Ag^I.[5a] In our four cases, an analogous weak interaction of the Ag^I atom with the tetrafluoroborate anion is reflected by P–Ag–N angles between ca. 149° and 167°. The smallest angle occurs in the case of $\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_2$, which exhibits two Ag···F contacts per silver atom. In the other three cases, a single such contact is observed and the deviation from linearity correlates roughly with the Ag···F distance, which ranges from ca. 2.67 Å to ca. 2.75 Å. These distances are well below the sum of the van der Waals radii of silver and fluorine (ca. 3.2 Å),[19] but considerably longer than the Ag–F distances in AgF (ca. 2.47 Å),[20] and it may be concluded that the Ag^I–anion interaction is mainly electrostatic in nature.

The surprisingly high solubilities of these silver complexes of ligands **1**–**3** in chloroform prompted us to probe their structures in solution by NMR spectroscopy. Metal *N*-coordination leads to a diagnostic shift of the ^1H NMR signal(s) due to the α-pyridyl proton(s). Likewise, metal *P*-coordination is reflected by a shift of the ^{31}P NMR signal due to the PPh_2 substituent of the respective ligand. Pertinent NMR spectroscopic data are collected in Table 2. Both *P*- and *N*-coordination are clearly indicated by substantial coordination-induced shifts in each case. The ^{31}P NMR spectra of silver(I) phosphine complexes are typically characterised by a diagnostic doublet of doublets type pattern, which results from the coupling of phosphorus to each of the spin $I = ½$ silver isotopes (^{107}Ag, 51.8 % natural abundance; ^{109}Ag, 48.2 % natural abundance), the $^1J(^{31}P,^{109}Ag)/^1J(^{31}P,^{107}Ag)$ ratio being close to the $\gamma(^{109}Ag)/\gamma(^{107}Ag)$ gyromagnetic ratio of 1.149.[21] This coupling is often unresolved at room temperature, which is due to rapid phosphine exchange processes which frequently occur with monodentate phosphine ligands.[22] In our three cases, we are not in the fast exchange regime, since slightly broadened doublets are observed, which reflect averaged coupling constants $^1J(^{31}P,^{109/107}Ag,)$, in line with observations reported by *Pettinari* and co-workers for a large number of *P,N*-coordinated silver(I) complexes with a single *P*-coordination.[12,23] These coupling constant values are close to 700 Hz (Table 2), which is nicely compatible with the notion that the Ag^I atoms exhibit a single *P*-coordination.[22–24] Dissolving $\{[Ag(\mu\text{-}\mathbf{3})][BF_4]\}_2$ in chloroform most likely leaves the dimeric complex unit $[Ag(\mu\text{-}\mathbf{3})]_2^{2+}$ intact. In the case of the chain-like coordination polymers $\{[Ag(\mu\text{-}\mathbf{1})][BF_4]\}_n$ and $\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_n$ partial de-

Table 2. NMR spectroscopic data indicative of the coordination of the respective *P,N*-ligand in the silver(I) complexes of the general composition $[Ag(L)][BF_4]$ (L = **1**–**3**) in $CDCl_3$ solution.

	^1H NMR signal(s) of α-pyridyl proton(s)	^{31}P NMR signal
1	8.47	–17.7
L = **1**	8.87	11.3 (658)$^{a)}$
Δ*δ*	0.40	29.0
2	8.48	–16.2
L = **2**	8.77	7.1 (702)$^{a)}$
Δ*δ*	0.29	23.3
3	8.61, 8.40	–17.8
L = **3**	9.00, 8.08	11.1 (691)$^{a)}$
Δ*δ*	0.39, –0.32	28.9

a) $|^1J(^{31}P,^{109/107}Ag)|$ in Hz.

Table 1. Selected bond lengths /Å and angles /° for the silver complexes with general composition $[Ag(L)][BF_4]$.

	L = **1** $\{[Ag(\mu\text{-}\mathbf{1})][BF_4]\}_n$	L = **2** $\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_n$	L = **2** $\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_2$	L = **3** $\{[Ag(\mu\text{-}\mathbf{3})][BF_4]\}_2$
Ag–N	2.174(3)	2.162(6)	2.177(5)	2.173(3)
Ag–P	2.3708(8)	2.358(2)	2.3571(16)	2.3591(10)
Ag···F	2.737(2)	2.752(6)	2.750(5), 2.987(4)	2.666(5)
P–Ag–N	164.21(6)	166.9(2)	149.14(11)	156.61(10)

polymerisation occurs upon dissolution. In view of the very similar NMR spectroscopic features of all three compounds, we surmise that in these two cases cyclic oligomers are dominant in solution.

Gold Complexes

The reaction of ligands **1**–**3** with one equivalent of [AuCl(tht)] (tht = tetrahydrothiophene) in dichloromethane afforded products of the expected composition [AuCl(L)] (L = **1**–**3**) according to elemental analysis. In the case of L = **1**, single-crystals were obtained by recrystallisation from diethyl ether. In the other two cases, single-crystals were obtained by liquid phase diffusion of *n*-hexane into a dichloromethane solution (L = **2**) or of diethyl ether into a chloroform solution (L = **3**) of the respective compound. X-ray diffraction analyses showed that the three molecular structures are very similar, and that of [AuCl(**1**)] is shown in Figure 5 as a representative example. Pertinent bond parameters are collected in Table 3.

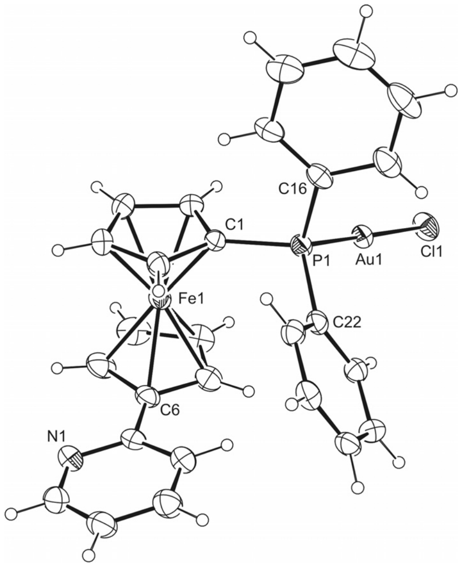

Figure 5. Molecular structure of [AuCl(**1**)] in the crystal.

