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FULL PAPER

Binuclear silver(I) complexes with polydentate phosphine ligands 2-(diphenylphosphino)-6-[3-(2′-pyridyl)pyrazol-1-yl]pyridine and 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine

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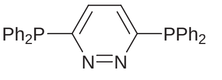
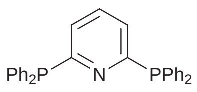
The new polydentate, pyridine-based phosphine ligand 2-(diphenylphosphino)-6-[3-(2′-pyridyl)-pyrazol-1-yl]-pyridine (L^2) has been synthesized. The reaction of L^2 with $[Ag(MeCN)_4][ClO_4]$ resulted in the formation of the binuclear silver(I) complex $[Ag_2(\mu\text{-}L^2)_2(ClO_4)_2]$, which is stabilized by significant π–π stacking interactions between its inter-ligand pyridyl fragments. In contrast, the reaction of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L^1) with $[Ag(MeCN)_4][ClO_4]$ gave the binuclear complex $[Ag_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$, which exhibits a weak metal–metal interaction.

Introduction

In our previous work, we have successfully synthesized polymeric silver(I) complexes $\{[Ag_2(MeCN)_2(\mu\text{-}L^1)]_n\}[ClO_4]_{2n}$ and $\{[Ag(MeCN)_2(\mu\text{-}L^2)]_n\}[ClO_4]_n$ by the self-assembly reaction of polydentate phosphine ligands 3,6-bis(diphenylphosphino)-pyridazine (I) and 2,6-bis(diphenylphosphino)pyridine (II) with $[Ag(MeCN)_4][ClO_4]$.[1] We have also recently reported several binuclear copper(I) complexes with 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L^1), although the synthesis of this polydentate phosphine ligand was only briefly sketched.[2]



I



II

Here we report our subsequent study on the design of a related ligand, 2-(diphenylphosphino)-6-[3-(2′-pyridyl)pyrazol-1-yl]pyridine (L^2), and its reaction with $[Ag(MeCN)_4][ClO_4]$ in comparison with L^1, the synthesis of which is now described in detail.

Experimental

General procedure, measurement and materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker-300 NMR spectrometer using $SiMe_4$ as the external standard and $CDCl_3$ as solvent. The $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker-500 NMR spectrometer at 202.45 MHz using 85% H_3PO_4 as the external standard and $CDCl_3$ as solvent. The compounds $[Ag(MeCN)_4][ClO_4]$[3] and 3-(2-pyridyl)pyrazole[4] were prepared from literature procedures.

CAUTION: while none of these perchlorate complexes has proved to be shock sensitive, nevertheless proper care should always be taken.[5]

Preparations

2-Chloro-6-(diphenylphosphino)pyridine. A solution of $LiBu^n$ in hexane (1.60 M, 36.0 mL) was added dropwise to a solution of Ph_2PH (9.30 g, 0.05 mol) in tetrahydrofuran (50 mL) at 0 °C. The resulting mixture was added dropwise to a solution of 2,6-dichloropyridine (7.40 g, 0.05 mol) in tetrahydrofuran at −78 °C, after which the mixture was stirred for 1 h at this temperature and then allowed to warm slowly to room temperature. The solvent was removed in vacuum and water (100 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL) and the organic phase dried with anhydrous Na_2SO_4 overnight. Most of the CH_2Cl_2 was removed under vacuum and hexane (100 mL) was added to deposit a colorless solid, which upon recrystallization from CH_2Cl_2–hexane afforded an analytically pure product (yield 9.40 g, 63%). Mp: 82–83 °C. ^1H NMR ($CDCl_3$): δ 7.49 (d, $J = 1.2$, 1 H, pyridyl-H^5), 7.38 (m, 10 H, phenyl), 7.20 (m, 1 H, pyridyl-H^4), 6.95 (d, $J = 1.5$ Hz, 1 H, pyridyl-H^3). $^{31}P\text{-}\{^1H\}$ NMR: δ 34.20 (Found: C, 68.50; H, 4.21; N, 4.51. Calc. for $C_{17}H_{13}ClNP$: C, 65.58; H, 4.40; N, 4.71%).

