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Coordination Behaviour of a Hexadentate 1,1′-Ferrocenylene-Bridged Bisphosphole towards Coinage Metal Centres

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Dedicated to Professor Edgar Niecke on the occasion of his 75th birthday

We describe the synthesis of a ferrocenylene-bridged bis[2,5-bis(2-pyridyl)]phosphole ligand that shows additional rotational degrees of freedom relative to its previously described *p*-phenylene-bridged congener. The coordination behaviour of this ferrocenylene-based bis-N,P,N pincer towards coinage metal centres M^I with M = Cu and Au was explored, revealing different coordination modes with and without involvement of N donation. Upon coordination of Au^I metal centres, different isomers of a bimetallic Au^I complex were isolated in the crystalline solid state that showed (or did not) intramolecular aurophilic interaction. Aurophilic as well as Au–N interactions have been investigated by means of ab initio calculations.

Introduction

In the past few decades, metallophilic interactions between d^{10} closed-shell metal ions have emerged as a field of increasing interest in crystal engineering and material sciences on account of new physical and chemical properties that cannot be observed in their monomeric counterparts. Indeed, in the toolbox of noncovalent interactions that is available in supramolecular chemistry, these metal–metal interactions have been used to complement hydrogen-bonding, van der Waals or π–π interactions to direct the relative conformation of isolated molecules and self-assembly processes that lead to complex superstructures including metallomacrocycles.[1] Moreover, rich emission properties often arise from these d^{10}–d^{10} closed-shell metal–metal interactions, which open interesting prospects for such derivatives as active molecular materials for optoelectronic applications.[2]

Au^I is one element of choice for the observation of these effects owing to its most pronounced relativistic effects. Aurophilic interaction is the strongest metallophilic interaction with a strength of about 7–12 kcal mol^{-1} comparable to that of a hydrogen bond. These rather strong metal–metal interactions have allowed the synthesis of a variety of polymetallic Au^I complexes with short Au^I–Au^I distances[3] that display great intrinsic stability, large structural diversity, rich photophysical properties and potential applications in material sciences.[4] In this area, linear coordination and aurophilic interactions between metal centres are two key factors in the use of gold complexes in the formation of complex molecular structures by self-assembly.[1k–1m,3c,5] Notably, the other closed-shell d^{10} ions of the group 11 triad, Ag^I and Cu^I, are also expected to display metallophilic interactions[3b,4] that are generally weaker than the aurophilic ones but are sometimes associated with rich photophysical properties.[3b,6] In contrast to Au^I, the coordination behaviour of Ag^I and Cu^I ions shows no strong geometrical preferences, which implies less predictive self-recognition processes associated with cuprophilic and argentophilic interactions.

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The bis(2-pyridyl)phosphole derivative 1[7] (Figure 1) is a powerful assembling N,P,N pincer for the stabilization of bimetallic complexes 2–5 (Figure 1) of monovalent metal ions with different coordination geometries (Pd^I, Pt^I, Cu^I, Ag^I) according to a very unusual bridging phosphane coordination mode.[8] As a consequence of this bridging phosphane coordination mode, short intermetallic distances entail metallophilic interactions in this series of complexes. Ligand 1 can also form stable neutral monometallic Au^I complex 6 (Figure 1) upon reaction with (tht)·AuCl (tht = tetrahydrothiophene).[9] In this complex, the coordination of ligand 1 involves only the phosphorus atom of the phosphole ring, whereas the nitrogen atoms of the pyridyl fragments remain uncoordinated. It was further demonstrated that the reaction of derivative 6 with one equivalent of AgPF$_6$ affords the emissive bimetallic Au^I complex 7 (Figure 1).[8g] In this complex, the Au^I centres are involved in aurophilic interactions [intermetallic distance, 3.1232(9) Å] and coordinated to two equivalents of ligand 1 that act as 1κN:2κP chelates, thereby leaving one pyridyl fragment of each ligand 1 free from coordination. To investigate whether the reactivity of such an N,P,N multitopic fragment could be combined with the self-assembly processes that arise from the formation of metallophilic interactions within complex molecular assemblies, we have studied the coordination chemistry of the new multitopic P,N ligand 8 (Figure 1) based on two bis(2-pyridyl)phosphole fragments connected by a ferrocene unit with the series of the closed-shell d^{10} ions of group 11 (Cu^I, Ag^I and Au^I). The presence of the ferrocene fragment within this multitopic assembling ligand provides attractive additional features such as redox activity and the availability of unique donor sites at the cyclopentadienyl (Cp) rings as well as at the central iron

atom.[10] These redox properties might be helpful in tailoring the overall charge and magnetism of supramolecular assemblies derived therefrom. The first ferrocenyl and ferrocenylene phospholes have been reported by Mathey and co-workers in a seminal report.[11] Very recently, Lang and co-workers demonstrated weak to moderate type II coupled redox-active centres in poly-ferrocenyl-substituted five-membered heterocycles of pyrroles and phospholes.[12] Moreover, the additional donor sites are likely to modify the coordinative properties of these ligands. Recently, the behaviour of 1,1′-ferrocenylene-bridged isonitriles and diacetylides towards gold was investigated and revealed a rich and unexpected coordination chemistry.[13]