Table 3. Selected bond lengths /Å and angles /° for the complexes of the type [AuCl(L-κ*P*)].

	L = **1**	L = **2**	L = **3**
Au–P	2.242(2)	2.2371(16)	2.2344(12)
Au–Cl	2.296(2)	2.301(2)	2.3047(12)
P–Au–Cl	176.59(6)	176.75(6)	175.30(4)

The Au bond parameters lie in the range commonly observed for linear dicoordinate complexes of the type [AuCl(P*R*$_3$)]. For example, the parent [AuCl(PPh$_3$)] exhibits Au-P and Au–Cl bond lengths of 2.235(3) Å and 2.279(3) Å and a P–Au–Cl angle of 179.63(8)°.[25] With PPh$_2$(CH$_2$Ph) as ligand, the corresponding values are 2.2292(7) Å, 2.2983(7) Å and 173.62(2)° for Au–P, Au–Cl and P–Au–Cl, respectively.[26]

Robust *P*-coordination is indicated in each case by the pronounced downfield shift of the ^{31}P NMR signal of ca. 45 ppm with respect to the uncoordinated ligand. Not surprisingly, the ^{1}H NMR signals diagnostic for *N*-coordination remain unshifted. *N*-coordination can be induced by removing the chlorido ligand present in these complexes. This was achieved by reaction with one equivalent of Ag[BF$_4$], which afforded products of the expected general composition [Au(L)][BF$_4$] according to elemental analysis. Owing to their poor solubility, characterisation by solution NMR spectroscopy was not possible. Fortuitously, single-crystals were obtained in the case of L = **1**. This was achieved by treating the solid with hot chloroform and layering the filtered extract with *n*-hexane at room temperature. Apparently, this procedure separated a more soluble minor component from the remaining insoluble, and therefore probably polymeric, product. The result of the X-ray diffraction study is shown in Figure 6.

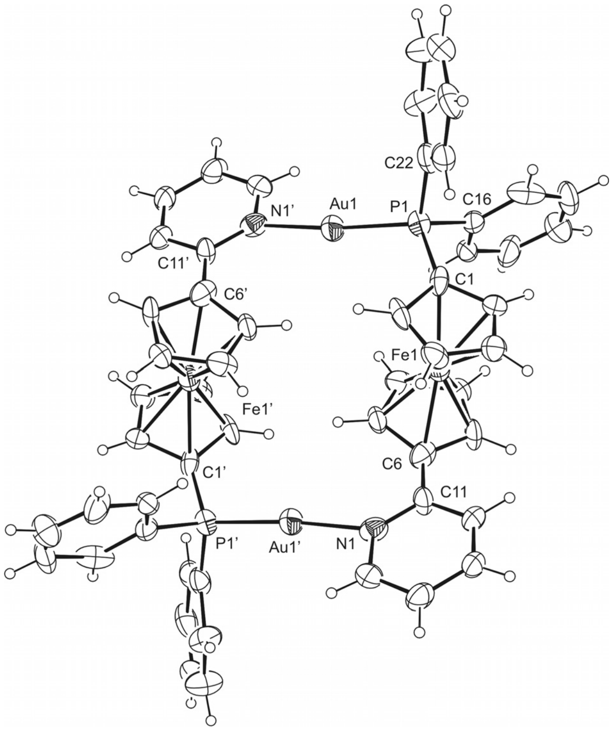

Figure 6. Molecular structure of the cationic unit of {[Au(μ-**1**)][BF$_4$]}$_2$ in the crystal.

The quality of the crystal structure determination was affected by weak scattering of the needle-shaped crystal, which resulted in a mediocre ratio of data with $I > 2\sigma$ (I) to refined parameters. The compound adopts a cyclic dimeric molecular structure, reminiscent of that of the closely related silver compound {[Ag(μ-**3**)][BF$_4$]}$_2$ (vide supra). Metal–anion interactions analogous to those found for the dimeric Ag^I complex are absent here. The Au–P and Au–N bond lengths are 2.252(4) Å and 2.159(14) Å, respectively, and the gold coordination angle has a value of 174.5(4)°. The corresponding values for the parent [Au(PPh$_3$)(Py)][BF$_4$] (Py = pyridine) are 2.2364(8) Å, 2.073(3) Å and 178.09(8)°,[27] and very similar values have been reported for closely related complexes,[28] including also the ferrocenyl (Fc)-containing compound [Au(PPh$_3$)(Fc-3-py)](OTf).[29] The Au-N distance of

2.159(14) Å found for $\{[Au(\mu\text{-}\mathbf{1})][BF_4]\}_2$ is at the high end of such bond length values for this type of complexes. A comparison of the metal bond lengths of $\{[Au(\mu\text{-}\mathbf{1})][BF_4]\}_2$ and $\{[Ag(\mu\text{-}\mathbf{3})][BF_4]\}_2$ (Table 1) provides further evidence for the notion that the *P*-philicity of Au^I is considerably higher than that of Ag^I (vide supra). *Schmidbaur* and co-workers have shown that the covalent radii of two-coordinate Ag^I and Au^I are 1.33 Å and 1.25 Å, respectively, which means that the radius of gold(I) is smaller than that of silver(I) by 0.08 Å.[30] In our case, the *M*–P bond length difference of ca. 0.11 Å is significantly larger than this value, while the *M*–N bond lengths are indistinguishable within experimental error.