2-(Diphenylphosphino)-6-[3-(2′-pyridyl)pyrazol-1-yl]pyridine L^2. A solution of 3-(2-pyridyl)pyrazole (4.43 g, 0.03 mmol) in anhydrous 2-methoxyethyl ether (40 mL) was mixed with 1.17 g (0.03 mol) of potassium and stirred at 70 °C until the metal dissolved. To this solution was added 7.44 g (0.025 mol) of 2-chloro-6-(diphenylphosphino)pyridine in one portion. The resulting mixture was stirred at 110 °C for 7 d. The solvent was removed under reduced pressure and water (100 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL) and the organic phase dried with anhydrous Na_2SO_4 overnight. Most of the CH_2Cl_2 was removed under vacuum and hexane (100 mL) was added to give a crude product which could be purified by column chromatography using 6:1 hexane–diethyl ether as the eluent. The product was obtained as colorless microcrystals (yield 7.80 g, 64%). ^1H NMR ($CDCl_3$): δ 8.31 (d, $J = 0.7$, 1 H, pyridyl-H^6), 7.80 (d, $J = 1.7$, 1 H, pyrazolyl-H^3), 7.62 (m, 2 H, pyridyl-H^3 and pyridyl-H^5), 7.31–7.39 (m, 13 H, phenyl, pyridyl-H^4, P-pyridyl-H^3 and P-pyridyl-H^5), 7.00 (d, $J = 1.4$, 1 H, pyrazolyl-H^4), 6.32 (t, $J = 0.5$ Hz, 1 H, P-pyridyl-H^4). $^{31}P\text{-}\{^1H\}$ NMR: δ 10.13 (Found: C, 73.78; H, 4.68; N, 13.72. Calc for $C_{25}H_{19}N_4P$: C, 73.88; H, 4.71; N, 13.79%).

2-(Diphenylphosphino)-6-(pyrazol-1-yl)pyridine L^1. The procedure was similar to that given above, except that 2.04 g (0.03 mol) of pyrazole was used instead of 3-(2-pyridyl)pyrazole. The product was obtained as colorless microcrystals (yield 6.70 g, 81%). ^1H NMR ($CDCl_3$): δ 8.36 (d, $J = 0.7$, 1 H, pyrazolyl-H^3), 7.87 (m, 1 H, pyrazolyl-H^5), 7.65 (m, 2 H, pyrazolyl-H^4 and pyridyl-H^5), 7.35–7.46 (m, 10 H, phenyl), 7.04 (m, 1 H, pyridyl-H^3), 6.36 (t, $J = 0.6$ Hz, 1 H, pyridyl-H^4). $^{31}P\text{-}\{^1H\}$ NMR: δ 9.31 (Found: C, 73.02; H, 5.08; N, 12.60. Calc. for $C_{20}H_{16}N_3P$: C, 72.94; H, 4.90; N, 12.76%).

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1		**2**	
Ag(1)–P(1)	2.359(1)	Ag(1)–P(1a)	2.375(2)
Ag(1)–N(3a)	2.395(5)	Ag(1)–N(1)	2.405(6)
Ag(1)–N(4a)	2.395(5)	Ag(1)–N(3)	2.324(5)
Ag(1)–O(3)	2.652(5)	Ag(1)–N(4)	2.412(8)
Ag(1)···Ag(1a)	7.630(1)	Ag(1)···Ag(1a)	2.964(1)
P(1)–Ag(1)–N(3a)	120.5(1)	P(1a)–Ag(1)–N(1)	110.7(2)
P(1)–Ag(1)–N(4a)	144.3(1)	P(1a)–Ag(1)–N(3)	155.1(1)
N(3a)–Ag(1)–N(4a)	71.3(2)	N(1)–Ag(1)–N(3)	70.0(2)

Symmetry code: compound **1**, a $y, x, \frac{1}{2} - z$; compound **2**, a $1 - x, -y, -z$.

