

Bis[μ -diphenyl(2-pyridylmethyl)phosphine- $\kappa^2 N, P$]bis[nitratosilver(I)](Ag—Ag)

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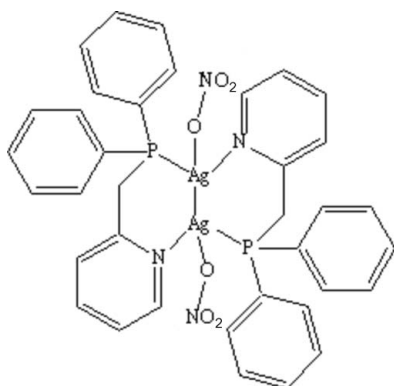
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Key indicators: single-crystal X-ray study; $T = 110$ K; mean $\sigma(\text{C}—\text{C}) = 0.006$ Å;
 R factor = 0.038; wR factor = 0.099; data-to-parameter ratio = 13.8.

In the title molecular structure, $[\text{Ag}_2(\text{NO}_3)_2(\text{C}_{18}\text{H}_{16}\text{NP})_2]$, the Ag^{I} atoms are held in close proximity by the chelating effect of the diphenyl(2-pyridylmethyl)phosphine ligand, with an Ag—Ag bond distance of 2.9171 (7) Å. The angles around the metal centers describe a distorted tetrahedral geometry, with the NO_3^- ions bound to the Ag^{I} atoms in a monodentate fashion. The molecule is centrosymmetric.

Related literature

For related literature, see: Cingolani *et al.* (2006); Feazell *et al.* (2005); Klausmeyer *et al.* (2004); Murso & Stalke (2004); Sandee & Reek (2006).



Experimental

Crystal data

$[\text{Ag}_2(\text{NO}_3)_2(\text{C}_{18}\text{H}_{16}\text{NP})_2]$ $a = 13.7678$ (19) Å
 $M_r = 894.34$ $b = 12.7143$ (17) Å
Monoclinic, $C2/c$ $c = 20.364$ (3) Å

$\beta = 95.251$ (5)°
 $V = 3549.7$ (9) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 1.25$ mm^{−1}
 $T = 110$ (2) K
 $0.32 \times 0.10 \times 0.09$ mm

Data collection

Bruker APEX X8 CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.70$, $T_{\text{max}} = 0.89$

17376 measured reflections
3109 independent reflections
2726 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.099$
 $S = 1.03$
3109 reflections

226 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 2.89$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.74$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Ag1—N1	2.247 (3)	Ag1—Ag1 ⁱ	2.9171 (7)
Ag1—P1	2.3980 (11)		
N1—Ag1—O1	116.02 (13)	O1—Ag1—Ag1 ⁱ	89.21 (11)
N1—Ag1—P1	132.06 (9)	P1—Ag1—Ag1 ⁱ	87.23 (3)
O1—Ag1—P1	111.77 (10)	C13—P1—C7	103.83 (18)
N1—Ag1—Ag1 ⁱ	89.81 (9)		

Symmetry code: (i) $-x, -y, -z$.

Data collection: APEX2 (Bruker, 2003); cell refinement: APEX2; data reduction: SAINT-Plus (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2000); software used to prepare material for publication: SHELXTL.

The diffractometer was purchased with funds received from the National Science Foundation Major Research Instrumentation Program Grant CHE-0321214. KK thanks the Robert A. Welch Foundation for support (AA-1508).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2178).