As a sideline of our investigation of the bidentate *P*,*N*-ligands **1–3** in the coordination chemistry of gold(I), we have also briefly addressed the tridentate *P*,*N*,*P*-analogue **4** in this context. Neutral *P*,*N*,*P*-ligands based on a central pyridine unit are currently attracting great interest as versatile non-innocent scaffolds for homogeneous catalysis.[31] Compound **4** was synthesised in analogy to **1** by Negishi cross-coupling of $Ph_2PfcZnCl$ with 2,6-dibromopyridine.[4a] It was structurally characterised by single-crystal X-ray diffraction analysis (Figure 7). The quality of the crystal structure determination was affected by weak scattering of the crystal, which resulted in a poor ratio of data with $I > 2\sigma(I)$ to refined parameters. Although a detailed discussion of bond parameters is not meaningful, the connectivities are established unequivocally. The two disubstituted ferrocene units are each in an approximately eclipsed conformation, one of them synclinal and the other one anticlinal.

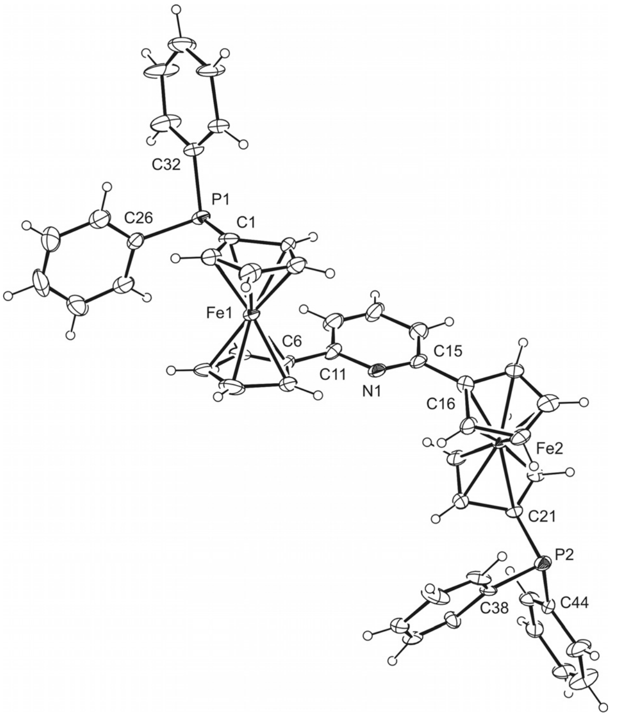

Figure 7. Molecular structure of compound **4** in the crystal.

Reaction of **4** with a slight excess of [AuCl(tht)] in dichloromethane afforded the expected dinuclear gold(I) complex $[(AuCl)_2(\mu\text{-}\mathbf{4}\text{-}\kappa^2P,P)]$, which was characterised by NMR spectroscopy and high-resolution mass spectrometry (HRMS). Robust *P*-coordination is clearly indicated by the pronounced downfield shift of the ^{31}P NMR signal (δ = 28.3) of ca. 46 ppm with respect to uncoordinated **4** (δ = –17.7).

The mononuclear *P*,*P*-coordinated gold(I) complex $[Au(\mathbf{4}\text{-}\kappa^2P,P)][SbF_6]$ was obtained in a one-pot reaction of **4** in dichloromethane solution with one equivalent of [AuCl(tht)] and subsequently with one equivalent of $Ag[SbF_6]$. The complex gives rise to a single ^{31}P NMR signal at δ = 42.6, which corresponds to a coordination induced shift of ca. 60 ppm. This agrees well with data published for closely related dicoordinate complexes of the type $[Au(PR_3)_2]^+$.[32] Recrystallisation from dichloromethane afforded single-crystals suitable for an X-ray diffraction study. The molecular structure of the cation is shown in Figure 8. The gold atom is in a quasi-linear dicoordinate environment. The Au–P bond lengths are 2.314(4) Å and 2.315(4) Å, and the gold coordination angle is 162.52(13)°. This compares well to values reported for closely related compounds such as, for example, $[Au(PPh_3)_2][BF_4]$, which exhibits Au–P bond lengths of 2.321(3) Å and 2.322(3) Å and a P–Au–P angle of 167.3(1)°.[33] The fairly pronounced, but not unusual, deviation of the P–Au–P unit from linearity in $[Au(\mathbf{4}\text{-}\kappa^2P,P)][SbF_6]$ is neither due to Au···F nor to Au···N contacts. The closest interatomic gold-fluorine distance is ca. 3.60 Å, which is well above the sum of the van der Waals radii of gold and fluorine (ca. 3.2 Å), and the intramolecular gold-nitrogen distance of ca. 4.39 Å is even further beyond the sum of the corresponding van der Waals radii (ca. 3.3 Å).[19]

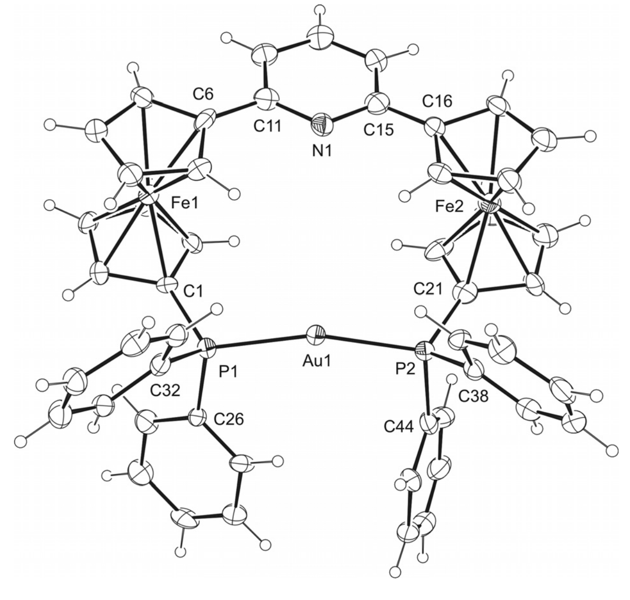

Figure 8. Molecular structure of the cation of $[Au(\mathbf{4}\text{-}\kappa^2P,P)][SbF_6]$ in the crystal.