[Ag$_2$(μ-L^2)$_2$(ClO$_4$)$_2$] 1. To a solution containing 0.40 g (1 mmol) of L^2 in CH$_3$CN (20 mL) was added solid [Ag(MeCN)$_4$][ClO$_4$] (0.37 g, 1 mmol). The resulting solution was stirred at room temperature for 30 min. Subsequent diffusion of diethyl ether into the concentrated solution gave **1** as colorless crystals (yield 0.32 g, 89%). ^{1}H NMR (CDCl$_3$): δ 8.31 (d, $J = 1.0$, 2 H, pyridyl-H^6), 7.52 (d, $J = 1.6$, 2 H, pyrazolyl-H^3), 7.50 (m, 4 H, pyridyl-H^3 and pyridyl-H^5), 7.13–7.37 (m, 26 H, phenyl, pyridyl-H^4, *P*-pyridyl-H^3 and *P*-pyridyl-H^5), 6.47 (d, $J = 0.7$, 2 H, pyrazolyl-H^4), 6.30 (t, $J = 0.4$ Hz, 2 H, *P*-pyridyl-H^4). ^{31}P-{^{1}H} NMR: δ 27.31 (Found: C, 48.75; H, 3.07; N, 9.05. Calc. for C$_{25}$H$_{19}$AgClN$_4$O$_4$P: C, 48.92; H, 3.12; N, 9.13%).

[Ag$_2$(μ-L^1)$_2$(MeCN)$_2$][ClO$_4$]$_2$ 2. The procedure was similar to that above, except for 0.33 g (1 mmol) of L^1 was used instead of L^2. The product was obtained as colorless crystals (yield 0.46 g, 91%). IR (CH$_2$Cl$_2$): ν(C≡N) 2306.7 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.56 (d, $J = 0.7$, 2 H, pyrazolyl-H^3), 8.12 (m, 2 H, pyrazolyl-H^5), 8.00 (m, 4 H, pyrazolyl-H^4 and pyridyl-H^5), 7.28 (m, 20 H, phenyl), 6.99 (m, 2 H, pyridyl-H^3), 6.54 (t, $J = 1.0$ Hz, 2 H, pyridyl-H^4), 2.02 (s, 6 H, methyl). ^{31}P-{^{1}H} NMR: δ 36.92 (Found: C, 45.70; H, 3.31; N, 9.45. Calc. for C$_{22}$H$_{19}$ClAgN$_4$O$_4$P: C, 45.74; H, 3.32; N, 9.70%).

Crystal structure determinations

Complex 1. C$_{50}$H$_{38}$Ag$_2$Cl$_2$N$_8$O$_8$P$_2$, $M = 1227.5$, trigonal, $a = 23.173(3)$, $b = 23.173(3)$, $c = 18.795(4)$ Å, $U = 8742(4)$ Å^3, $T = 294$ K, space group $P\bar{3}_{c1}$(no. 165), $Z = 6$, μ(Mo-Kα) = 0.872 mm^{-1}, 5210 reflections measured, 4258 unique ($R_{int} = 0.043$) which were used in all calculations. The final $wR(F^2)$ was 0.088. $R1 = 0.058$. Rigaku RAXIS IIC imaging-plate diffractometer was used.

Complex 2. C$_{44}$H$_{38}$Ag$_2$Cl$_2$N$_8$O$_8$P$_2$, $M = 1155.4$, monoclinic, $a = 9.663(1)$, $b = 11.557(1)$, $c = 21.344(7)$ Å, $\beta = 99.88(3)$°, $U = 2348.0(9)$ Å^3, $T = 294$ K, space group $P2_1/c$ (no. 14), $Z = 2$, μ(Mo-Kα) = 1.077 mm^{-1}, 5409 reflections measured, 3726 unique ($R_{int} = 0.034$) which were used in all calculations. The final $wR(F^2)$ was 0.092. $R1 = 0.055$. Siemens P4/PC four-circle diffractometer was used.