In previous work, ligand 9, the p-phenylene analogue of 8 (Figure 1), was treated with Cu^I ions to afford a tetrametallic complex in which two dimeric Cu^I units are linked together by the p-phenylene group similar to complex 4 (Scheme 1).[14] It is important to note that the P atoms of phospholes have considerable pyramidal character, since the formation of P–C bonds mainly involves phosphorus p orbitals.[15] As a consequence, the p-phenylene moiety of 1 is almost perpendicular to the two coordinating N,P,N moieties to afford two potential N,P,N chelates with a free rotation about the P–C$_6$H$_4$–P pin. Indeed, it was demonstrated that such a precursor can be used as a molecular tetrametallic Cu^I clip. This derivative can act as a "swivel pin" to afford coordination polymers based on π-stacked metallocyclophane motifs as a result of the reaction of cyanocapped π-conjugated homoditopic linkers with the independent Cu^I dimer subunits. Interestingly, the supramolecular framework is constructed from coordination polymers that exist either as an unfolded or as a folded structure upon establishment of cooperative π–π interactions along the
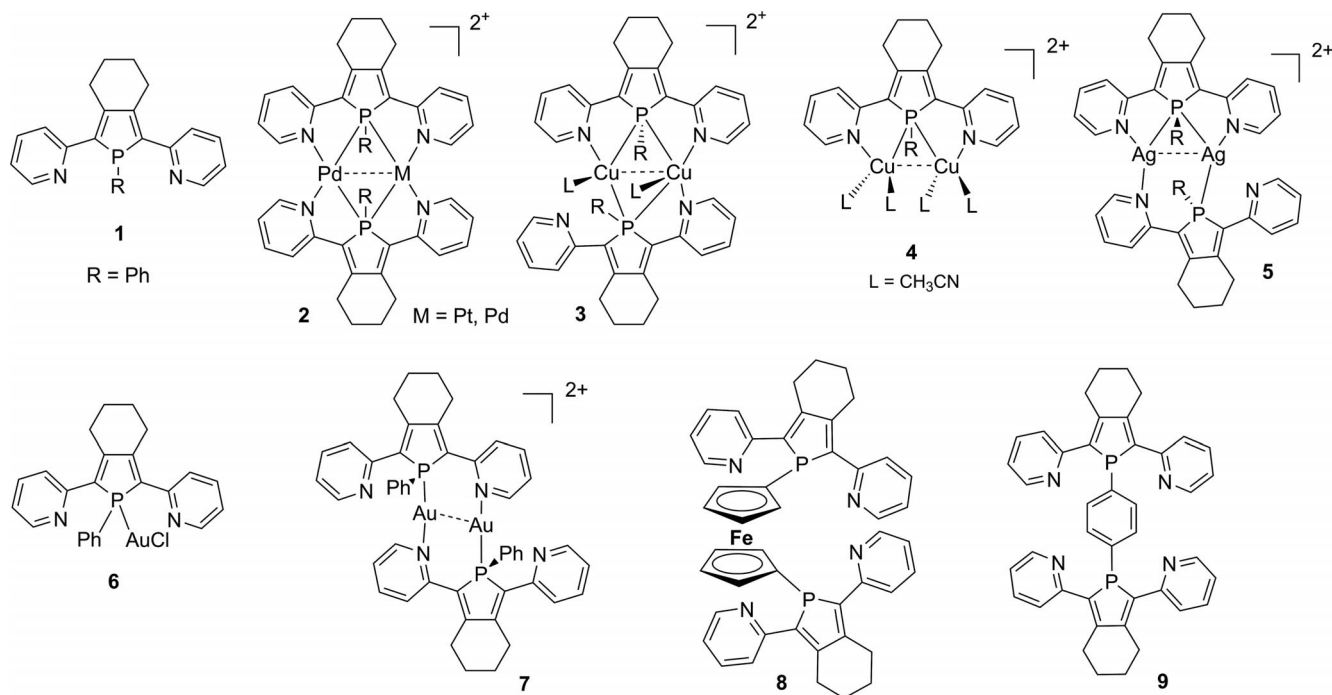

Figure 1. Structure of the N,P,N ligands 1, 8, 9; of the neutral complex 6 and of the dicationic complexes 2–5, 7.

polymer backbone.[14] Conversely, the assembling ligand **8** is expected to allow much larger directional motion between the two N,P,N units due to the free rotation expected about the two P–C$_{Cp}$ bonds in addition to the free rotation of the Cp ring about the "Cp–Fe–Cp" axis. Therefore, the question arises whether the larger rotational flexibility in **8** will allow the two different N,P,N units to behave as independent coordination sites, as observed in the case of ligand **9**.[14] Alternatively, these units might act in a more cooperative way to afford species in which the extent of the metallophilic interactions could allow the formation of new coordination modes within original polymetallic complexes, or direct the organization of several metal centres and ligands in complex supramolecular assemblies. In this paper, we describe the synthesis and the characterization of derivative **8** together with the study of the coordination chemistry of this multitopic N,P,N ligand with Cu^I, Ag^I and Au^I metal centres.
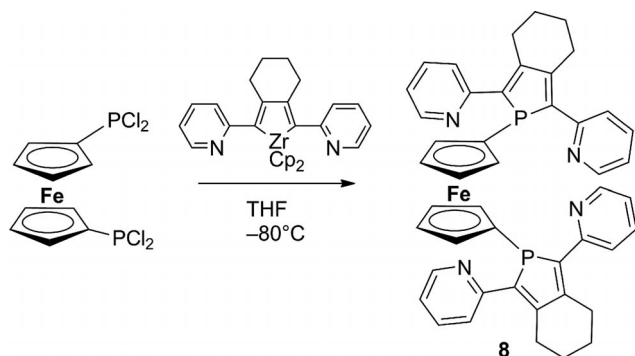
Scheme 1. Synthesis of 1,1′-ferrocenylene-bridged bisphosphole (**8**) from 1,1′-ferrocenyl bis-dichlorophosphane.

Results and Discussion

Synthesis of the target 1,1′-ferrocenylene-bridged bisphosphole **8** was achieved starting from readily available ferrocenyl bis-dichlorophosphane **10** and intermediately generated zirconacyclopentadiene (Scheme 1) that results from the stepwise reaction of [Cp$_2$ZrCl$_2$] with nBuLi (2 equiv.) and 1,8-di(2-pyridyl)octa-1,7-diyne (1 equiv.).[7] Derivative **8** was purified by column chromatography on neutral alumina and fully characterized by heteronuclear NMR spectroscopy and HRMS. Compound **8** displays a single ^{31}P NMR spectroscopic resonance at δ = 3.2 ppm and a symmetrical ^{1}H NMR spectrum, which indicates a non-constrained structure for **8**, in which each of the two N,P,N moieties most likely act independently in solution.