Ligand **4** is able to act as a *trans*-spanning *P*,*P*-chelate ligand. Only a surprisingly limited number of such ligands is known to date, and most of them have proved useful for applications in catalysis.[34] The large chelate ring size of 12 atoms present in $[Au(\mathbf{4}\text{-}\kappa^2P,P)]^+$, although not unprecedented for *P*,*P*-chelates,[35] is remarkable. Close relatives of **4** among the *trans*-chelating diphosphine ligands are the biferrocene-based TRAP ligands introduced by *Ito*,[36] which, however, form nine-membered chelate rings.

Conclusions

P,*N*-ligands **1–3** form coordination polymers or cyclic dimers with two-coordinate Ag^I and Au^I. Ligands **1** and **2** had previously been shown to form chelates with four-coordinate metal centres, with bite angles ranging from ca. 90° to 125°.[4] The absence of chelate structures was not unexpected with the Group 11 metal atoms investigated here, although with low-coordinate Ag^I, coordination angles down to, or even slightly below, 150° have been reported even in the absence of structurally relevant silver-anion interactions.[5a] Owing to the presence of the methylene bridge between the ferrocene moiety and the pyridyl group, ligand **2** is more flexible than **1** and **3**. Consequently, its coordination behaviour is more temperamental, and different structure types can result with the same metal-ligand fragment. The results obtained with the *P*,*N*,*P*-ligand **4**, which formed gold(I) complexes in a $\kappa^2 P,P$ coordination mode in this preliminary study, augur well for the development of a rich coordination chemistry of this compound, and this issue will be addressed in due course.

Experimental Section

Ligands **1**–**3** were prepared as described previously.[4c,d] [AuCl(tht)],[37] 1-bromo-1′-(diphenylphosphanyl)ferrocene[38] and [ZnCl$_2$(1,4-dioxane)][39] were prepared according to established procedures. All other materials were procured from standard commercial sources and used as received. Reactions were routinely performed under an atmosphere of dry nitrogen by using standard Schlenk techniques or a conventional glove-box. Solvents and reagents were appropriately dried and purified. Details concerning methods and instrumentation used for compound characterisation have already been described in detail elsewhere.[4d]

Preparative Work

Synthesis of 4: A 1.58 M solution of *n*-butyllithium in hexanes (4.1 mL, 6.5 mmol) was slowly added at –70 °C to a stirred solution of 1-bromo-1′-(diphenylphosphanyl)ferrocene (2.89 g, 6.4 mmol) in THF (40 mL). The mixture was kept at this temperature for 0.5 h. [ZnCl$_2$(1,4-dioxane)] (1.58 g, 7.1 mmol) was added. After 0.5 h the mixture was allowed to warm to room temperature and stirred for a further 2.5 h. 2,6-Dibromopyridine (734 mg, 3.1 mmol) and [Pd(PPh$_3$)$_4$] (133 mg, 0.1 mmol) were added sequentially. The stirred reaction mixture was heated to 60 °C for 72 h and subsequently allowed to cool to room temperature. Silica gel (ca. 2 g) was added. Volatile components were removed in vacuo to afford the crude product adsorbed on silica gel. The product was purified by column chromatography on silica gel. Less polar components were removed by elution with a 10:1 mixture of petroleum ether and diethyl ether. The product was subsequently eluted with dichloromethane containing 0.5 % NEt$_3$. Removal of the eluent in vacuo afforded the product as a foamy solid. This procedure afforded **4**·¼CH$_2$Cl$_2$. Yield 824 mg (33 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a concentrated dichloromethane solution (0.7 mL) placed in a 5 mm NMR tube with a small amount of pure dichloromethane and then with *n*-hexane. **^{1}H NMR** (CDCl$_3$): δ = 3.94 (s, 4 H, fc), 4.17 (s, 4 H, fc), 4.26 (s, 4 H, fc), 4.88 (s, 4 H, fc), 7.01 (m, 2 H, C$_5$H$_3$N), 7.30–7.38 (m, 21 H, Ph and C$_5$H$_3$N). **^{13}C{^{1}H} NMR** (CDCl$_3$): δ = 68.50 (s), 71.20 (d, J_{PC} = 1 Hz), 73.23 (d, J_{PC} = 4 Hz), 74.28 (d, J_{PC} = 15 Hz), 76.72 (d, J_{PC} = 7 Hz), 85.19 (s), 117.04 (s), 128.28 (d, J_{PC} = 7 Hz), 128.61 (s), 133.63 (d, J_{PC} = 20 Hz), 135.93 (s), 139.15 (d, J_{PC} = 10 Hz), 157.60 (s). **^{31}P NMR** (CDCl$_3$): δ = –17.7 (s). **MS/MALDI(+):** *m*/*z* (%) = 815 (100) [M]$^+$. **Elemental analysis:** C$_{49}$H$_{39}$NFe$_2$P$_2$·¼CH$_2$Cl$_2$ (836.7): C 70.85 (calcd. 70.70), H 4.78 (4.76), N 1.64 (1.67) %.

