A hemilabile binucleating pincer ligand for self-assembly of coordination oligomers and polymers†‡

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The *bis*(PNP)-donor pincer ligand 1,4-$C_6H_4\{N(CH_2CH_2PPh_2)_2\}_2$, **1**, contains weakly basic nitrogen donor atoms because the lone pairs of electrons are conjugated to the bridging phenylene group, and this feature is used in the synthesis of oligomers and polymers. The complexes $[Pd_2X_2(\mu\text{-}\mathbf{1})](OTf)_2$, X = Cl, Br or OTf, contain the ligand **1** in *bis*(pincer) binding mode (μ-κ^6-P_4N_2), but $[Pd_4Cl_6(\mu_3\text{-}\mathbf{1})_2]Cl_2$ contains the ligand in an unusual unsymmetrical μ_3-κ^5-P_4N binding mode. The bromide complex is suggested to exist as a polymer $[\{Pd_2Br_4(\mu_4\text{-}\mathbf{1})\}_n]$ with the ligands **1** in μ_4-κ^4-P_4 binding mode. The methylplatinum(II) complexes $[Pt_2Me_4(\mu\text{-}\mathbf{1})]$ and $[Pt_2Me_2(\mu\text{-}\mathbf{1})](O_2CCF_3)_2$ contain the ligand **1** in μ-κ^4-P_4 and μ-κ^6-P_4N_2 bonding modes, while the silver(I) complex $[Ag_2(O_2CCF_3)_2(\mu\text{-}\mathbf{1})]$ contains the ligand **1** in an intermediate bonding mode in which the nitrogen donors are very weakly coordinated. The complexes $[Pd_2(OTf)_2(\mu\text{-}\mathbf{1})](OTf)_2$ and $[Ag_2(O_2CCF_3)_2(\mu\text{-}\mathbf{1})]$ react with 4,4′-bipyridine to give polymers $[Pd_2(\mu\text{-bipy})(\mu\text{-}\mathbf{1})](OTf)_4$ and $[Ag_2(\mu\text{-bipy})(\mu\text{-}\mathbf{1})](O_2CCF_3)_2$.

Introduction

Tridentate pincer ligands have proved to have many useful roles in coordination chemistry, with applications in catalysis and molecular materials.[1,2] Within this class of ligand, the hemilabile PNP-donor pincer ligands have been widely studied and the presence of the weak nitrogen-donor centre in promoting some catalytic reactions has been well established.[1–3] The reversibility of the N-donor group in ligands of the type $RN(CH_2CH_2PPh_2)_2$ is illustrated by the complexes shown in Chart 1. Tridentate coordination is illustrated by the cationic square planar palladium(II) and platinum(II) complexes **A–E**, but the N-donor can be displaced reversibly by ligands such as chloride to give the complexes such as **F**, which contains an eight-membered chelate ring with a *cis*-bidentate ligand, or **G**, which contains a sixteen-membered macrocycle and in which the ligand bridges between palladium(II) centres.[4] The preference for formation of **F** (M = Pt) *versus* **G** (M = Pd) appears to depend on the preference of the metal centre for *cis* or *trans* stereochemistry, under conditions where the chelate effect is not dominant. If the anions X^- are weakly binding, such as the triflate ion, the compounds of type **E** are formed exclusively.[4f] When X = Cl, the complex which crystallizes may depend on the substituent R in the ligand $RN(CH_2CH_2PPh_2)_2$, so that complex **A** or **D** is formed if R = H or benzyl, but complex **G** is formed if R = C(=O)-4-C_6H_4Me.[4d,e] Thus, it is known that the preference for forming the cationic complexes **A–E** with tridentate ligands or the neutral complexes **F** or **G** with bidentate ligands (Chart 1) can be controlled by modifying the relative donor strength of the nitrogen donor (by adjusting the electron donating or withdrawing ability of the substituent R) and of the anion X^-.[4] In catalysis, the easy, reversible M–N bond cleavage offers a low energy route for coordination of reagents and displacement of products in a catalytic cycle.[1–4]

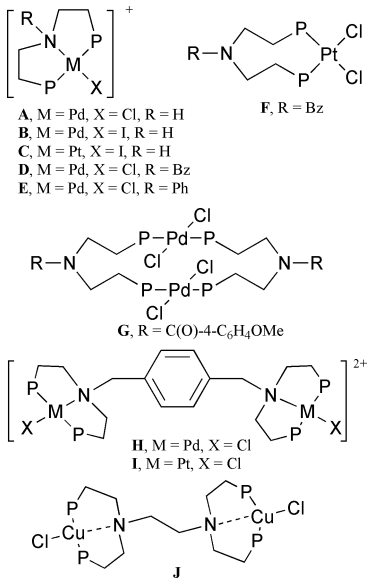

Chart 1 Representative complexes with PNP pincer ligands.

The hemilabile PNP-donor pincer ligands have not been used to such a great extent in forming polymeric molecular materials, although more rigidly binding pincer ligands have proved to be exceptionally useful in this field.[1,2] However, several binucleating PNP-donor pincer ligands have been synthesized and used in coordination chemistry. The palladium(II), platinum(II) and copper(I) complexes **H–J** (Chart 1) are representative examples.[5] This paper reports a new *bis*(PNP)-donor ligand 1,4-$C_6H_4\{N(CH_2CH_2PPh_2)_2\}_2$ and a study of its use in forming oligomeric and polymeric transition metal complexes.

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† The HTML version of this article has been enhanced with colour images.

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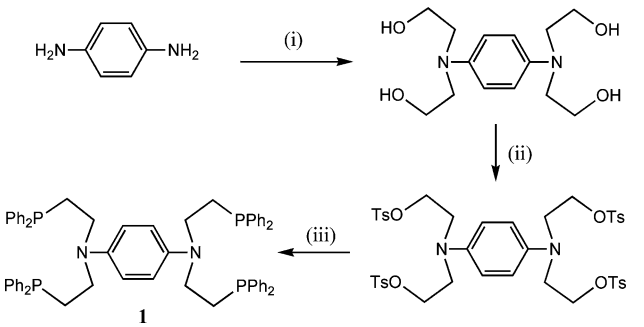
Results and discussion