Reaction of Ligand 8 with Cu^I Metal Centres

The Cu^I complex of the phenylene-bridged analogue of **8** has been reported to act as a molecular clip that promotes folded supramolecular frameworks on account of the presence of a swiveling axis (phenylene).[14] Therefore we wanted to explore the coordination behaviour of the new

bisphosphole **8**, which provides a potential similar swiveling axis (ferrocenylene) – which, in contrast to **9**, is not identical to the C$_{ipso}$–P axis – and moreover provides a redox activity that might be useful to modify the overall charge of the resulting aggregates. Nevertheless, once derivative **8** was treated with [Cu(CH$_3$CN)$_4$BF$_4$] (4 equiv.) in dichloromethane at room temperature, a deep red insoluble precipitate was almost instantaneously obtained together with a colourless solution that did not present a signal in its ^{31}P NMR spectrum. Indeed this reaction afforded a material that is insoluble in organic solvents (CH$_2$Cl$_2$, THF, CH$_3$OH, acetone), probably due to its polymeric structure. All attempts to obtain single crystals of this derivative were unsuccessful and therefore its molecular structure is unknown. This result is in marked contrast with the reaction of ligand **9** with [Cu(CH$_3$CN)$_4$BF$_4$] (4 equiv.), which afforded a readily soluble discrete tetrametallic complex based on two independent bimetallic Cu^I fragments comparable to complex **4** (Scheme 1) that are linked by the central –PC$_6$H$_4$P– moiety of ligand **9**. Therefore, the coordination chemistry accessible from ligand **8** gives different results from its p-phenylene analogue **8**. This motivated us to explore further the reactivity of **8** to understand the reason for such differences. The bis(diphenylphosphanyl)methane (dppm) ligand was then used as ancillary ligand together with **8** along with its reaction with Cu^I metal centres. Indeed, the dppm ligand was expected to compete with ligand **8** and act as a blocking ligand in the coordination sphere of the metal centre to inhibit the direct formation of insoluble material. Therefore, coordination to Cu^I was accomplished by treating **8** with [Cu(CH$_3$CN)$_4$BF$_4$] (4 equiv.) in the presence of dppm (2 equiv.) (Scheme 2) to afford a clear red solution. The ^{31}P NMR spectra obtained from this crude solution show a very large set of signals, which most probably reveals multiple equilibriums between several labile species. Upon pentane vapour diffusion on the crude reaction, a heterogeneous batch of polycrystalline crystals was obtained: a very few brown crystals of derivative **11** (which appeared after a few days) and a larger amount of dark red crystals of derivative **12** (which appeared after one week).

On account of the initial formation of product mixtures, further characterization of derivative **11** was limited to single-crystal analysis, whereas heteronuclear NMR spectroscopic data of compound **12** could be obtained from a pure sample obtained through careful manual selection of single crystals.

X-ray diffraction studies were performed on the limited material available of derivative **11**. Despite several attempts on different samples obtained from different reactions, we were not able to obtain single crystals of satisfactory quality. In one case, data collection could be performed from a sample that bore a weak diffraction pattern due to moderate crystalline quality. However, X-ray structure resolution carried out from that data collection strongly suggested that this crystalline sample was twinned, which did not allow us to establish the molecular structure of derivative **11** in a space group of high and accurate symmetry (presumably space group $P2_1/n$). Nevertheless, working in the $P2_1$ space
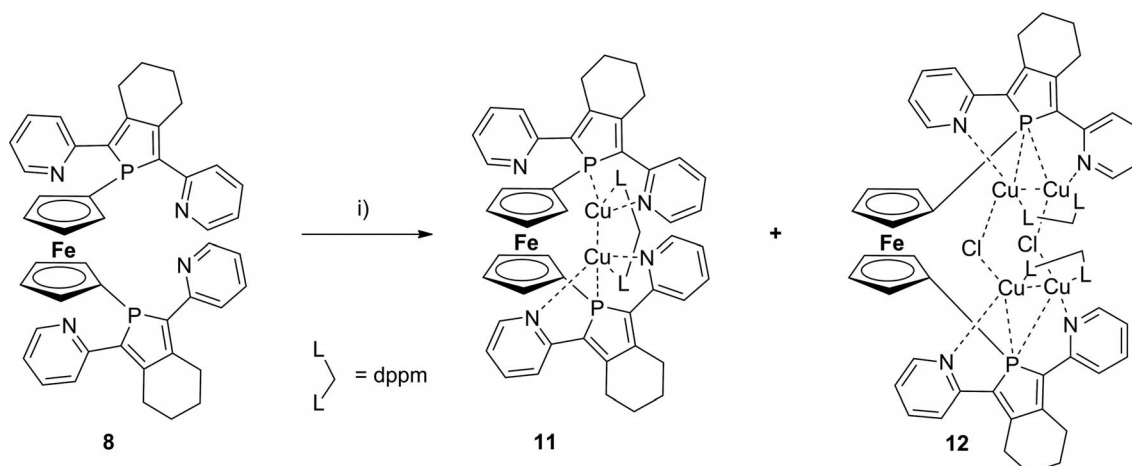
Scheme 2. Synthesis of Cu complexes **11** and **12** from 1,1′-ferrocenylene-bridged bisphosphole **8**: i) (1) dppm (2 equiv.), CH_2Cl_2; (2) [Cu(CH$_3$CN)$_4$BF$_4$] (4 equiv.).