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supplementary materials

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Bis[μ -diphenyl(2-pyridylmethyl)phosphine- κ^2N,P]bis[nitratosilver(I)](*Ag-Ag*)

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Comment

The study of silver coordinated complexes using P,*N* based ligands is a well established field of research, with reports that describe the formation of a large variety of coordination modes associated with variation in the ligand/metal ratio or by changes in the solvent or counterion in charged systems (Cingolani *et al.*, 2006; Feazell *et al.*, 2005). The well known 2-(phosphinomethyl)pyridyl family of ligands of the type PPh_xCH₂py_{3-x} (*x* = 0, 1, 2) have been widely used in coordination chemistry associated with transition metals and applications in the catalysis arena, due to the geometrical flexibility and electronic properties that these phosphine ligands exhibit (Murso & Stalke, 2004; Sandee & Reek, 2006). The diphenyl(2-pyridylmethyl)phosphine is of special interest because as a bidentate ligand it can connect two identical or different metal centers, allowing for a close proximity and direct metal-metal interactions. The use of silver starting materials and these P,*N* based ligands have received great attention lately because of the flexible coordination sphere of the silver centers, allowing it to take different structural motifs (Klausmeyer *et al.*, 2004). Thus, following this research line we present in this study the synthesis of a silver-based dinuclear complex, obtained by the reaction of the diphenyl(2-pyridylmethyl)phosphine ligand with silver nitrate in a 1:1 ratio.

The title compound, (I), consists of two phosphine ligands coordinated head-to-tail to two silver atoms across the Ag—Ag axis, and the nitrate anions bound to the metal centers in a unidentate fashion. Accordingly, the Ag^I atom in (I) is four-coordinated by one P atom, one N atom, an O atom from the nitrate anion, and a Ag atom with which the metallophilic interaction occurs. The coordination sphere of the metal centers reveal a distorted tetrahedral environment with angles ranging between 87.23 (3) and 132.1 (9)°. The flexibility of the ligand is evidenced by a twisting angle of 77.4 (4)° for P1—C1—C2—N1. The Ag—P and Ag—N distances fall in the range of reported values. The NO₃ anions coordinated to the corresponding silver atoms through one of the oxygen atoms, are bounded perpendicular to the Ag—Ag bond with an angle of 89.21 (11)° for O1—Ag1—Ag1ⁱ [symmetry code: (i) $-x, -y, -z$].

Experimental

The title compound was obtained by mixing AgNO₃ (0.051 g, 0.3 mmol) and PPh₂(2-CH₂C₅H₄N) (0.083 g, 0.3 mmol) in 20 ml of acetonitrile. The mixture was stirred for 10 min and pulled dry under vacuum. Diffraction-quality crystals were obtained by slow diffusion of diethyl ether into a concentrated *N,N*-dimethylformamide solution of (I) in the presence of air.

Refinement

All H atoms were included in calculated positions (C—H = 0.95–0.99 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest residual electron density peak is located 1.11 Å from atom Ag1.

Figures

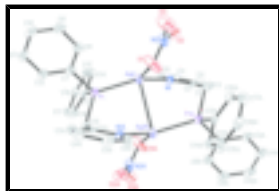


Fig. 1. A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. The suffix A corresponds to symmetry code $(-x, -y, -z)$.

Bis[μ -diphenyl(2-pyridylmethyl)phosphine- κ^2N,P]bis[nitrat silver(I)](Ag—Ag)

Crystal data

$[\text{Ag}_2(\text{NO}_3)_2(\text{C}_{18}\text{H}_{16}\text{NP})_2]$

$M_r = 894.34$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 13.7678\ (19)\ \text{\AA}$

$b = 12.7143\ (17)\ \text{\AA}$

$c = 20.364\ (3)\ \text{\AA}$

$\beta = 95.251\ (5)^\circ$

$V = 3549.7\ (9)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1792$

$D_x = 1.673\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 7549 reflections

$\theta = 2.9\text{--}27.9^\circ$

$\mu = 1.25\ \text{mm}^{-1}$

$T = 110\ (2)\ \text{K}$

Block, colorless

$0.32 \times 0.10 \times 0.09\ \text{mm}$

Data collection

Bruker APEX X8 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 110\ (2)\ \text{K}$