Synthesis of [Ag(1)][BF$_4$]: Ag[BF$_4$] (19.5 mg, 0.1 mmol) was added to a solution of **1** (44.7 mg, 0.1 mmol) in methanol (4 mL). The reaction mixture was stirred in the dark for 5 h. Volatile components were removed in vacuo. The residue was dissolved in dichloromethane (2 mL) and *n*-hexane (15 mL) was added. The precipitate was isolated by filtration, washed with diethyl ether (3 mL) and *n*-hexane (3 mL) and dried in vacuo. Yield: 54.8 mg (85 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by recrystallisation from hot chloroform. **^{1}H NMR** (CDCl$_3$): δ = 4.16 (s, 2 H, fc), 4.34 (s, 2 H, fc), 4.55 (s, 2 H, fc), 4.90 (s, 2 H, fc), 7.37 (m, 1 H, 2-py), 7.47 (m, 7 H, Ph and 2-py), 7.61 (m, 4 H, Ph), 7.75 (m, 1 H, 2-py), 8.87 (s, 1 H, 2-py). **^{31}P NMR** (CDCl$_3$): δ = 6.8 (br. d, J_{PAg} ≈ 712 Hz). **MS/ESI(+):** *m*/*z* (%) = 556 (100) [Ag(**1**)]$^+$. **MS/ESI(–):** *m*/*z* (%) = 87 (100) [BF$_4$]$^–$. **Elemental analysis:** C$_{27}$H$_{22}$NAgBF$_4$FeP (641.9): C 50.50 (calcd. 50.52), H 3.66 (3.45), N 2.17 (2.18) %.

Synthesis of [Ag(2)][BF$_4$]: Ag[BF$_4$] (19.5 mg, 0.1 mmol) was added to a solution of **2** (46.2 mg, 0.1 mmol) in methanol (5 mL). The reaction mixture was stirred in the dark for 3 h and *n*-hexane (10 mL) was added. The precipitate was isolated by filtration, washed with *n*-hexane (3 mL) and dried in vacuo. This procedure afforded [Ag(**2**)][BF$_4$]·½C$_6$H$_{14}$. Yield 58.0 mg (89 %). Single-crystals of the coordination polymer {[Ag(μ-**2**)][BF$_4$]}$_n$ were obtained by layering a nearly saturated chloroform solution of the product placed in a 5 mm NMR tube with a small amount of pure chloroform and then with *n*-hexane. Layering a dichloromethane solution with diethyl ether afforded single-crystals of the cyclic dimer {[Ag(μ-**2**)][BF$_4$]}$_2$. **^{1}H NMR** (CDCl$_3$): δ = 3.93, 4.06, 4.13, 4.23, 4.54 (5 × s, 5 × 2 H, fc and CH$_2$), 7.30 (m, 1 H, py), 7.39–7.44 (m, 7 H, Ph and 2-py), 7.50 (m, 4 H, Ph), 7.79 (m, 1 H, 2-py), 8.77 (s, 1 H, 2-py). **^{31}P NMR** (CDCl$_3$): δ = 7.1 (br. d, J_{PAg} ≈ 702 Hz). **MS/ESI(+):** *m*/*z* (%) = 558 (100) [Ag(**2**)]$^+$. **MS/ESI(–):** *m*/*z* (%) = 87 (100) [BF$_4$]$^–$. **Elemental analysis:** C$_{28}$H$_{24}$NAgBF$_4$FeP·½C$_6$H$_{14}$ (698.1): C 53.38 (cald. 53.34), H 4.25 (4.33), N 2.25 (2.01) %.

Synthesis of [Ag(3)][BF$_4$]: Ag[BF$_4$] (19.5 mg, 0.1 mmol) was added to a solution of **3** (44.7 mg, 0.1 mmol) in methanol (4 mL). The reaction mixture was stirred in the dark for 14 h. The orange solid was isolated by filtration, washed with methanol (1 mL), diethyl ether (3 mL) and finally *n*-hexane (3 mL) and dried in vacuo. Yield 41.9 mg (65 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a nearly saturated chloroform solution of the product placed in a 5 mm NMR tube with a small amount of pure chloroform and then with *n*-hexane. **^{1}H NMR** (CDCl$_3$): δ = 4.05 (s, 2 H, fc), 4.17 (s, 2 H, fc), 4.75 (s, 2 H, fc), 4.87 (s, 2 H, fc), 7.43 (m, 6 H, Ph), 7.60 (m, 4 H, Ph), 7.66 (s, 1 H, 3-py), 7.92 (s, 1 H, 3-py), 8.08 (s, 1 H, 3-py), 9.00 (br. s, 1 H, 3-py). **^{31}P NMR** (CDCl$_3$): δ = 11.1 (br. d, J_{PAg} ≈ 691 Hz). **MS/ESI(+):** *m*/*z* (%) = 556 (100) [Ag(**3**)]$^+$. **MS/ESI(–):** *m*/*z* (%) = 87 (100) [BF$_4$]$^–$. **Elemental analysis:** C$_{27}$H$_{22}$NAgBF$_4$FeP (641.9): C 50.49 (calcd. 50.52), H 3.46 (3.45), N 2.30 (2.18) %.

Synthesis of [AuCl(1-κ*P*)]: 1 (44.7 mg, 0.1 mmol) was added to a solution of [AuCl(tht)] (32.0 mg, 0.1 mmol) in dichloromethane

(5 mL) The reaction mixture was stirred for 3 h. The solvent volume was reduced to slightly less than half in vacuo and *n*-hexane (25 mL) was added. The precipitate was isolated by filtration, washed with diethyl ether (2 mL) and *n*-hexane (2 mL) and dried in vacuo. Yield 26.0 mg (38 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by recrystallisation from diethyl ether. **^{1}H NMR** ($CDCl_3$): δ = 4.18 (s, 2 H, fc), 4.35 (s, 2 H, fc), 4.44 (s, 2 H, fc), 5.00 (s, 2 H, fc), 7.09 (m, 1 H, 2-py), 7.39 (m, 1 H, 2-py), 7.44 (m, 4 H, Ph), 7.49 (m, 1 H, 2-py), 7.57 (m, 6 H, Ph), 8.48 (m, 1 H, 2-py). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 69.25 (s), 70.05 (d, J_{PC} = 74 Hz), 72.28 (s), 74.78 (d, J_{PC} = 9 Hz), 74.95 (d, J_{PC} = 14 Hz), 85.71 (s), 120.80 (s), 121.45 (s), 129.70 (d, J_{PC} = 12 Hz), 130.64 (s), 131.19 (s), 131.81 (d, J_{PC} = 64 Hz), 133.71 (d, J_{PC} = 14 Hz), 136.79 (s), 149.46 (s), 157.10 (s). **^{31}P NMR** ($CDCl_3$): δ = 27.6 (s). **MS/APCI(+):** *m/z* (%) = 679 (5) [M]$^+$, 644 (100) [M – Cl]$^+$. **Elemental analysis:** $C_{27}H_{22}NAuClFeP$ (679.7): C 47.52 (calcd. 47.71), H 3.25 (3.26), N 2.09 (2.06) %.