group of the monoclinic system, a model could be established that revealed the molecular structure of complex **11** even though metric data for **11** can clearly not be discussed in detail. Derivative **11** is a discrete dimetallic complex that gathers one ligand **8**, one dppm ligand and two Cu^I metal centres involved in close-contact interactions (Figure 2, a). Quite unexpectedly, the two N,P,N fragments of ligand **8** are coordinated on the same Cu^I dimer, one of which acts as a bridging phosphane six-electron μ-1κN:1,2κP:2κN-N,P,N donor and one acting as a four-electron 1κN:2κP-P,N ligand. Due to this coordination scheme, the two N,P,N fragments present a *cisoid* orientation (P–Fe–P, ca. 66°) associated with an almost eclipsed conformation of the ferrocenylene unit. The dppm ligand completes the distorted-tetrahedral coordination sphere of Cu^I metal centres acting as a four-electron 1κP:2κP-P,P donor. Therefore, the coordination behaviour of ligand **8** toward Cu^I metal centres is clearly different from those observed for ligand **9** for which the two N,P,N units act independently, thereby selectively supplying a tetrametallic Cu^I complex.[14] Interestingly, the coordination modes adapted by the N,P,N moieties of **8** in this Cu^I dimer reproduce those observed in dimer **3** (Scheme 1) stabilized by two equivalents of the monophosphole ligand **1**.[8a,8c] Finally one can note that in derivative **11**, the Fe–Cu intermetallic distances are clearly too large for any short contact interactions [d(Fe–Cu) > 4.2 Å].

The ^{31}P{^{1}H} NMR spectra of **12** show a broad doublet at δ = +1.0 ppm and a triplet at δ = +13.8 ppm with a coupling constant of 85.3 Hz in an approximate ratio of 2:1. Such a ^{31}P{^{1}H} NMR spectrum is very similar to those recorded for complexes bearing a Cu$_2$(**1**)(dppm) fragment in which ligand **1** and dppm act as a six-electron μ-1κN:1,2κP:2κN donor and four-electron 1κP:2κP donors toward a Cu^I dimer, respectively.[8a,8c,14] Moreover, the ^{1}H and ^{13}C NMR spectroscopic data are indicative of a high complexity in this compound and together with the ^{31}P NMR spectroscopic data suggest incorporation of a dppm unit in these polymetallic complexes of Cu^I stabilized by
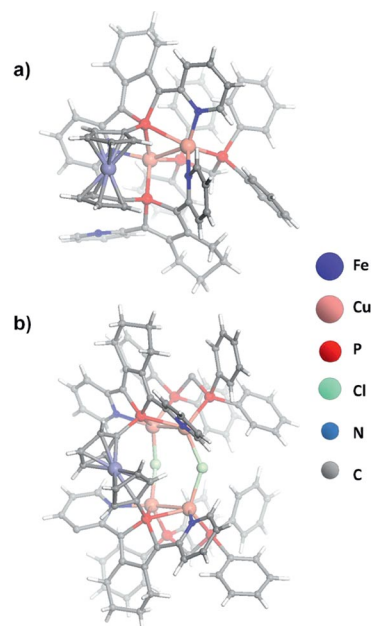

Figure 2. Molecular structure of Cu complexes (a) **11** and (b) **12** in the solid state. Included solvent molecules and counteranions have been omitted for clarity.

ligand **8**. Broadening of the ^{31}P and ^{13}C NMR spectroscopic signals also indicates a dynamic behaviour in solution at room temperature (room temp.). Interestingly, no signals for coordinating MeCN ligands were observed, which could be expected to saturate the open coordination site. Ultimately, only single-crystal X-ray diffraction allowed us to fully deduce the structure of **12**. On account of the small size and rapid decomposition of the crystals by solvent loss, the collected data did not allow extensive analysis of this structure. However, the identity and connectivity of all atoms could be unambiguously determined.

Each of the N,P,N sites bridges a Cu$^I_2$ dimer (Figure 2, b) [intermetallic Cu^I–Cu^I distances, 2.683(3) and 2.726(3) Å] similar to related Cu$_2$(**1**)(dppm) fragments,

which might be interpreted as metallophilic interactions.[8a,8c,14] Furthermore, the bimetallic Cu^I_2 dimer is symmetrically coordinated by one dppm ligand. Surprisingly, two Cl^- ions connect the two Cu^I_2 dimers to afford a non-planar six-membered Cu_4Cl_2 ring. These chloride ions most likely might originate from abstraction from the solvent (CH_2Cl_2) under the crystallization conditions in the presence of daylight. Similar examples that involve chloride abstraction have also been recently observed for other multinuclear copper complexes.[16] Consequently, only two BF_4^- counterions were found per formula unit. On account of this coordination scheme, in this derivative the two N,P,N units also adopt a *cisoid* orientation (P–Fe–P, ca. 102°) associated with an almost eclipsed conformation of the ferrocenylene unit. Finally, also note that in complex **12**, Fe–Cu intermetallic distances are again too long for metal–metal interactions [d(Fe–Cu) > 4.67 Å].

The characterization of these two derivatives **11** and **12** highlights the very different coordination chemistry toward Cu^I metal centres of the two ligands **8** and **9**. Whereas the reaction of **9** with this metal centre selectively afforded a discrete tetrametallic Cu^I complex, a similar reaction using **8** produced an insoluble derivative of presumably a polymeric nature. However, the use of dppm as ancillary blocking ligand allowed the isolation of discrete assemblies starting from **8**. Although the reactivity of **8** is not selective in this case, it demonstrates the ability of this bis(N,P,N) ligand to make multiple chelates on a Cu^I dimer (complex **11**) or on a Cu^I tetramer (complex **12**). Such different behaviour can be probably assigned to the higher geometrical flexibility of ligand **8** that bears more rotational degrees of freedom than ligand **9**. An alternative way to describe the coordination chemistry of ligand **8** would be to state that it adapts its geometry to act as a pincer ligand to trap either a Cu_2(dppm) unit (derivative **11**) or a larger Cu_4Cl_2-(dppm)$_2$ fragment (derivative **12**). Nevertheless, such a diversity in the coordination chemistry of ligand **8** is only possible at the expense of selectivity. These observation have triggered us to investigate in the next step the reaction of the ligand **8** to Ag^I and Au^I metal centres, which previously afforded a rich coordination chemistry upon reaction with the monophosphole N,P,N chelate **1**.[8f,8g]