Synthesis of the ligand 1

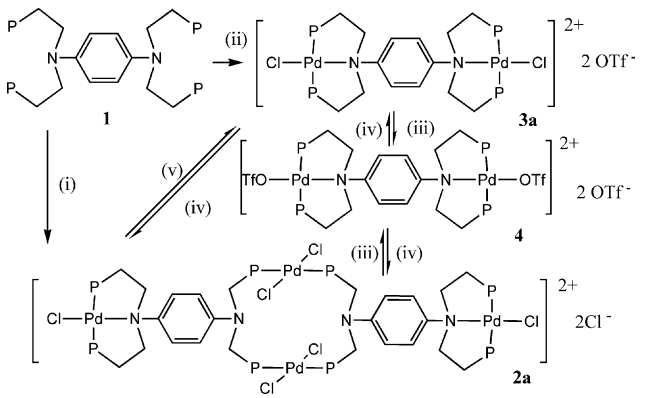
The synthesis of the ligand 1,4-$C_6H_4\{N(CH_2CH_2PPh_2)_2\}_2$ is shown in Scheme 1. The precursor 1,4-$C_6H_4\{N(CH_2CH_2OH)_2\}_2$ was prepared by the literature method.[6] It is reported to be unstable so it was immediately converted to the tosylate derivative 1,4-$C_6H_4\{N(CH_2CH_2OTs)_2\}_2$ by reaction with tosyl chloride in the presence of pyridine as base. Treatment of the tosylate with lithium diphenylphosphide then gave the new ligand 1,4-$C_6H_4\{N(CH_2CH_2PPh_2)_2\}_2$, **1**. The ligand **1** was isolated as a white solid and was characterized in the ^{31}P NMR spectrum by a singlet at $\delta(^{31}P) = -20.0$, which is the typical range for ligands of this type.[4,5]



Scheme 1 Synthesis of the ligand **1**. Reagents are: (i) $ClCH_2CH_2OH$–NaOH; (ii) tosyl chloride–pyridine; (iii) Ph_2PLi.

Palladium chloride and triflate complexes

The reaction of ligand **1** with two equivalents of $[PdCl_2(COD)]$ occurred cleanly to give a complex which was identified as $[Pd_4Cl_6(\mu_3\text{-}\mathbf{1})_2]Cl_2$, **2a** (Scheme 2). In the ^{31}P NMR spectrum, complex **2a** gave two equal intensity singlet resonances at $\delta(^{31}P) =$ 10.8 and 32.4, assigned to the phosphorus atoms in the central macrocycle (compare to complex **G** in Chart 1 with average $\delta(^{31}P) = 11.6$)[4e] and the terminal units (compare to complexes **D** and **E** in Chart 1 with $\delta(^{31}P) = 32.2$ and 32.6 respectively)[4b,e] respectively. The reaction of ligand **1** with an equimolar mixture of $PdCl_2$ and $[Pd(acac)_2]$ in the presence of triflic acid gave the complex $[Pd_2Cl_2(\mu\text{-}\mathbf{1})](OTf)_2$, **3a**, which was characterized by a single resonance in the $\delta(^{31}P)$ NMR spectrum at $\delta(^{31}P) = 32.3$. Complex **3a** could also be formed by reaction of complex **2a** with triflic acid. Reaction of complex **3a** with silver triflate occurred by abstraction of the chloride ligands to give the triflate complex $[Pd_2(OTf)_2(\mu\text{-}\mathbf{1})](OTf)_2$, **4**, which was characterized by a single resonance in the $\delta(^{31}P)$ NMR spectrum at $\delta(^{31}P) = 43.6$. These reactions were reversible. Thus, treatment of complex **4** with two or four equivalents of lithium chloride gave back the complexes **3a** and **2a** respectively, as monitored by ^{31}P NMR spectroscopy.



Scheme 2 Reagents are: (i) $[PdCl_2(COD)]$, – COD; (ii) $PdCl_2$ + $[Pd(acac)_2]$ + HOTf; (iii) AgOTf, – AgCl; (iv) LiCl, – LiOTf; (v) HOTf, – HCl.

The complexes **2a** and **3a** were characterized by structure determinations. The structure of **3a** is shown in Fig. 1. There is a centre of symmetry at the middle of the C_6H_4 group, such that the two square planar palladium(II) centres are equivalent. Each palladium has stereochemistry similar to that in the mononuclear complexes such as **A** (Chart 1).[4h] There are no close contacts between palladium centres and the triflate anions. Compared to complex **A**, the Pd–N distance in **3a** is slightly longer [2.114(3) *versus* 2.065(5) Å] while the Pd–Cl is slightly shorter [2.2866(9) *versus* 2.3082(2) Å]. This difference can be rationalised in terms of the C_6H_4 substituent in **3a** making the nitrogen a weaker donor than in **A** with a resulting decrease in the *trans*-influence.

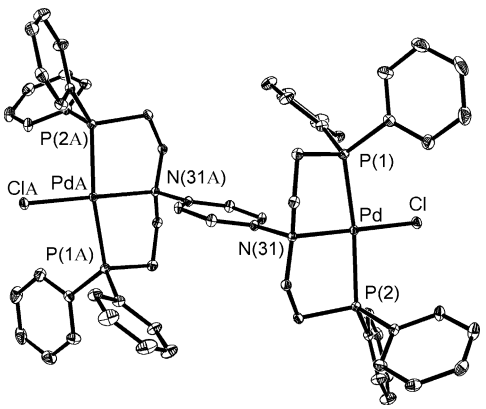


Fig. 1 Structure of the dicationic complex **3a**. Selected bond parameters: Pd–N(31) 2.114(3); Pd–Cl 2.2866(9); Pd–P(2) 2.2968(9); Pd–P(1) 2.3227(10) Å; N(31)–Pd–Cl 178.23(7); N(31)–Pd–P(2) 85.77(8); Cl–Pd–P(2) 94.75(3); N(31)–Pd–P(1) 83.76(8); Cl–Pd–P(1) 95.89(3); P(2)–Pd–P(1) 168.19(3)°. Symmetry equivalent atoms: $1.5 - x$, $1.5 - y$, $4 - z$.

The structure of the dicationic complex **2a** is shown in Fig. 2(a). There is an inversion centre in the centre of the molecule. However, the central palladium(II) centres, Pd(2) and Pd(2A), have *trans*-$PdCl_2P_2$ coordination. This part of the structure is analogous to the structure of complex **G** (Chart 1), and the bond parameters are also similar.[4e] An unusual feature is the presence of a pair of dichloromethane molecules which bridge weakly between the two $PdCl_2$ units through secondary bonding interactions of the type Pd(2)–Cl(4)···H(61D)CHCl–Cl(6D)···Pd(2A), with Pd(2A)···Cl(6D) = 3.499 Å and Cl(4)···H(61D) = 2.62 Å, as shown in Fig. 2(b). The terminal palladium(II) centres, Pd(1) and Pd(1A) with $PdClNP_2$ coordination, have similar stereochemistry and bond parameters as in complex **3a** as well as to **A** (Chart 1). The Pd–N bond is slightly shorter in **2a** than in **3a** [2.103(7) *versus* 2.114(3) Å] while the Pd–Cl bond is slightly longer [2.295(2) *versus* 2.2866(9) Å]. A likely reason for these small differences is that