Synthesis of [AuCl(2-κ*P*)]: 2 (46.1 mg, 0.1 mmol) was added to a solution of [AuCl(tht)] (32.0 mg, 0.1 mmol) in dichloromethane (5 mL) The reaction mixture was stirred for 6 h. *n*-Hexane (25 mL) was added and the precipitate was isolated by filtration, washed with diethyl ether (2 mL) and *n*-hexane (2 mL) and dried in vacuo. Yield 33.4 mg (48 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a dichloromethane solution of the product (0.7 mL) placed in a 5 mm NMR tube with *n*-hexane. **^{1}H NMR** ($CDCl_3$): δ = 3.67 (s, 2 H, fc), 4.11 (m, 2 H, fc), 4.27 (m, 4 H, CH_2 and fc), 4.51 (m, 2 H, fc), 7.10 (m, 2 H, 2-py), 7.41–7.52 (m, 6 H, Ph), 7.54–7.62 (m, 5 H, Ph and 2-py), 8.47 (m, 1 H, 2-py). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 38.01 (s), 68.91 (d, J_{PC} = 74 Hz), 70.02 (s), 71.01 (s), 73.54 (d, J_{PC} = 9 Hz), 74.19 (d, J_{PC} = 14 Hz), 88.23 (s), 121.36 (s), 122.78 (s), 128.95 (d, J_{PC} = 12 Hz), 130.98 (d, J_{PC} = 63 Hz), 131.62 (d, J_{PC} = 3 Hz), 133.47 (d, J_{PC} = 14 Hz), 136.58 (s), 149.01 (s), 160.27 (s). **^{31}P NMR** ($CDCl_3$): δ = 29.2 (s). **MS/ESI(+):** *m/z* (%) = 695 (15) [M]$^+$, 658 (100) [M – Cl]$^+$. **Elemental analysis:** $C_{28}H_{24}NAuClFeP$ (693.7): C 48.39 (calcd. 48.48), H 3.53 (3.49), N 1.84 (2.02) %.

Synthesis of [AuCl(3-κ*P*)]: 3 (44.7 mg, 0.1 mmol) was added to a solution of [AuCl(tht)] (32.0 mg, 0.1 mmol) in dichloromethane (5 mL) The reaction mixture was stirred for 6 h and *n*-hexane (25 mL) was added. The precipitate was isolated by filtration, washed with diethyl ether (2 mL) and *n*-hexane (2 mL) and dried in vacuo. Yield 33.5 mg (49 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a chloroform solution of the product (0.7 mL) placed in a 5 mm NMR tube with diethyl ether. **^{1}H NMR** ($CDCl_3$): δ = 4.20 (s, 2 H, fc), 4.42 (s, 2 H, fc), 4.44 (s, 2 H, fc), 4.71 (s, 2 H, fc), 7.20 (s, 1 H, 3-py), 7.44 (m, 4 H, Ph), 7.49–7.58 (m, 6 H, Ph), 7.65 (m, 1 H, 3-py), 8.42 (s, 1 H, Ph), 8.54 (s, 1 H, 3-py). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 68.34 (s), 70.37 (d, J_{PC} = 73 Hz), 72.03 (s), 74.78 (d, J_{PC} = 9 Hz), 75.06 (d, J_{PC} = 14 Hz), 83.76 (s), 123.77 (s), 129.13 (d, J_{PC} = 12 Hz), 129.31 (d, J_{PC} = 12 Hz), 130.50 (s), 131.02 (s), 131.93 (d, J_{PC} = 3 Hz), 133.59 (s), 133.68 (d, J_{PC} = 14 Hz), 147.29 (s), 147.87 (s). **^{31}P NMR** ($CDCl_3$): δ = 28.26 (s). **MS/ESI(+):** *m/z* (%) = 644 (100) [M – Cl]$^+$. **Elemental analysis:** $C_{27}H_{22}NAuClFeP$ (679.7): C 47.43 (calcd. 47.71), H 3.27 (3.26), N 2.15 (2.06).

Synthesis of [Au(1)][BF$_4$]: 1 (44.7 mg, 0.1 mmol) was added to a solution of [AuCl(tht)] (32.0 mg, 0.1 mmol) in dichloromethane (5 mL) The reaction mixture was stirred for 1.5 h in the dark. Ag[BF$_4$] (21.3 mg, 0.11 mmol) was added and stirring was continued in the dark for 14 h. Dichloromethane (10 mL) was added and the mixture filtered to remove insoluble components. The volume of the filtrate was reduced to slightly less than half in vacuo and diethyl ether (10 mL) was added. The precipitate was isolated by filtration, washed with diethyl ether (2 mL) and dried in vacuo. Yield 28.3 mg (39 %). Single-crystals suitable for an X-ray diffraction analysis were obtained by treatment of the product with hot chloroform, which dissolved part of the material, and layering of the solution obtained after filtration at room temperature with *n*-hexane. **MS/ESI(+):** *m/z* (%) = 1091 (85) [Au(**1**)$_2$]$^+$, 644 (100) [Au(**1**)]$^+$. **Elemental analysis:** $C_{27}H_{22}NAuBF_4FeP$ (731.1): C 44.76 (calcd. 44.36), H 3.07 (3.03), N 2.01 (1.92) %.