Reaction of Ligand 8 with Ag^I Metal Centres

Coordination to Ag^I was explored by treating **8** with $AgBF_4$, which results in unspecific decomposition of the ligand system, probably induced by initial oxidation of the ferrocenylene unit. To corroborate this hypothesis, the oxidation potential of bisphosphole **8** was investigated using cyclic voltammetry. The half-wave potential of the ferrocenylene unit in **8** is observed at +0.53 V in CH_2Cl_2 versus Cp^*_2Fe (Cp^* = pentamethylcyclopentadienyl), which corresponds to –0.02 V versus ferrocene. In addition to this reversible redox process, further irreversible processes are observed at higher potential starting at +0.15 V (versus ferrocene). The oxidation potential of Ag^+ is, however, +0.65 V

(versus ferrocene) in CH_2Cl_2, which suggests that **8** is unsuitable for coordination of Ag^I.

Reaction of Ligand 8 with Au^I Metal Centres

Although the redox potential of Au/Au^+ is even more positive than that of Ag/Ag^+, coordination of bisphosphole **8** towards Au^I can be achieved in almost quantitative yield by using a suitable gold precursor. For this purpose, **8** was treated with [(tht)AuCl] (2 equiv.) to afford the neutral bimetallic Au^I complex **13** (Scheme 3). This reaction was conducted for 12 h in dichloromethane at room temperature and afforded a light yellow clear solution. After precipitation with pentane, the novel complex **13** was isolated from the reaction mixture as an air-stable hygroscopic light yellow powder in 85% yield.
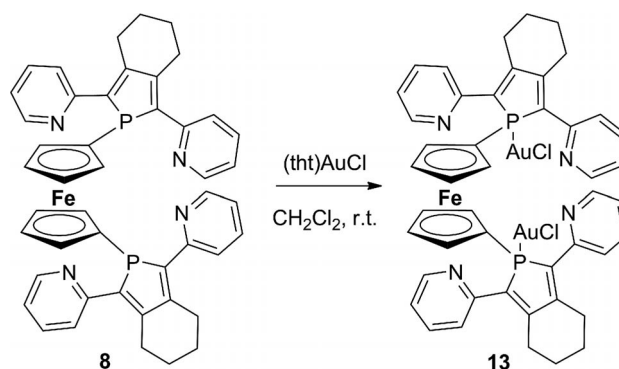
Scheme 3. Synthesis of the Au complex (**13**) from 1,1′-ferrocenylene-bridged bisphosphole **8**.

The $^{31}P\{^1H\}$ NMR spectrum of the crude solution displays one signal at δ = +32.0 ppm, which suggests a very selective reaction. This NMR spectroscopic signal is shifted to lower field relative to the resonance of the uncomplexed ligand **8**. Interestingly, the coordination shift $\Delta\delta(^{31}P) \approx$ 30 ppm is similar to that of ligand **1** and its monometallic Au^I complex **6** (δ = +39.9 ppm). This suggests a similar coordination mode of the Au^I metal centres on the phosphorus atoms of ligand **8** in derivative **13** as observed in complex **6**. The ^1H NMR spectrum of derivative **13** recorded at room temperature displays one set of signals indicative of ligand **8**, which suggests high molecular symmetry. The ^{13}C NMR spectra of **13** also indicate a symmetric nature. However the ferrocene (Fc)-carbon atoms could not be resolved or assigned and appear as heavily overlapping signals.

To confirm the proposed coordination mode, crystallization experiments were performed at room temperature with pentane vapour diffusion into a solution of **13** in dichloromethane. Quite surprisingly, after a few weeks, single crystals with different shapes and colours were collected: **13a** (orange prisms), **13b** (yellow prisms) and **13c** (yellow plates). X-ray diffraction analysis was successfully performed for these three polymorphs (see Table S1 in the Supporting Information) and revealed the solid-state crystal

Table 1. Selected structural parameters of **13a**–**c**.

	AuP[a]	PC$_{Fc}$[a]	Au–Au[a]	AuPCCl[b]	PAuC$_{Fc}$[b]	PFeP[c]
13a	2.2227(13)	1.793(5)	8.520(1)	177.83(4)	117.66(15)	180
13b	2.2294(16)/2.2299(17)	1.800(7)	8.349(1)	175.68(10)/177.40(8)	113.0(2)/120.9(2)	152
13c	2.2294(16)/2.2311(17)	1.792(6)/1.806(6)	3.0766(4)	164.33(7)/168.43(7)	121.8(2)/123.5(2)	90

[a] Distances [Å]. [b] Angles [°]. [c] Dihedral angle between the P substituents along the Fc axis [°].

structure of three different conformers of **13**, which differ from the relative orientation of the two N,P,N moieties coordinated to an "AuCl" fragment.