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.70$, $T_{\max} = 0.89$

17376 measured reflections

3109 independent reflections

2726 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 2.5^\circ$

$h = -16 \rightarrow 16$

$k = -11 \rightarrow 15$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.099$

$S = 1.03$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 24.9163P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

3109 reflections $\Delta\rho_{\max} = 2.89 \text{ e } \text{\AA}^{-3}$
226 parameters $\Delta\rho_{\min} = -0.74 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag1	0.04440 (2)	−0.01171 (2)	0.067423 (15)	0.02050 (13)
P1	−0.08720 (8)	0.09272 (8)	0.10130 (5)	0.0171 (2)
N1	0.1901 (2)	0.0319 (3)	0.03379 (16)	0.0177 (7)
C1	0.1915 (3)	−0.1181 (3)	−0.04038 (18)	0.0179 (8)
H1A	0.1696	−0.1612	−0.0041	0.021*
H1B	0.2414	−0.1589	−0.0616	0.021*
C2	0.2369 (3)	−0.0183 (3)	−0.01233 (19)	0.0170 (9)
C3	0.3233 (3)	0.0199 (3)	−0.0336 (2)	0.0227 (9)
H3	0.3542	−0.0157	−0.0670	0.027*
C4	0.3636 (3)	0.1110 (4)	−0.0050 (2)	0.0280 (10)
H4	0.4228	0.1383	−0.0187	0.034*
C5	0.3172 (3)	0.1616 (3)	0.0433 (2)	0.0234 (9)
H5	0.3441	0.2233	0.0641	0.028*
C6	0.2310 (3)	0.1200 (3)	0.0604 (2)	0.0219 (9)
H6	0.1983	0.1556	0.0930	0.026*
C7	−0.1431 (3)	0.0425 (3)	0.17266 (19)	0.0199 (9)
C8	−0.1145 (3)	−0.0544 (4)	0.1985 (2)	0.0268 (10)
H8	−0.0682	−0.0952	0.1777	0.032*
C9	−0.1528 (3)	−0.0925 (4)	0.2546 (2)	0.0316 (11)
H9	−0.1318	−0.1584	0.2726	0.038*
C10	−0.2218 (3)	−0.0344 (4)	0.2844 (2)	0.0306 (11)
H10	−0.2477	−0.0601	0.3230	0.037*
C11	−0.2527 (3)	0.0612 (4)	0.2576 (2)	0.0284 (10)
H11	−0.3010	0.1004	0.2774	0.034*
C12	−0.2140 (3)	0.1003 (4)	0.2022 (2)	0.0230 (9)
H12	−0.2354	0.1661	0.1842	0.028*
C13	−0.0448 (3)	0.2231 (3)	0.12690 (18)	0.0166 (8)
C14	0.0418 (3)	0.2276 (3)	0.1691 (2)	0.0225 (9)