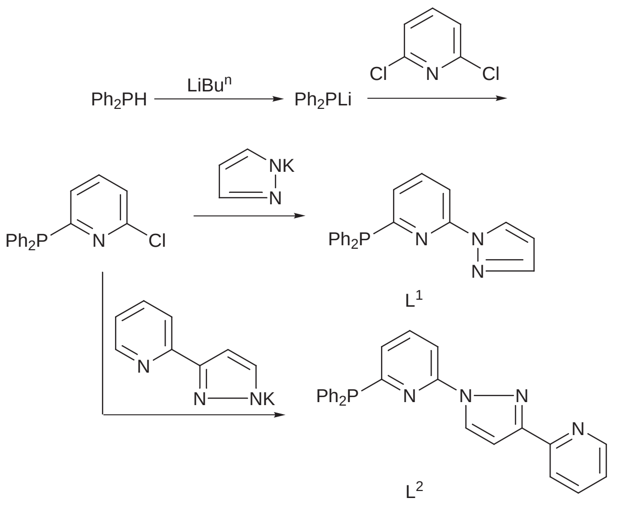
Selected bond distances and angles are presented in Table 1.

CCDC reference number 186/1087.

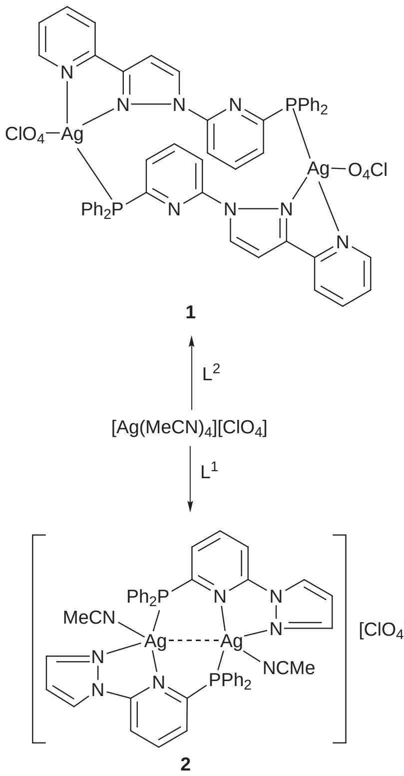
See http://www.rsc.org/suppdata/dt/1998/2927/ for crystallographic files in .cif format.

Results and discussion

The P,N-polydentate ligands 2-(diphenylphosphino)-6-[3-(2′-pyridyl)pyrazol-1-yl]pyridine (L^2) and 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L^1), which possess rigid, narrow bites, have been synthesized in good yields in two steps. Reaction of Ph$_2$PLi (prepared "*in situ*" from Ph$_2$PH and LiBu^n) with 2,6-dichloropyridine at low temperature gave the mono-substituted product 2-chloro-6-(diphenylphosphino)pyridine, which in turn reacted with potassium 3-(2-pyridyl)pyrazolate or potassium pyrazolate to furnish the desired phosphine ligands (Scheme 1). The composition of the intermediate 2-chloro-6-(diphenylphosphino)pyridine, L^2 and L^1 were all confirmed by elemental analysis, ^{1}H NMR and ^{31}P-{^{1}H} NMR spectroscopy.



Scheme 1



Scheme 2

Treatment of L^2 with 1 equivalent of [Ag(MeCN)$_4$][ClO$_4$] resulted in the formation of [Ag$_2$(μ-L^2)$_2$(ClO$_4$)$_2$] **1**, in which the two L^2 ligands are arranged in a head-to-tail configuration and one of the two pyridyl nitrogen atoms in each does not participate in metal co-ordination (Scheme 2).