Conformers **13a** and **13b** crystallize in the triclinic space group P1̄, whereas **13c** crystallizes in the monoclinic space group P2$_1$/c. Besides molecules of **13**, the unit cells contain two included molecules of dichloromethane (solvent) for **13a**, one molecule of dichloromethane and one disordered molecule of water for **13b** and two molecules of dichloromethane for **13c**. None of these included molecules shows short contact interaction with the neutral complex **13**. In all these polymorphs, the expected bimetallic Au^I complex is observed as a result of the coordination of an AuCl moiety at the phosphorus atoms of ligand **8**. As observed in complex **6**, all the nitrogen atoms of the four pyridyl rings are free from coordination on the Au^I metal centres. The coordination spheres of the Au^I metal centres are almost linear (Table 1) and the P–Au bond lengths are classical for terminal two-electron P donors coordinated on Au^I metal centres (Table 1).[8g,9] The geometry around the P atoms is slightly pyramidal with obtuse Au–P–C$_{ferrocene}$ angles (Table 1). As usually observed in the coordination chemistry of the 2,5-bis(2-pyridyl)phosphole unit, the pyridyl rings and the phosphole rings are not coplanar and present quite a large range of interplanar torsion angles (from 5.9 to 51.2°). In all these conformers, the N,P,N moieties coordinated to the AuCl fragments are connected through the central ferrocenyl fragments of ligand **8**. The P–C$_{ferrocene}$ bond lengths (Table 1) are comparable to the P–C$_{Phenyl}$ bond length [1.813(4) Å] observed for complex **6**[9] and are typical of a P–C single bond. The ferrocenyl units bear cyclopentadienyl moieties that are planar and parallel, thereby revealing that neither the substitution of the cyclopentadienyl ring by 2,5-bis(2-pyridyl)phosphole fragments nor the coordination of the Au^I metal centres on the P centres induce steric strains in the central ferrocenyl groups. Finally, the P atoms are almost coplanar to the plane of the adjacent cyclopentadienyl groups (distance of the P atoms from the mean planes of the cyclopentadienyl groups in **13a**: 0.017 Å, **13b**: 0.031 and 0.110 Å, **13c**: 0.046 and 0.115 Å). All in all, these metric data are comparable for all the three conformers observed in the solid state. Finally one can note that in all the solid-state structures of the conformers of derivative **13**, the Fe–Au intermetallic distances are too large for short contact interactions [d(Fe–Au) > 4.2–4.5 Å]. The structural differences between **13a**–**c** lie in the orientation of the two N,P,N units coordinated to the Au^I metal centre relative to the central ferrocenylene moiety. Whereas in **13a**, these units have a strict *anti* orientation (P–Fe–P, 180°) associated with a staggered conformation of the ferrocenylene unit, the

two N,P,N units get "more *cisoid*" in the solid-state structure of **13b** (P–Fe–P, 152°, in which the ferrocenylene moiety has an eclipsed conformation) and in the conformer **13c** (P–Fe–P, 90°; eclipsed conformation). The fact that these three different conformations can crystallize from the same mother solution suggests an energetically and sterically free rotation about the "Cp–Fe–Cp" axis in complex **13**. Interestingly, in conformer **13c**, the Au^I centres present short intermetallic distances [3.0766(4) Å] indicative of an aurophilic interaction (Figure 3). Intermetallic distances are 8.520(1) Å in **13a** and 8.349(1) Å in **13b** and therefore too large for aurophilic interactions. Apparently, in compound **13** the factors that favour this aurophilic interaction can be easily counterbalanced.
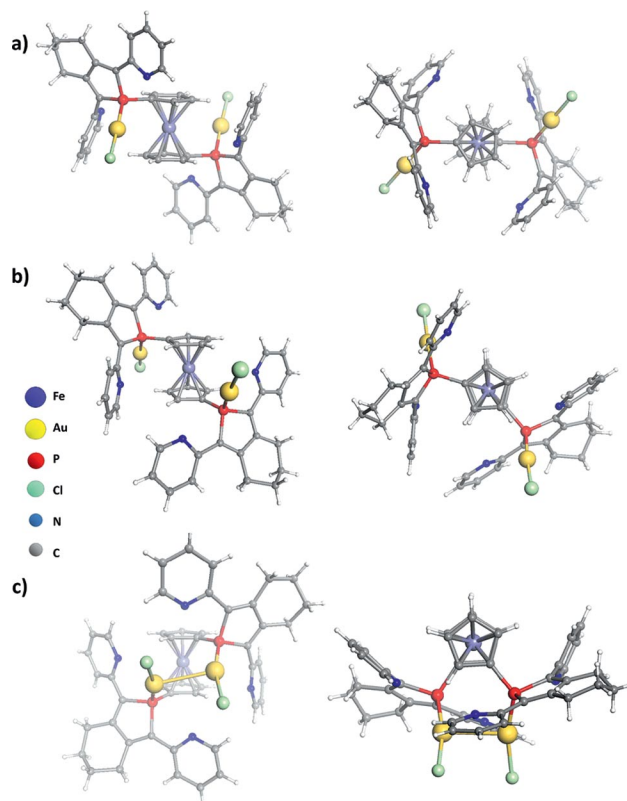

Figure 3. Two views of the molecular structure of Au complex **13**: (a) conformer **13a**, (b) conformer **13b**, (c) conformer **13c** in the solid state. Included solvent molecules have been omitted for clarity.

Computational Studies

Nevertheless, exploratory density functional theory (DFT) calculations indicate that for single molecules of the

different isomers the arrangement found for **13c** is energetically preferred over the isomers without aurophilic interactions, which confirms that the short Au···Au contact in **13c** is not simply a packing effect in the crystal. Calculated geometries slightly overestimate bonding towards the metal centre [i.e., for **M13c** Au···Au (2.71 Å), Au···Cl (2.27 Å)], and Au···P (2.21 Å) contacts are shortened relative to the experimental data. The *transoid* isomer **M13b** shows Au–Au distances of 7.11 Å and has a similar orientation of the substituents to the solid-state structure of **13b**. Interestingly, we also found an additional *trans* isomer **M13d** on the potential-energy surface (PES) in which one of the Au atom exhibits coordination towards a pyridine fragment, whereas no intermetallic interactions are observed. This interaction leads to a relatively short Au··N distance of 2.48 Å, whereas the Au···P distance remains essentially unchanged (ca. 2.21 Å). This coordination requires a reorientation of the Au–Cl unit, which leads to a highly distorted coordination to the phosphole. However, this calculated isomer is almost isoenergetic to **M13b** and destabilized by approximately 13 kcal mol^{-1} relative to the energetically most favoured isomer **M13c**.