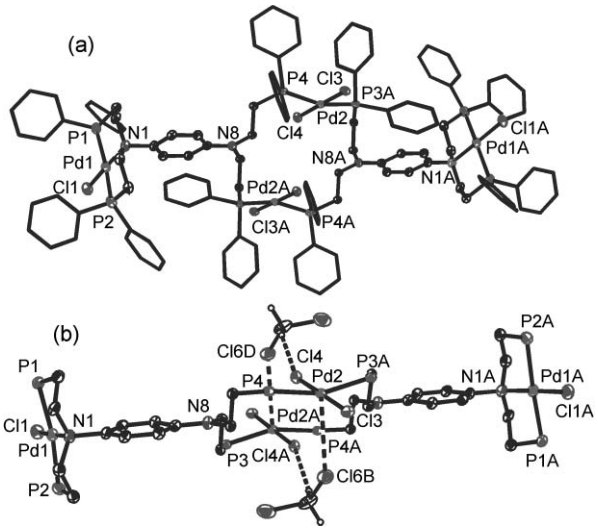


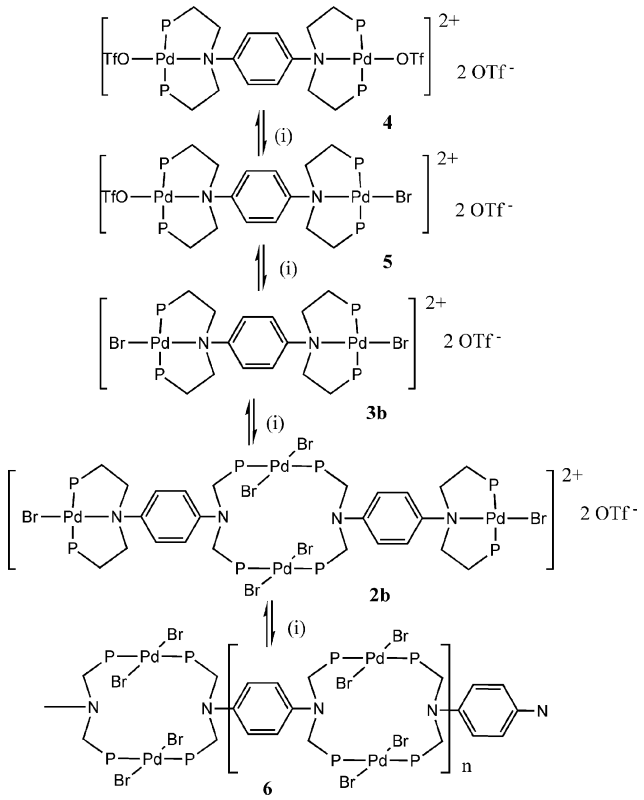
Fig. 2 The structure of complex **2a**: (a) structure of the dication; (b) structure with phenyl groups omitted, showing the secondary bonding to dichloromethane solvate molecules. Selected bond parameters: Pd(1)–N(1) 2.103(7); Pd(1)–P(2) 2.293(3); Pd(1)–P(1) 2.293(3); Pd(1)–Cl(1) 2.295(2); Pd(2)–Cl(4) 2.295(2); Pd(2)–Cl(3) 2.298(2); Pd(2)–P(3A) 2.310(2); Pd(2)–P(4) 2.313(2) Å; N(1)–Pd(1)–P(2) 85.4(2); N(1)–Pd(1)–P(1) 85.4(2); P(2)–Pd(1)–P(1) 165.2(1); N(1)–Pd(1)–Cl(1) 177.1(2); P(2)–Pd(1)–Cl(1) 95.62(9); P(1)–Pd(1)–Cl(1) 94.1(1); Cl(4)–Pd(2)–Cl(3) 179.36(8); Cl(4)–Pd(2)–P(3A) 88.81(7); Cl(3)–Pd(2)–P(3A) 91.33(7); Cl(4)–Pd(2)–P(4) 89.50(7); Cl(3)–Pd(2)–P(4) 90.56(7); P(3A)–Pd(2)–P(4) 161.21(7)°. Symmetry equivalent atoms: A, $-x$, $-y$, $-1-z$.

the lone pair of the free nitrogen atom N(8) in **2a** is conjugated with the phenylene group[7] and this leads to an increase in electron density at N(1), thus increasing the donor power when compared to the two nitrogen donors in **3a**. We will discuss this effect in greater depth below.

The structure of complex **2a** illustrates very clearly the fine balance in the competition between coordination of chloride and the nitrogen atom of the pincer ligand to palladium(II) to give either the *trans*-$PdCl_2P_2$(freeN) or the $[PdClNP_2]^+Cl^-$ unit. Complex **2** contains two units of each type (Fig. 2). This observation prompted a study of the corresponding bromide complexes, assuming that the softer bromide would compete more effectively than chloride for coordination to palladium(II).

Palladium bromide complexes

The reaction of complex **4** with two equivalents of *n*-Bu_4NBr gave the complex $[Pd_2Br_2(\mu\text{-}\mathbf{1})](OTf)_2$, **3b** (Scheme 3), which was characterized spectroscopically by comparison to the chloride analog **3a**. For example, the ^{31}P NMR spectrum contained a singlet at $\delta(^{31}P) = 36.8$, in the range expected for a pincer complex [**3a**, $\delta(^{31}P) = 32.3$]. However, a new reaction occurred on reaction of complex **4** with four equivalents of *n*-Bu_4NBr in acetonitrile solution. Most of the product precipitated as a yellow solid, which analysed as $Pd_2Br_4(\mu\text{-}\mathbf{1})$, **6**. The formula is analogous to that of complex **2a**, but complex **6** is much less soluble than **2a** and has different spectroscopic features. Thus, the ^{31}P NMR spectrum contained only a single broad resonance at $\delta(^{31}P) = 12.3$, in the region found for the central unit in complex **2a** [$\delta(^{31}P) = 10.8$] and no resonance in the region expected for pincer ligation [$\delta(^{31}P) =$ 36.8 for **3b**]. The ESI-MS, recorded in the presence of formic acid to aid ionization, gave the highest mass peak at $m/z = 4373$ corresponding to the ion $[Pd_6Br_{11}(\mathbf{1})_3^+]$. We have not been able to grow single crystals of **6** suited to structure determination, but the spectroscopic data indicates an oligomeric or polymeric structure as indicated for **6** in Scheme 3.