A perspective view of the binuclear complex **1**, which has molecular symmetry 2, is displayed in Fig. 1 with atom numbering. The adopted cyclic structure results from stabilization through π–π stacking of a pair of pyridyl moieties from different phosphine ligands. As anticipated, L^2 bridges between two metal centers. Each silver(I) center is bound to a pyridylpyrazole unit from one ligand and a phosphorus atom from the other, resulting in the formation of a dimeric M$_2$L$_2$ species (Fig. 2). The pseudo-tetrahedral co-ordination sphere of each metal center is completed by a weakly co-ordinated perchlorate ligand

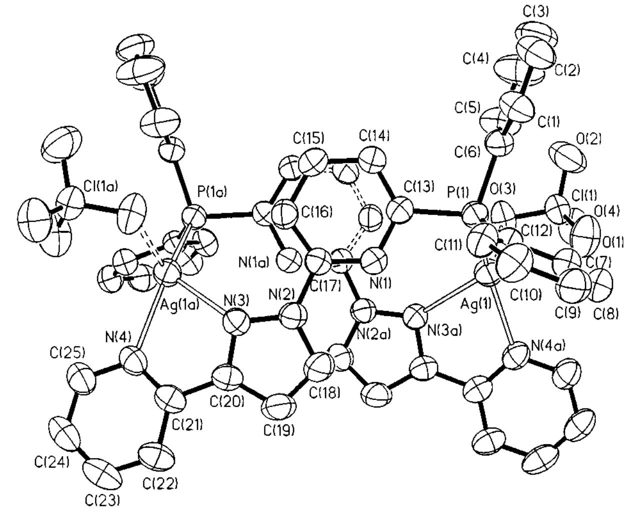


Fig. 1 Perspective view (35% thermal ellipsoids) of the molecular structure of $[\mathrm{Ag_2(\mu\text{-}L^2)_2(ClO_4)_2}]$ **1** with atom labelling scheme (H atoms have been omitted for clarity). A crystallographic C_2 axis runs vertically and bisects a line joining the silver atoms. Symmetry code: a $y, x, \frac{1}{2} - z$.

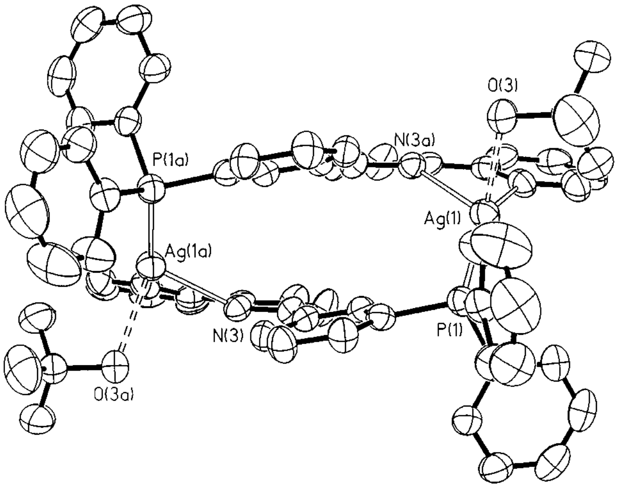


Fig. 2 View of the molecular structure of **1** showing the π–π separation between pyridyl fragments of the pair of co-ordinated L^2 ligands.

bound through a single O atom. The metal–ligand bond lengths and angles are unremarkable and the non-bonded Ag···Ag distance is 7.630 Å. The inter-ligand π–π stacking interaction distance between the pyridyl units is 3.759 Å, which is a little longer than that (3.380 Å) in $\{[\mathrm{AgL(MeCN)_2}]_n\}[\mathrm{BF_4}]_n$ (L = 2,7-diazapyrene).[6] The Ag–O distance of 2.625(5) Å is shorter than those [2.762(13)–3.489(12) Å] found in $[\mathrm{Ag_3(dppp)_2(MeCN)_2(ClO_4)_2}][\mathrm{ClO_4}]$ [dppp = bis(diphenylphosphinomethyl)phenylphosphine)].[7]

In contrast, reaction of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine with 1 equivalent of $[\mathrm{Ag(MeCN)_4}][\mathrm{ClO_4}]$ resulted in the formation of $[\mathrm{Ag_2(\mu\text{-}L^1)_2(MeCN)_2}][\mathrm{ClO_4}]_2$ **2**, in which the two L^1 ligands are in a head-to-tail configuration and the two metal atoms have a weak metal–metal interaction as revealed by X-ray crystallography.