In solution there is most probably an equilibrium between the different conformations observed in the solid state and possibly others as well. This is also in agreement with NMR spectroscopic characterizations in solution that suggest a single symmetrical species as a result of fast conformational exchange on the NMR spectroscopic timescale even at low temperature (–50 °C). This result confirms that the possibility of the free rotation about the "Cp–Fe–Cp" axis in ligand **8** offers a structural diversity to the complex formed from this ligand, which is larger than those associated with the phenylene-bridged bisphosphole ligand **9**. Apparently, this flexibility is a consequence of the balanced steric situation in **8**, which differs from the situation in diaurated ferrocenylene bisphosphane Fc′(PHPh)$_2$ for which three diastereomers have been reported on the basis of ^{31}P NMR spectroscopy.[17]

Careful examination of the structural data obtained for **13a–c** reveals that the free rotation about the P–C$_{ferrocenyl}$ bond also contributes to this structural diversity as the orientation of the N,P,N unit presents quite a large range of orientations toward the planes of the cyclopentadienyl fragments to which they are bonded. More particularly, the two 2,5-bis(2-pyridyl)phosphole fragments present an almost "face-to-face" organization in conformer **13c** in which the aurophilic interaction is observed. Such organization probably allows the metal centres to become involved in metallophilic interactions.

Conclusion

We have prepared a novel N,P,N-chelating bisphosphole ligand **8** based on ferrocene and explored its reactivity towards Cu^I, Ag^I and Au^I metal centres. The high rotational flexibility in **8** yields a different coordination behaviour relative to its phenylene analogue **9**, as exemplified by

the coordination mode toward Cu^I. In turn, the redox properties of **8** are unsuitable for the formation of diamagnetic complexes with Ag^I. Most interestingly, ligand **8** is well suited to coordination to Au^I centres. These gold complexes can show intramolecular aurophilic interactions as confirmed by X-ray crystallography. However, these aurophilic interactions are overcome by rotational motion about the Cp–Fe–Cp axis in solution, and isomers of **13** without aurophilic interactions have been confirmed in the solid state as well. The effect of the larger structural flexibility of ferrocenylene bisphosphole **8** than phenylene bisphosphole **9** shall be explored with respect to supramolecular assemblies of tetrametallic Cu^I clips in the future. Moreover, we will explore the possibility to interconvert the open (**13a**,**b**) and closed (**13c**) isomeric forms to gain access to an "aurophilic switch".

Experimental Section

General: All experiments were carried out under an inert atmosphere using modified Schlenk techniques and dried deoxygenated solvents unless otherwise stated. NMR spectra were recorded with a JEOL Eclipse+ or Varian MR-400 and VNMRS-500 instrument operating at proton frequencies of 400 and 500 MHz, respectively. Spectra were referenced internally to solvent residual peaks (^{1}H, ^{13}C) or externally to 85% H$_3$PO$_4$. Chemicals have been purchased from Sigma–Aldrich and used as received if not otherwise stated. Deuterated solvents were purchased from Eurisotop. All solvents were dried using appropriate methods.

Bisphosphole 8: A solution of 1,8-bis(pyridin-2-yl)octa-1,7-diyne[7a] (2.25 g, 8.7 mmol) and [Cp$_2$ZrCl$_2$] (2.53 g, 8.7 mmol) in THF (30 mL) was cooled to –78 °C and slowly treated with *n*BuLi (7.62 mL, 19.1 mmol). Upon addition, stirring was continued for 2 h at –78 °C and then the mixture was allowed to reach room temperature with stirring for an additional 10 h (e.g., overnight). The mixture was cooled to –78 °C again and 1,1-bisdichlorophosphano ferrocene[18] (1.68 g, 4.3 mmol) dissolved in THF (15 mL) was added dropwise over 15 min. Upon addition, the mixture was allowed to reach room temperature followed by additional stirring for 3–5 h. The resulting suspension was filtered through basic alumina and the solvent was removed under vacuum. Product **8** was obtained as an orange oil or solid, which could be purified by trituration with small amounts of Et$_2$O (yield: 1.66 g, 50%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.67–2.58 (m, 8 H, CH$_2$), 3.17–3.08 (m, 8 H, CH$_2$), 3.54 (m, 4 H, Cp), 3.59 (m, 4 H, Cp), 7.11 (ddd, $J_{H,H}$ = 7.4, 4.8, 1.0 Hz, 4 H, Py), 7.47 (ddd, $J_{H,H}$ = 7.9, 1.1, 1.0 Hz, 4 H, Py), 7.67 (ddd, $J_{H,H}$ = 8.1, 7.7, 1.9 Hz, 4 H, Py), 8.62 (ddd, $J_{H,H}$ = 4.8, 1.8, 0.9 Hz, 4 H, Py) ppm. ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ = 23.39 (s, CH$_2$), 28.42 (s, CH$_2$), 71.31 [dd, $J_{C,P}$ = 3.7, 0.9 Hz, Cp], 71.60 (d, $J_{C,P}$ = 11.4 Hz, Cp), 74.57 (d, $J_{C,P}$ = 14.5 Hz, C$_q$–Cp), 120.99 (s, Py), 124.29 (d, $J_{C,P}$ = 7.4 Hz, Py), 136.11 (d, $J_{C,P}$ = 1.3 Hz, Py), 145.30 (d, $J_{C,P}$ = 2.9 Hz, C$_q$), 146.53 (d, $J_{C,P}$ = 10.0 Hz, C$_q$), 149.83 (d, $J_{C,P}$ = 1.1 Hz, Py), 156.85 (d, $J_{C,P}$ = 17.9 Hz, C$_q$–Py) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$): δ = 3.2 (s) ppm. MS (MALDI, DCTB): *m/z* (%) = 766.034 (100) [M$^{+\cdot}$]. CV (CD$_2$Cl$_2$, Bu$_4$NPF$_6$): $U_{1/2}$ = 0.53 V (versus Cp*$_2$Fe). Microanalytical data show slight deviations owing to solvent content. Purity based on ^{1}H NMR spectroscopy is >97%.