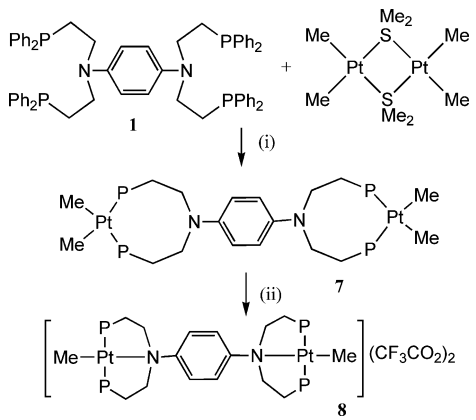


Scheme 3 Bromide complexes of palladium(II). Reagents: (i) Bu_4NBr, – Bu_4NOTf.

In another experiment, a solution of complex **4** in CD_3CN in an NMR tube was treated with successive one equivalent amounts of *n*-Bu_4NBr and the reaction was monitored by ^{31}P NMR spectroscopy. With one equivalent, the peak due to complex **4** at $\delta(^{31}P) = 44$ [$PdONP_2$] was replaced by two peaks assigned to complex **5** (Scheme 3) at $\delta(^{31}P) = 37$ [$PdBrNP_2$] and 46 [$PdONP_2$]. After addition of two equivalents, the spectrum contained only a singlet resonance for complex **3b** at $\delta(^{31}P) = 37$ [$PdBrNP_2$]. Note that the chemical shifts of the ^{31}P NMR resonances for complex **5** ($\delta = 37$ and 46) are similar to those of **4** ($\delta = 44$) and **3b** ($\delta = 37$), so the spectrum assigned to **5** could also be assigned to a mixture of these three complexes. After addition of three equivalents of bromide, there were again two resonances at $\delta(^{31}P) =$ 13 [$PdBr_2P_2$] and 37 [$PdBrNP_2$], which are assigned to complex **2b** because the spectrum is similar to that of **2a**. After four equivalents, precipitation of **6** occurred but the remaining solution contained only a singlet at $\delta(^{31}P) = 12$ [$PdBr_2P_2$]. Similar steps were observed in the addition of chloride to **4** except that the last addition gave no precipitation or spectral change, indicating that **2a** was unreactive towards chloride addition. It is remarkable that the change from chloride to bromide causes such a difference, but the chemistry does show how the hemilabile nature of the nitrogen donor in **1** can be used to make oligomeric or polymeric molecular compounds.

Synthesis of methylplatinum(II) complexes

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligand **1** occurred easily to give the methylplatinum(II) complex $[Pt_2Me_4(\mu\text{-}\mathbf{1})]$, **7** (Scheme 4). In the ^{1}H NMR spectrum, the methylplatinum resonance occurred at $\delta(^1H) = 0.09$ with coupling constant $^2J(PtH) = 68$ Hz and, in the ^{31}P NMR spectrum, there was a single resonance at $\delta(^{31}P) = 18.1$ with coupling constant $^1J(PtP) = 2280$ Hz. These parameters are characteristic for square planar platinum(II) complexes with *cis*-$PtMe_2P_2$ coordination, so it is clear that the nitrogen atoms of **1** are not coordinated.[8] Reaction of complex **7** with trifluoracetic acid occurred to give methane and the pincer complex $[Pt_2Me_2(\mu\text{-}\mathbf{1})](CF_3CO_2)_2$, **8**. Complex **8** gave a single resonance in the ^{31}P NMR spectrum at $\delta(^{31}P) = 31.5$, in the range expected for a pincer complex,[4] with a coupling constant $^1J(PtP) = 3760$ Hz, much higher than in **7**. The methylplatinum resonance for **8** appeared at $\delta(^1H) = 0.79$, as a triplet [$^3J(PH) = 6$ Hz] with satellites due to coupling to ^{195}Pt with $^2J(PtH) = 80$ Hz. The increase in the coupling constant $^2J(PtH)$ in complex **8** compared to **7** is consistent with the *trans*-NPtMe stereochemistry. Reaction of complex **8** with excess trifluoroacetic acid led to loss of the methylplatinum resonances, but a mixture of platinum-containing products was formed from which no pure compounds could be isolated.

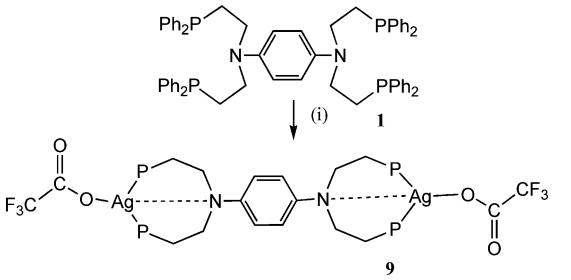


Scheme 4 Synthesis of methylplatinum complexes: (i) $-2SMe_2$; (ii) $2CF_3CO_2H, -2CH_4$.

Synthesis and structure of a disilver(I) complex

The direct reaction between silver trifluoroacetate and ligand **1** gave the complex $[Ag_2(O_2CCF_3)_2(\mu\text{-}\mathbf{1})]$, **9**. Complex **9** was sparingly soluble in common organic solvents. It gave only a broad single resonance in the ^{31}P NMR spectrum at $\delta(^{31}P) = -2$, with no resolved coupling to silver. In the ^{1}H NMR spectrum the resonances for the CH_2N and CH_2P protons were also broad, and the combined data indicate easy fluxionality of the complex in solution. The low solubility did not allow a low temperature NMR study. The structure was found to be **9** (Scheme 5) by X-ray structure determination.

The structure of complex **9** is shown in Fig. 3. The two halves of the molecule are related by an inversion centre. There do not appear to be any related structures of silver(I) but complex **J** (Chart 1) is a copper(I) analogue.[5c] The binding mode of the PNP ligand **1** is different from complexes **2a** and **3a** in the sense that the



Scheme 5 Synthesis if the disilver(I) complex **9**. Reagent: (i) AgO_2CCF_3.

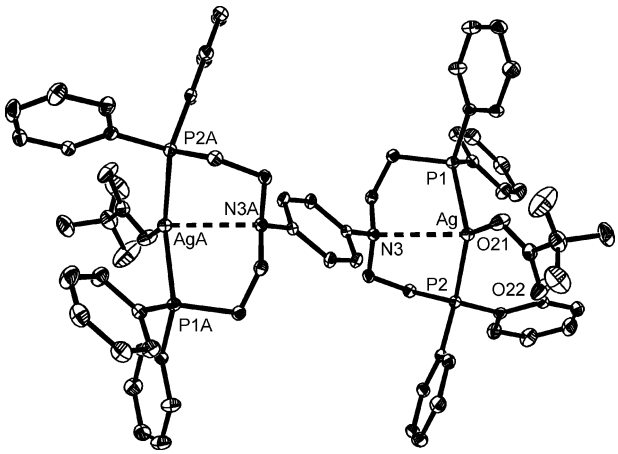
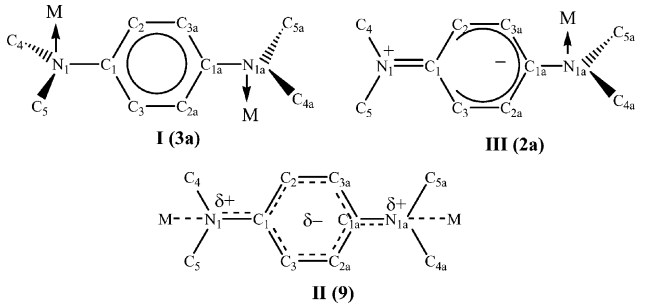