A perspective view of the centrosymmetric binuclear cation of complex **2** is displayed in Fig. 3. Each Ag(I) atom exhibits distorted tetrahedral geometry with ligation by two N atoms from one phosphine ligand and one P atom from the other, and further stabilization was accomplished by the co-ordination of an acetonitrile ligand. The structure is isostructural to $[\mathrm{Cu_2(\mu\text{-}L^1)_2(MeCN)_2}][\mathrm{ClO_4}]_2$,[2b] although the two compounds are not isomorphous. The Ag···Ag separation of 2.964(1) Å is much shorter than the Cu···Cu separation [3.625(1) and 3.587(1) Å] in the analogous copper(I) complex, which is an unusual result.

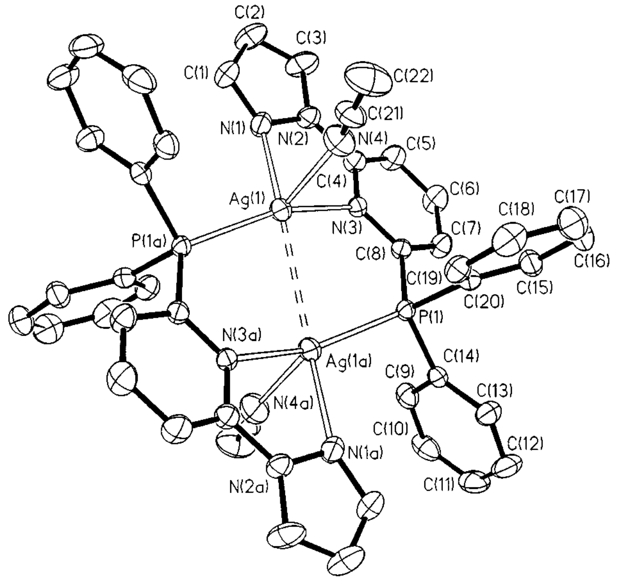


Fig. 3 Perspective view (35% thermal ellipsoids) and atom labelling scheme of the centrosymmetric $[\mathrm{Ag_2(\mu\text{-}L^1)_2(MeCN)_2}]^{2+}$ cation in **2** (H atoms have been omitted for clarity). Symmetry code: a $1 - x, -y, -z$.

This value, however, is in agreement with those [2.943(2)–3.014(2) Å] in $[\mathrm{Ag_3(dppp)_2(MeCN)_2(ClO_4)_2}][\mathrm{ClO_4}]$,[7] but shorter than those found in $\{[\mathrm{Ag_2(MeCN)_2(\mu\text{-}L)}]_n\}[\mathrm{ClO_4}]_{2n}$ [L = 3,6-bis(diphenylphosphino)pyridazine] [3.005(2), 3.184(2) Å],[1] $[\mathrm{Ag\{HC(PPh_2)_3\}_2Cl}][\mathrm{ClO_4}]_2\cdot 2\mathrm{MeCN}$ [3.162(1)–3.223(1) Å],[8] and $[\mathrm{Ag_2(dppm)_2(NO_3)_2}]$ (3.085 Å),[9] indicating the possibility of a weak metal–metal interaction in this binuclear complex.

Conclusion

We have taken advantage of the different site-specific ligating behavior of the newly-designed polydentate P,N-ligands L^2 and L^1 to generate binuclear complexes with $[\mathrm{Ag(MeCN)_4}][\mathrm{ClO_4}]$. The adopted structure of **1** is favored by significant inter-ligand π–π stacking interactions involving one pyridyl group of L^2, while a weak metal–metal interaction in **2** is imposed by simultaneous tight binding of L^1 to two metal centers.

Acknowledgements

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