Copper Complex 11 and 12: [CuBF$_4$(MeCN)$_4$] (2 equiv., 83 mg, 0.26 mmol, 5 mL of CH$_2$Cl$_2$) was added to a solution of **8** (46 mg,

0.06 mmol) and dppm (50 mg, 0.13 mmol) in CH_2Cl_2 (10 mL). Compound **11** could not be isolated in pure form. Hence characterization was limited to X-ray crystallographic analysis of crystals that were manually picked. Compound **12**: ^1H NMR (400 MHz, CDCl$_3$): δ = 1.62 (m, 4 H), 1.95–2.05 (m, 4 H, CH_2), 2.55–2.65 (m, 4 H, CH_2), 3.25–3.35 (m, 4 H, CH_2), 3.49 (br. s, 4 H, Fc), 3.85 (br. s, 4 H, Fc), 6.72 (m, 8 H), 6.90 (t, $^3J_{H,H}$ = 7.5 Hz, 8 H), 7.11 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H), 7.26–7.41 (m, 20 H), 7.92–8.07 (m, 8 H), 8.33 (d, J = 4.5 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.99 (s, CH_2), 27.50 (br. s, CH_2) 71.26–71.96 (Fc), 117.72 (s), 124.07 (s), 124.88 (s), 129.00 (dm, J = 49.6 Hz), 130.79 (d, J = 19.0 Hz), 132.22 (m), 137.30 (d, J = 84.3 Hz), 139.69 (br. s), 140.70 (d, J = 41.6 Hz), 143.84 (d, J = 43.0 Hz), 150.77 (multiple overlapping signals), 151.45 (d, J = 14.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$): δ = 1.1 (br. d, J = 88 Hz), 13.4 (br. t, J = 88 Hz) ppm. Microanalytical data show slight deviations due to solvent content. Purity based on ^1H NMR spectroscopy is >90%.

Gold Complex 13: AuCl·(tht)[19] (2 equiv., 26 mg, 0.08 mmol) was added to a solution of **8** (36 mg, 0.04 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was protected from light and stirred overnight to give the gold chloride complex **13** in quantitative yields. After removal of all volatiles the product was obtained by diffusion of pentane into a saturated solution of **13** in CH_2Cl_2 as a slightly light- and air-sensitive compound, yield 85% (34 mg). ^1H NMR (400 MHz, CDCl$_3$): δ = 1.60–1.80 (m, 8 H), 2.60–2.70 (m, 4 H), 2.95–3.05 (m, 4 H), 3.75 (br. s, 4 H, Fc), 4.14 (br. s, 4 H, Fc), 7.22 (t, $J_{H,H}$ = 6.9 Hz, 4 H), 7.76 (t, $J_{H,H}$ = 7.1 Hz, 4 H), 7.83 (d, $J_{H,H}$ = 7.7 Hz, 4 H), 8.86 (d, $J_{H,H}$ = 4.4 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 22.23 (s, CH_2), 22.69 (d, $^3J_{P,C}$ = 9.6 Hz, CH_2), 73.60–73.89 (Fc), 122.59 (br. s), 124.98 (d, J = 5.3 Hz), 136.66 (d, J = 2.1 Hz), 149.62 (br. s), 151.73 (d, J = 16.7 Hz), 152.79 (d, J = 15.8 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$): δ = 32.0 ppm. Microanalytical data show slight deviations due to solvent content. Purity based on ^1H NMR spectroscopy is >95%.

Crystallographic Details: Single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of vapours of pentane into a solution of the derivatives **11** and **13** or **12** in dichloromethane or chloroform at room temperature, respectively. Single-crystal data collection of **11** and **13** were performed at 150 K with a Nonius KappaCCD diffractometer and a Bruker AXS APEX-II (Centre de Diffractométrie, Université de Rennes 1, France) as well as with a Bruker D8 with an APEX-II setup at 100 K (Uppsala) with Mo-K_α radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program. Alternatively the Bruker suite of programs (SAINT, SADABS) was used for indexing, integration and scaling.[20] Structure **12** was solved with direct methods and refined using the SHELX suite of programs with the WinGX interface.[21] Structure determinations of **11** and **13** were performed by direct methods with the solving program SIR97,[22] which revealed all the non-hydrogen atoms. SHELXL program[21b] was used to refine the structures by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. In the crystal lattices of some of coordination complexes studied, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and to their counteranions. These solvent molecules in most cases have a strong tendency to leave the bulk crystal by means of evaporation once the crystals are removed from their mother solution, a process that induces a rapid degradation of the single-crystal integrity of the

crystals investigated. To slow this process, single crystals of all these derivatives were always coated in Fomblin oil once removed from the mother solution, mounted at low temperature as quickly as possible on the diffractometer goniometer and X-ray data collection was performed at low temperature. In most of the cases, X-ray crystal-structure resolution revealed these solvent molecules to be highly disordered. In addition, with regard to the data collection for derivatives **11** and **12**, due to the small size and/or the weak crystalline quality of the crystal obtained, a satisfactory crystal-structure resolution could not be performed (see above for more details). In the case of the solid-state structure of derivative **11**, a correct modelling of the disorders of these CH_2Cl_2 solvent molecules was not possible and we proceeded to a "squeeze" treatment[23] to remove the scattering contribution of these molecules that cannot be satisfactory modelled. Table S1 in the Supporting Information gives the crystallographic data for the solid-state structures **11**, **12**, **13a**, **13b** and **13c**. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[24]

CCDC reference numbers 963910 (for **11**), -963911 (for **12**), -963912 (for **13a**), -963913 (for **13b**) and -963914 (for **13c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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