Fig. 3 Structure of the complex $[Ag_2(O_2CCF_3)_2(\mu\text{-}\mathbf{1})]$, **9**. Selected bond parameters: Ag–O(21) 2.268(2); Ag–P(2) 2.4149(8); Ag–P(1) 2.4496(8) Å; O(21)–Ag–P(2) 130.69(6); O(21)–Ag–P(1) 109.10(6); P(2)–Ag–P(1) 120.03(3)°.

PMP angle is 120.03(3)° in **9** but always close to linear in **2a** and **3a**. The stereochemistry at silver(I) can be considered as trigonal planar, with the monodentate trifluoroacetate ligand occupying the third coordination site. The Ag···N(3) distance of 2.97 Å is too long for a normal covalent bond but it could represent a weak bonding interaction. For comparison the distances for **2a** are Pd(1)–N(1) = 2.104(7) Å for the covalent bond and Pd(2)···N(8) = 5.15 Å for the non-bonding interaction. The bond distances to the trifluoroacetate ligand, Ag–O(21) = 2.268(2) Å and Ag···O(22) = 3.18 Å, indicate an essentially monodentate binding mode.

Some bond parameters for the phenylenediamine units of the complexes **2a**, **3a** and **9** are listed in Table 1, and illustrate differences associated with the different bonding modes (note that a common atom labelling system, different from the figures, is used to facilitate comparisons). The simplest case is for complex **3a** for which the bonding can be described as in **I** (Table 1). The bond angles at the equivalent atoms N1 and N1a are close to tetrahedral [sum of the three CNC angles, $\sum CN(1)C = 328(1)°$, which is the expected value for an ideal tetrahedron], the distance N1–C1 = 1.482(4) Å corresponds well to a single bond, and the CC distances in the C_6H_4 unit are roughly equal. In this case the lone pairs on the nitrogen donors of the ligand **1** are fully engaged in σ-bonding to palladium, so there is no nitrogen-aryl π-bonding. Another extreme example is found in the unsymmetrical binding mode of the ligand in complex **2a**, which can be described as close to **III** (Table 1). Thus, the sums of the three CNC angles,

Table 1 Bond parameters for the *para*-phenylenediamine units in complexes **2a**, **3a** and **9**

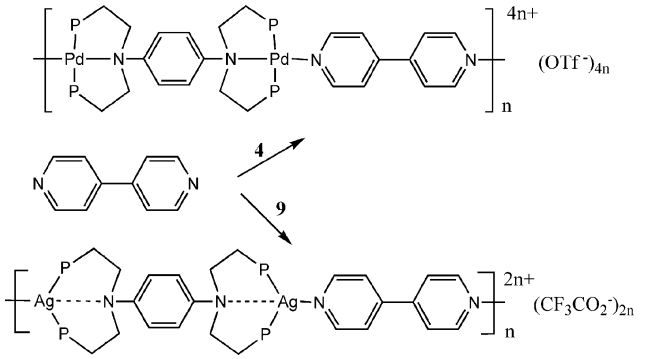


	3a	9	2a
N(1)–C(1)	1.482(4)	1.433(3)	1.365(10)
N(1a)–C(1a)	1.482(4)	1.433(3)	1.482(10)
C(1)–C(2)	1.382(5)	1.384(4)	1.409(10)
C(1a)–C(2a)	1.382(5)	1.384(4)	1.380(11)
C(1)–C(3)	1.386(5)	1.383(4)	1.406(11)
C(1a)–C(3a)	1.386(5)	1.383(4)	1.383(11)
C(2)–C(3a)	1.389(5)	1.392(4)	1.375(11)
C(2a)–C(3)	1.389(5)	1.392(4)	1.380(11)
∑CN(1)C	328(1)	342(1)	360(2)
∑CN(1a)C	328(1)	342(1)	327(2)

∑CN(1)C = 360(2)° and ∑CN(1a)C = 327(2)° for **2a** are close to the ideal trigonal planar and tetrahedral stereochemistries respectively. The distances C1a–N1a = 1.482(10) and C1–N1 = 1.365(10) Å are significantly different and closer to the expected values for a single and double bond respectively (C–N 1.47 Å, C=N 1.29 Å). In addition, the distances C1–C2 and C1–C3 appear longer than the other C–C distances in the C_6H_4 unit, though the differences are comparable to the error limits (Table 1). It is probably this communication between nitrogen donors through the phenylene bridge of ligand 1 which favours the unsymmetrical bridging mode, as found in **2a**, when compared to other *bis*(pincer) ligands such as those in complexes **H–J** (Chart 1). There is a symbiotic effect because the N1-aryl π-bonding makes the lone pair unavailable for coordination while increasing the electron density at N1a and enhancing its donor ability, and coordination of N1a draws electron density from the aryl group and enhances the N1-aryl π-bonding. In complex **9** the sum of the three CNC angles, ∑CN(1)C = 342(1)° and the distance C–N = 1.433(3) Å are intermediate values (Table 1). Therefore it seems that the lone pair on nitrogen is weakly involved both in π-bonding to the C_6H_4 group and in coordination to silver(I), as illustrated by **II** (Table 1).

Synthesis of 4,4′-bipyridine bridged oligomers or polymers

Part of the research plan was to use the hemilabile nature of the ligand **1** in forming polymers and network materials. This work was partly successful but was limited by difficulty in crystallizing and characterizing sparingly soluble products. The displacement of the weakly bound oxygen-donor ligand in $[Pd_2(OTf)_2(\mu\text{-}\mathbf{1})](OTf)_2$, **4**, or $[Ag_2(O_2CCF_3)_2(\mu\text{-}\mathbf{1})]$, **9**, by linear 4,4′-bipyridine gave the corresponding polymers $[Pd_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}\mathbf{1})](OTf)_4$, **10**, or $[Ag_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}\mathbf{1})](O_2CCF_3)_2$, **11**, respectively (Scheme 6). The ^1H and ^{31}P NMR data for the coordinated ligand **1** indicated



Scheme 6 Synthesis of 4,4′-bipyridine bridged oligomers or polymers.

that the binding mode of **1** did not change on coordination of the 4,4′-bipyridine ligand. For example, in the ^{31}P NMR, **4** and **10** gave resonances at $\delta(^{31}P) = 43.6$ [$PdONP_2$] and 37.2 [PdN_2P_2], and **9** and **11** gave resonances at $\delta(^{31}P) = -2.2$ [$AgOP_2$] and −3.2 [$AgNP_2$], respectively. In principle, reaction of **10** or **11** with more bipyridine ligand might convert the one dimensional polymer to a two dimensional sheet material by displacement of the nitrogen-donor of ligand **1**. The compounds did react but it was not possible to isolate pure materials.