Synthesis of [(AuCl)$_2$(μ-4-κ^2*P,P*)]: 4 (32.6 mg, 0.04 mmol) was added to a solution of [AuCl(tht)] (32.1 mg, 0.1 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 22 h. Volatile components were removed in vacuo. The crude product was dissolved in a minimal amount of ethyl acetate and purified by column chromatography (neutral alumina, ethyl acetate). The product was obtained as a yellow, microcrystalline solid. Yield 41.0 mg (80 %). **^{1}H NMR** ($CDCl_3$): δ = 4.18 (s, 4 H, fc), 4.39 (s, 8 H, fc), 5.00 (s, 4 H, fc), 7.12 (m, 2 H, C_5H_3N), 7.41–7.61 (m, 21 H, Ph and C_5H_3N). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 69.16 (s), 72.07 (s), 74.59 (s), 74.72 (s), 74.81 (s), 86.15 (s), 117.89 (s), 128.91 (d, J_{PC} = 12 Hz), 130.76 (d, J_{PC} = 64 Hz), 131.67 (d, J_{PC} = 2 Hz), 133.52 (d, J_{PC} = 14 Hz), 136.83 (s), 156.25 (s). **^{31}P NMR** ($CDCl_3$): δ = 28.3 (s). **HRMS/ESI(+):** *m/z* calcd. for $[C_{49}H_{39}NAu_2ClFe_2NP_2]^+$ ([M – Cl]$^+$) = 1244.0276, found: 1244.0273. **Elemental analysis:** $C_{49}H_{39}NAu_2Cl_2Fe_2P_2$ (1280.3): C 45.93 (calcd. 45.97), H 3.15 (3.07), N 0.99 (1.09) %.

Synthesis of [Au(4-κ^2*P,P*)][SbF$_6$]: 4 (81.6 mg, 0.1 mmol) was added to a solution of [AuCl(tht)] (32.1 mg, 0.1 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 22 h in the dark. Ag[SbF$_6$] (34.3 mg, 0.1 mmol) was added and the reaction mixture stirred in the dark for 1 h. The mixture was filtered through a 1 cm pad of Celite®. The filtrate was reduced to dryness in vacuo, affording the product as a yellow, microcrystalline solid. Single-crystals were obtained by recrystallisation from dichloromethane. Yield 121 mg (97 %). **^{1}H NMR** ($CDCl_3$): δ = 4.01 (s, 4 H, fc), 4.15 (s, 4 H, fc), 4.74 (s, 4 H, fc), 5.17 (s, 4 H, fc), 7.28 (d, *J* = 8 Hz, 2 H, C_5H_3N), 7.51–7.62 (m, 21 H, Ph and C_5H_3N). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 69.22 (s), 71.65 (s), 74.54 (t, J_{PC} = 4.5 Hz), 75.68 (t, J_{PC} = 8 Hz), 86.91 (s), 118.81 (s), 129.60 (t, J_{PC} = 6 Hz), 129.97 (t, J_{PC} = 30.6 Hz), 132.44 (s), 133.50 (t, J_{PC} = 7.4 Hz), 137.06 (s), 156.59 (s). **^{31}P NMR** ($CDCl_3$): δ = 42.6 (s). **HRMS/ESI(+):** *m/z* calcd. for $[C_{49}H_{39}Au_2Fe_2N_1P_2]^+$ ([Au(**4**)]$^+$) = 1212.0922, found: 1212.0917. **MS/ESI(–):** *m/z* (%) = 235 (100) [SbF$_6$]$^-$. **Elemental analysis:** $C_{49}H_{39}NAuF_6Fe_2P_2Sb \cdot ½CH_2Cl_2$ (1290.7): C 46.04 (calcd. 46.06), H 3.37 (3.12), N 0.95 (1.09) %.

X-ray Crystallography

For each data collection a single-crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo-K_α radiation (λ = 0.71073 Å) was made with a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red[40] except for {[Ag(μ-**2**)][BF$_4$]}$_n$·CHCl$_3$. Unfortunately, this data collection remains incomplete because the crystal was lost during the measurement and no new single-crystal suitable for crystal structure analysis could be obtained, despite many attempts. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL97).[41] All non-hydrogen atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters, except for the sol-

Table 4. Crystal data and structure refinement details for the silver(I) complexes of ligands **1**–**3**.

	$\{[Ag(\mu\text{-}\mathbf{1})][BF_4]\}_n{\cdot}2CHCl_3$	$\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_n{\cdot}CHCl_3$	$\{[Ag(\mu\text{-}\mathbf{2})][BF_4]\}_2{\cdot}CH_2Cl_2$	$\{[Ag(\mu\text{-}\mathbf{3})][BF_4]\}_2{\cdot}2CHCl_3$
Empirical formula	$C_{29}H_{24}AgBCl_6F_4FeNP$	$C_{29}H_{25}AgBCl_3F_4FeNP$	$C_{57}H_{50}Ag_2B_2Cl_2F_8Fe_2N_2P_2$	$C_{56}H_{46}Ag_2B_2Cl_6F_8Fe_2N_2P_2$
Molecular weight	880.69	775.35	1396.89	1522.65
T /K	100(2)	298(2)	100(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a /Å	10.5259(10)	13.2362(14)	9.0908(10)	9.1606(5)
b /Å	11.9401(16)	11.5572(13)	13.1685(13)	21.4054(9)
c /Å	26.573(3)	20.694(3)	13.3913(14)	15.4766(9)
α /°			112.067(8)	
β /°	93.193(7)	91.336(11)	92.560(8)	93.684(5)
γ /°			106.301(8)	
V /Å^3	3334.6(6)	3164.7(7)	1405.5(3)	3028.5(3)
Z	4	4	1	2
$D_{calcd.}$ /g·cm^{-1}	1.754	1.627	1.650	1.670
μ/mm^{-1}	1.596	1.425	1.411	1.488
θ range/°	1.53 to 25.00	1.54 to 25.00	1.66 to 25.00	1.63 to 25.63
Refl. measured	21156	2375	11332	19521
Unique refl.	5720	2074	4925	5387
R_{int}	0.0773	0.0254	0.0762	0.0304
Refl. observed	4955	1179	3271	4463
R_1, wR_2 ($I > 2\sigma(I)$)	0.0307, 0.0842	0.0321, 0.0494	0.0452, 0.0975	0.0409, 0.1115
R_1, wR_2 (all data)	0.0377, 0.0903	0.0738, 0.0555	0.0735, 0.1052	0.0499, 0.1158
$\Delta\rho_{min}/_{max}$ /e·Å^{-3}	–-0.867 / 0.974	–0.151 / 0.175	–0.779 / 0.707	–0.746 / 1.418