Conclusions

The *bis*(PNP)-donor pincer ligand 1,4-$C_6H_4\{N(CH_2CH_2PPh_2)_2\}_2$, **1**, contains weakly basic nitrogen donor atoms because the lone pairs of electrons are conjugated to the bridging phenylene group. For this reason, the ligand is more "hemilabile" than similar ligands containing hydrogen or alkyl groups in place of the 1,4-C_6H_4 group,[1–4] and this feature is particularly useful in the synthesis of oligomeric and polymeric coordination compounds. The ligand **1** can bind as a conventional *bis*(pincer) ligand in the μ_2-κ^6-P_4N_2 binding mode, as in the complex cation $[Pd_2Cl_2(\mu\text{-}\mathbf{1})]^{2+}$ but it can also bind in the μ_2-κ^4-P_4 and μ_4-κ^4-P_4 binding modes, as in the complexes $[Pt_2Me_4(\mu\text{-}\mathbf{1})]$ and $[\{Pd_2Br_4(\mu_4\text{-}\mathbf{1})\}_n]$, respectively. In the silver complex $[Ag_2(O_2CCF_3)_2(\mu\text{-}\mathbf{1})]$, the ligand binding mode is intermediate between the μ_2-κ^6-P_4N_2 and μ_2-κ^4-P_4 binding modes, with very weakly coordinated nitrogen atoms. Finally, there is a symbiotic effect which can favour an unsymmetrical μ_3-κ^5-P_4N bonding mode for the ligand **1** and this is found in the tetrapalladium complex $[Pd_4Cl_6(\mu_3\text{-}\mathbf{1})_2]Cl_2$. Two routes to polymeric complexes have been established, one relying on conventional pincer ligand chemistry and the other relying on the hemilabile nature of the ligand **1**.

Experimental

NMR spectra were recorded using a Varian Mercury 400 or Inova 400 MHz NMR spectrometer. ESI-MS were recorded using a Micromass LCT spectrometer in MeCN solution; MALDI-TOF data were acquired using a Micromass TofSpec 2E mass spectrometer in positive ion mode. The sensitive precursor 1,4-$C_6H_4\{N(CH_2CH_2OH)_2\}_2$ was prepared by the literature method[6] and it was used immediately for ligand synthesis.

N,*N*,*N*′,*N*′-Tetrakis(2-diphenylphosphinoethyl)-1, 4-phenylenediamine, 1

To an ice-cold solution of 1,4-$C_6H_4\{N(CH_2CH_2OH)_2\}_2$ (1.42 g, 5 mmol) in dry pyridine (10 mL) was added 4-toluenesulfonyl chloride (4.7 g, 25 mmol). The mixture was stirred at 0 °C for 16 h. Cold ether (30 mL) was added to the mixture to precipitate the product 1,4-$C_6H_4\{N(CH_2CH_2OTs)_2\}_2$ as a red solid, which was separated by filtration, washed with ether and water, and dried under vacuum. The yield was 3.9 g, 87%, and the product was used in the next step without further purification.

To an ice-cold solution of diphenylphosphine (2 mL, 11.5 mmol) in dry THF (20 mL), was added dropwise *n*-BuLi (1.60 M solution in hexane, 7.2 mL, 11.5 mmol). The mixture was stirred at 0 °C for 1 h, then 1,4-$C_6H_4\{N(CH_2CH_2OTs)_2\}_2$ (2.06 g, 2.3 mmol) was added. The mixture was stirred at 0 °C for 20 h, then hydrolysed with water (50 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed with water, dried over $MgSO_4$, filtered and the solvent evaporated to give the product 1,4-$C_6H_4\{N(CH_2CH_2PPh_2)_2\}_2$, which was recrystallized from hot acetone–methanol. The crystalline product was obtained as white needles. Yield: 1.4 g, 64%. Anal. Calc. for $C_{62}H_{60}N_2P_4$: C, 77.81; H, 6.32; N, 2.93. Found: C, 77.34; H, 6.01; N, 2.68%. NMR in $CDCl_3$: $\delta(^1H) = 3.20$ [m, 8H, CH_2]; 3.69 [m, 8H, CH_2]; 6.90 [s, 4H, C_6H_4]; 7.58–7.80 (m, 40H, Ph); $\delta(^{31}P) =$. −20.0 [s, P].

$[Pd_4Cl_6(\mu\text{-}1)_2]Cl_2$, 2

$PdCl_2$ (0.177 g, 1 mmol) was dissolved in hot MeCN (15 mL) with stirring. The solution was cooled to room temperature, and ligand **1** (0.478 g, 0.5 mmol) was added. The mixture was stirred for 24 h, the volume of solvent was reduced to *ca.* 5 mL, and the yellow solid product was separated by filtration, washed with MeCN and ether, and dried under vacuum. Yield: 0.56 g, 85%. Anal. Calc. for $C_{124}H_{120}Cl_8N_4P_8Pd_4$: C, 56.77; H, 4.61; N, 2.14. Found: C, 56.35; H, 4.33; N, 2.09%. NMR (d^6-acetone–CF_3COOH): $\delta(^1H) = 2.26$ [m, 2H, $^2J(HH) = 13$ Hz, CH^aH^bN]; 2.60 [m, 4H, CH_2N]; 2.92 [m, 2H, $^2J(HH) = 13$ Hz, CH^aH^bN]; 3.53 [m, 4H, CH_2P]; 3.87 [m, 2H, CH^aH^bP]; 4.06 [m, 2H, CH^aH^bP]; 7.28–7.92 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) = 10.8$ [s, $PdCl_2P_2$]; 32.4 [s, $PdClNP_2$].

$[Pd_2Cl_2(\mu\text{-}1)](OTf)_2$, 3a

A mixture of ligand **1** (96 mg, 0.1 mmol), HOTf (73% solution in water, 60 mg, 0.3 mmol), $[Pd(acac)_2]$ (30.4 mg, 0.1 mmol) and $PdCl_2$ (18 mg, 0.1 mmol) in MeCN (4 mL) was heated at 80 °C for 2 h. The solution was cooled to room temperature and ether (10 mL) was added to precipitate the product as a yellow solid. Yield: 120 mg, 78%. Anal. Calc. for $C_{64}H_{60}Cl_2F_6N_2O_6P_4Pd_2S_2$: C, 49.95; H, 3.93; N, 1.82. Found: C, 50.10; H, 4.06; N, 1.99%. NMR (d^6-acetone): $\delta(^1H) = 2.09$ [m, 4H, $^2J(HH) = 13$ Hz, CH^aH^bN]; 3.11 [m, 4H, $^2J(HH) = 13$ Hz, CH^aH^bN]; 4.08 [m, 4H, CH^aH^bP]; 4.19 [m, 4H, CH^aH^bP]; 7.4–7.95 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) =$ 32.3 [s, $PdClNP_2$].

$[Pd_2(OTf)_2(\mu\text{-}1)](OTf)_2$, 4

To a suspension of $[Pd_4Cl_6(\mu\text{-}\mathbf{1})_2]Cl_2$, **2a**, (260 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added a solution of AgOTf (230 mg, 0.9 mmol) in MeCN (10 mL). The mixture was stirred for 16 h, then filtered to remove insoluble material, and the solvent was evaporated under vacuum to give the product as a yellow solid. The solid was purified by extraction into CH_2Cl_2 (5 mL), followed by filtration to remove traces of insoluble material, concentration to *ca.* 1 mL, and addition of ether (10 mL) to precipitate the product. Yield: 350 mg, 99%. Anal. Calc. for $C_{66}H_{60}F_{12}N_2O_{12}P_4Pd_2S_4$: C, 44.89; H, 3.42; N, 1.59. Found: C, 44.54; H, 3.74; N, 1.35%. NMR (CD_3CN): $\delta(^1H) = 2.36$ [m, 4H, $^2J(HH) = 14$ Hz, CH^aH^bN]; 3.23 [m, 4H, $^2J(HH) = 14$ Hz, CH^aH^bN]; 4.05 [m, 4H, CH^aH^bP]; 4.20 [m, 4H, CH^aH^bP]; 7.5–7.9 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) = 43.6$ [s, $PdONP_2$].

$[Pd_2Br_2(\mu\text{-}1)](OTf)_2$, 3b

A mixture of complex **4** (88 mg, 0.05 mmol) and *n*-Bu_4NBr (32.2 mg, 0.1 mmol) in MeCN (10 mL) was stirred for 1 h, then the volume was reduced to *ca.* 3 mL and ether (10 mL) was added to precipitate the product as a yellow solid, which was separated, washed with methanol and ether, and dried under vacuum. Yield: 65 mg, 80%. Anal. Calc. for $C_{64}H_{60}Br_2F_6N_2O_6P_4Pd_2S_2$: C, 47.22; H, 3.72; N, 1.72. Found: C, 46.93; H, 3.88; N, 1.63%. NMR (d^6-acetone): $\delta(^1H) = 2.05$ [m, 4H, $^2J(HH) = 14$ Hz, CH^aH^bN]; 3.15 [m, 4H, $^2J(HH) = 14$ Hz, CH^aH^bN]; 4.01 [m, 4H, CH^aH^bP]; 4.24 [m, 4H, CH^aH^bP]; 7.3–7.9 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) = 36.8$ [s, $PdBrNP_2$].

$[\{Pd_2Br_4(\mu\text{-}1)\}_n]$, 6

To a solution of $[Pd_2(OTf)_2(\mu\text{-}\mathbf{1})](OTf)_2$, **4** (44 mg, 0.025 mmol) in CD_3CN (0.5 mL) was added *n*-Bu_4NBr (32.2 mg, 0.1 mmol). The ^{31}P NMR spectrum contained a single broad resonance at $\delta(^{31}P) = 12.3$. Most of the product precipitated as a yellow solid, which was separated by filtration, washed with MeCN and ether, and dried under vacuum. Yield: 26 mg, 70%. Anal. Calc. for $C_{62}H_{60}Br_4N_2P_4Pd_2$: C, 50.00; H, 4.06; N, 1.88. Found: C, 50.14; H, 4.05; N, 1.89%. NMR (CD_3CN–CF_3COOH): $\delta(^1H) = 2.55$ [m, 4H, CH_2N]; 3.50 [m, 4H, CH_2P]; 7.28–7.92 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) = 12.3$ [s, $PdBr_2P_2$]. ESI-MS (MeCN–HCO_2H): *m*/*z* (cited for Br79) = 1405 $[Pd_2Br_3(\mathbf{1})^+]$; 1485 $[Pd_2Br_4(\mathbf{1})H^+]$; 1669 $[Pd_3Br_5(\mathbf{1})^+]$; 2889 $[Pd_4Br_7(\mathbf{1})_2^+]$; 2969 $[Pd_4Br_8(\mathbf{1})_2H^+]$; 4373 $[Pd_6Br_{11}(\mathbf{1})_3^+]$.

In another experiment the *n*-Bu_4NBr was added to complex **4** in 1 equivalent amounts and the reaction was monitored by ^{31}P NMR. 0 equiv., $\delta(^{31}P) = 44$ [$PdONP_2$]; 1 equiv., $\delta(^{31}P) = 37$ [$PdBrNP_2$] and 46 [$PdONP_2$]; 2 equiv., $\delta(^{31}P) = 37$ [$PdBrNP_2$]; 3 equiv., $\delta(^{31}P) = 13$ [$PdBr_2P_2$] and 37 [$PdBrNP_2$]; 4 equiv., $\delta(^{31}P) =$ 12 [$PdBr_2P_2$], **6**. The solution remained homogeneous until the last step, when yellow solid formed in the NMR tube.

$[Pt_2Me_4(\mu\text{-}1)]$, 7

To a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.1 mmol) in acetone (5 mL) was added a solution of ligand **1** (95.7 mg, 0.1 mmol) in acetone (5 mL). The mixture was stirred for 3 h, then the solvent was evaporated to give the product as a white solid, which was recrystallized from acetone ether. Yield: 114 mg, 81%. Anal. Calc. for $C_{66}H_{72}N_2P_4Pt_2$: C, 56.33; H, 5.16; N, 1.99. Found: C, 56.10; H, 5.02; N, 1.82%. NMR (CD_2Cl_2): $\delta(^1H) = 0.09$ [m, 6H, $^2J(PtH) =$ 68 Hz, MePt]; 2.27 [m, 8H, CH_2N]; 3.38 [m, 4H, $^2J(PH) = 19$ Hz,

CH_2P]; 6.25 [2, 4H, C_6H_4]; 7.0–7.3 [m, 40H, Ph]; $\delta(^{31}P) = 18.1$ [s, $^1J(PtP) = 2280$ Hz, $PtMe_2P_2$].