Table 5. Crystal data and structure refinement details for gold(I) complexes of ligands **1**–**3**.

	$[AuCl(\mathbf{1})]$	$[AuCl(\mathbf{2})]$	$[AuCl(\mathbf{3})]$	$\{[Au(\mu\text{-}\mathbf{1})][BF_4]\}_2$
Empirical formula	$C_{27}H_{22}AuClFeNP$	$C_{28}H_{24}AuClFeNP$	$C_{27}H_{22}AuClFeNP$	$C_{54}H_{44}Au_2B_2F_8Fe_2N_2P_2$
Molecular weight	679.69	693.72	679.69	1462.10
T /K	218(2)	223(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a /Å	13.8398(9)	9.972(4)	8.7087(6)	13.332(2)
b /Å	10.7636(5)	22.351(9)	8.9472(7)	27.486(4)
c /Å	16.6681(12)	11.648(4)	16.2538(12)	8.8823(12)
α /°			94.250(6)	
β /°	107.505(5)	105.81(3)	103.269(6)	107.523(11)
γ /°			107.591(6)	
V /Å^3	2368.0(3)	2497.9(15)	1160.88(15)	3103.7(8)
Z	4	4	2	2
$D_{calcd.}$ /g·cm^{-1}	1.907	1.845	1.944	1.565
μ/mm^{-1}	6.997	6.635	7.136	5.278
θ range /°	1.68 to 25.00	1.82 to 25.00	1.30 to 25.20	1.48 to 25.00
Refl. measured	10860	15428	15146	19862
Unique refl.	4149	4384	4115	5481
R_{int}	0.0607	0.1663	0.0498	0.1531
Refl. observed	3172	4081	3967	2427
R_1, wR_2 ($I > 2\sigma(I)$)	0.0327, 0.0741	0.0521, 0.1370	0.0305, 0.0833	0.0798, 0.1720
R_1, wR_2 (all data)	0.0461, 0.0766	0.0550, 0.1400	0.0316, 0.0841	0.1504, 0.1948
$\Delta\rho_{min}/_{max}$ /e·Å^{-3}	–2.150 / 1.310	–3.026 / 2.484	–2.699 / 2.069	–0.955 / 2.977

vent molecules in $\{[Au(\mu\text{-}\mathbf{1})][BF_4]\}_2$ and $[Au(\mathbf{4}\text{-}\kappa^2P,P)][SbF_6]$, which have been removed from the data set using the squeeze routine from PLATON.[42] Furthermore, in $[Au(\mathbf{4}\text{-}\kappa^2P,P)][SbF_6]$ the anion appears to be located on two positions with occupancies of 2/3 and 1/3, respectively. In the minor occupied position the fluorine atoms are disordered over several positions and, hence, do not represent a chemically reasonable result, but may be regarded as a crude approximated model. The rather high residual electron densities are found close the $[SbF_6]^-$ anions. Hydrogen atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters. All figures represent the displacement ellipsoids at the 30 % probability level, except for the hydrogen atoms, which are drawn as circles of arbitrary radius. Graphical representations were made using ORTEP-3 win.[43] Pertinent crystallographic data are collected in Table 4, Table 5 and Table 6. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC-824177, -824178, -824179, -824180, -824181, -824182, -824183, -824184, -824185 and 830433. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-1223-336-033; E-mail for enquiry: fileserv@ccdc.cam.ac.uk).

Table 6. Crystal data and structure refinement details for ligand **4** and [Au(**4**-κ^2*P*,*P*)][SbF$_6$].

	4	[Au(**4**-κ^2*P*,*P*)][SbF$_6$]
Empirical formula	$C_{49}H_{39}Fe_2NP_2$	$C_{49}H_{39}AuF_6Fe_2NP_2Sb$
Molecular weight	815.45	1248.17
T /K	193(2)	100(2)
Crystal system	triclinic	trigonal
Space group	$P\bar{1}$	$P\bar{3}$
a /Å	8.635(2)	26.9441(10)
b /Å	12.721(3)	26.9441(10)
c /Å	18.684(5)	11.2362(6)
α /°	102.60(2)	90
β /°	91.03(2)	90
γ /°	95.93(2)	120
V /Å^3	1990.4(9)	7064.4(5)
Z	2	6
$D_{calcd.}$ /g·cm^{-1}	1.361	1.760
μ /mm^{-1}	0.845	4.403
θ range /°	1.65 to 25.00	1.51 to 24.98
Refl. measured	12726	15917
Unique refl.	6591	8296
R_{int}	0.2092	0.0950
Refl. observed	1956	4361
R_1, wR_2 ($I > 2\sigma(I)$)	0.1169, 0.2847	0.0716, 0.1647
R_1, wR_2 (all data)	0.2343, 0.3740	0.1299, 0.1881
$\Delta\rho_{\text{min}}/_{\text{max}}$ /e·Å^{-3}	–2.106 / 1.059	–4.287 / 2.381

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