[Pt_2Me_2(μ-**1**)](CF_3CO_2)$_2$, **8**

To a solution of [Pt_2Me_4(μ-**1**)], **7**, (35 mg, 0.025 mmol) in CH_2Cl_2 (2 mL) was added CF_3CO_2H (3.8 μL, 0.05 mmol). The mixture was stirred for 15 min, then ether (10 mL) was added to precipitate the product as a white solid. Yield: 26 mg, 64%. NMR (CD_2Cl_2): $\delta(^1H) = 0.79$ [t, 6H, $^3J(PH) = 6$ Hz, $^2J(PtH) = 80$ Hz, MePt]; 1.88 [m, 4H, $^2J(HH) = 14$ Hz, CH^aH^bN]; 2.77 [m, 4H, $^2J(HH) = 14$ Hz, CH^aH^bN]; 3.29 [m, 4H, $^2J(HH) = 13$ Hz, $^2J(PH) = 21$ Hz, CH^aH^bP]; 4.32 [m, 4H, $^2J(HH) = 13$ Hz, $^2J(PH) = 21$ Hz, CH^aH^bP]; 7.0–7.6 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) = 31.5$ [s, $^1J(PtP) = 3760$ Hz, $PtNMeP_2$].

[$Ag_2(O_2CCF_3)_2$(μ-**1**)], **9**

To a solution of AgO_2CCF_3 (111 mg, 0.5 mmol) in acetone (5 mL) was added ligand **1** (239 mg, 0.25 mmol). The mixture was stirred for 3 h, then the volume of solvent was reduced to 3 mL and ether (10 mL) was added to precipitate the product as a white solid. Yield: 270 mg, 72%. Anal. Calc. for $C_{66}H_{60}Ag_2F_6N_2O_4P_4$: C, 56.67; H, 4.32; N, 2.00. Found: C, 56.44; H, 4.09; N, 2.00%. NMR (d^6-acetone): $\delta(^1H) = 2.60$ [m, 8H, CH_2N]; 3.58 [m, 8H, CH_2P]; 7.2–7.8 [m, 44H, Ph + C_6H_4]; $\delta(^{31}P) = -2.2$ [br s, $AgOP_2$].

[Pd_2(μ-4,4′-bipy)(μ-**1**)](OTf)$_4$, **10**

To a solution of [Pd_2(OTf)$_2$(μ-**1**)](OTf)$_2$, **4** (35.2 mg, 0.02 mmol) in MeCN (1 mL) was added 4,4′-bipyridine (3.2 mg, 0.02 mmol) in MeCN (1 mL). The mixture was stirred for 30 min, then the product was precipitated as a yellow solid by addition of ether (5 mL). Yield: 21 mg, 55%. Anal. Calc. for $C_{76}H_{68}F_{12}N_4O_{12}P_4Pd_2S_4$: C, 47.49; H, 3.57; N, 2.91. Found: C, 47.03; H, 3.37; N, 2.78%. NMR (CD_3CN): $\delta(^1H) = 2.04$ [m, 4H, CH^aH^bN]; 2.91 [m, 4H, CH^aH^bN]; 3.76 [m, 4H, CH^aH^bP]; 4.01 [m, 4H, CH^aH^bP]; 7.5–8.5 [m, 52H, bipy + Ph + C_6H_4]; $\delta(^{31}P) = 37.2$ [s, PdN_2P_2].

[Ag_2(μ-4,4′-bipy)(μ-**1**)] (O_2CCF_3)$_2$, **11**

To a solution of [$Ag_2(O_2CCF_3)_2$(μ-**1**)], **9** (28 mg, 0.02 mmol) in acetone (5 mL) was added 4,4′-bipyridine (3.2 mg, 0.02 mmol) in acetone (2 mL). The mixture was stirred for 3 h, then the volume of solvent was reduced to 2 mL and ether (10 mL) was added to precipitate the product as a white solid. Yield: 25 mg, 80%. Anal. Calc. for $C_{76}H_{68}Ag_2F_6N_4O_4P_4$: C, 58.70; H, 4.41; N, 3.60. Found: C, 58.47; H, 4.26; N, 3.38%. NMR (d^6-acetone): $\delta(^1H) = 2.35$ [m, 8H, CH_2N]; 3.45 [m, 8H, CH_2P]; 7.2–8.5 [m, 52H, bipy + Ph + C_6H_4]; $\delta(^{31}P) = -3.2$ [br s, $AgNP_2$].

X-Ray structure determinations

Crystals were mounted on glass fibres. Data were collected at 150 K using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B.V., 1998).[9] The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998).[9] The SHELXTL-NT V6.1 suite of programs was used to solve the structures by direct methods.[9] Subsequent difference Fourier syntheses allowed the remaining atoms to be located. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Details of the crystal data and refinements are in Table 2.

A yellow block crystal of **2a**·2CH_2Cl_2·2$C_2H_4Cl_2$·6$CHCl_3$ was grown from a dichloromethane–dichloroethane–chloroform solution by slow diffusion of pentane. The crystal was grown with difficulty after many trials and it diffracted weakly. The dichloroethane solvate molecule was disordered (60/40) and the C–Cl distances were fixed (1.72 Å). A yellow block crystal of **3a** was grown from $CHCl_3$–hexane. There were no unusual features in the structure solution. A colourless block crystal of **9** was grown from acetone solution by slow evaporation. There was disorder of the fluorine atoms of the trifluoroacetate groups (80/20) and the C–F bonds were restrained to be equal using the SADI command.

CCDC reference numbers 664675–664677.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716035f

Table 2 Crystal data and refinement details

Complex	**2a**·2CH_2Cl_2·2$C_2H_4Cl_2$·6$CHCl_3$	**3a**	**9**
Formula	$C_{136}H_{138}Cl_{34}N_4P_8Pd_4$	$C_{64}H_{60}Cl_2F_6N_2O_6P_4Pd_2S_2$	$C_{66}H_{60}Ag_2F_6N_2O_4P_4$
FW	3707.16	1538.84	1398.78
T/K	150(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a/Å	15.9810(2)	31.9519(5)	12.3770(2)
b/Å	12.3410(2)	12.4261(2)	11.8752(2)
c/Å	41.0338(7)	17.3210(3)	21.1926(4)
β/°	99.264(1)	111.707(1)	100.225(1)
V/Å^3	7987.2(2)	6389.4(2)	3065.41(9)
Z	2	4	2
d(calc.)/Mg m^{-3}	1.541	1.600	1.515
μ/mm^{-1}	1.139	0.883	0.811
Data/restr./param.	13870/252/769	7334/0/349	6271/51/358
R(int)	0.057	0.049	0.046
$R1$ [$I > 2\sigma(I)$]	0.081	0.041	0.036
$wR2$ (all data)	0.242	0.110	0.091

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