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H14	0.0736	0.1644	0.1838	0.027*
C15	0.0809 (3)	0.3234 (4)	0.1895 (2)	0.0272 (10)
H15	0.1393	0.3255	0.2182	0.033*
C16	0.0364 (3)	0.4161 (4)	0.1687 (2)	0.0260 (10)
H16	0.0641	0.4817	0.1826	0.031*
C17	−0.0494 (3)	0.4128 (3)	0.1271 (2)	0.0258 (10)
H17	−0.0807	0.4765	0.1127	0.031*
C18	−0.0896 (3)	0.3170 (3)	0.1064 (2)	0.0234 (9)
H18	−0.1482	0.3156	0.0779	0.028*
N2	0.0698 (3)	−0.2472 (3)	0.0958 (2)	0.0291 (9)
O1	0.0043 (3)	−0.1936 (3)	0.0628 (2)	0.0543 (12)
O2	0.1523 (2)	−0.2084 (3)	0.10666 (15)	0.0378 (8)
O3	0.0526 (3)	−0.3363 (3)	0.1142 (2)	0.0573 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0186 (2)	0.0202 (2)	0.0234 (2)	0.00012 (12)	0.00551 (13)	−0.00150 (13)
P1	0.0180 (5)	0.0182 (5)	0.0153 (5)	−0.0019 (4)	0.0028 (4)	0.0005 (4)
N1	0.0172 (18)	0.0183 (18)	0.0178 (17)	−0.0016 (14)	0.0034 (14)	0.0005 (14)
C1	0.020 (2)	0.021 (2)	0.0127 (19)	−0.0006 (17)	0.0026 (16)	−0.0003 (16)
C2	0.017 (2)	0.020 (2)	0.014 (2)	0.0001 (16)	0.0010 (16)	0.0046 (16)
C3	0.017 (2)	0.034 (2)	0.017 (2)	−0.0004 (18)	0.0047 (17)	0.0016 (18)
C4	0.019 (2)	0.034 (3)	0.032 (2)	−0.0074 (19)	0.0040 (19)	0.005 (2)
C5	0.023 (2)	0.022 (2)	0.024 (2)	−0.0072 (18)	−0.0028 (18)	−0.0006 (18)
C6	0.024 (2)	0.019 (2)	0.022 (2)	0.0002 (18)	0.0007 (18)	0.0003 (17)
C7	0.021 (2)	0.024 (2)	0.015 (2)	−0.0066 (18)	−0.0007 (17)	0.0004 (17)
C8	0.026 (2)	0.029 (2)	0.025 (2)	0.0004 (19)	0.0032 (19)	0.0058 (19)
C9	0.032 (3)	0.037 (3)	0.025 (2)	−0.003 (2)	0.003 (2)	0.012 (2)
C10	0.031 (3)	0.043 (3)	0.017 (2)	−0.015 (2)	0.0010 (19)	0.008 (2)
C11	0.019 (2)	0.046 (3)	0.021 (2)	−0.006 (2)	0.0048 (18)	−0.004 (2)
C12	0.023 (2)	0.029 (2)	0.017 (2)	−0.0048 (18)	−0.0002 (18)	−0.0008 (18)
C13	0.018 (2)	0.017 (2)	0.015 (2)	−0.0018 (16)	0.0059 (16)	−0.0002 (16)
C14	0.019 (2)	0.025 (2)	0.023 (2)	0.0014 (17)	0.0031 (18)	−0.0035 (18)
C15	0.024 (2)	0.034 (3)	0.024 (2)	−0.006 (2)	0.0004 (19)	−0.008 (2)
C16	0.032 (3)	0.025 (2)	0.023 (2)	−0.0107 (19)	0.011 (2)	−0.0064 (18)
C17	0.035 (3)	0.016 (2)	0.027 (2)	−0.0011 (18)	0.008 (2)	0.0001 (18)
C18	0.022 (2)	0.025 (2)	0.024 (2)	−0.0018 (18)	0.0022 (18)	−0.0014 (18)
N2	0.030 (2)	0.017 (2)	0.042 (2)	−0.0030 (17)	0.0130 (18)	−0.0056 (17)
O1	0.0246 (19)	0.0224 (18)	0.114 (4)	−0.0011 (15)	−0.001 (2)	0.017 (2)
O2	0.038 (2)	0.049 (2)	0.0263 (17)	−0.0196 (17)	−0.0024 (15)	0.0013 (15)
O3	0.046 (2)	0.025 (2)	0.099 (3)	−0.0062 (17)	−0.004 (2)	0.017 (2)

Geometric parameters (\AA , $^\circ$)

Ag1—N1	2.247 (3)	C8—C9	1.389 (6)
Ag1—O1	2.378 (3)	C8—H8	0.9500
Ag1—P1	2.3980 (11)	C9—C10	1.386 (7)

Ag1—Ag1 ⁱ	2.9171 (7)	C9—H9	0.9500
P1—C13	1.818 (4)	C10—C11	1.383 (7)
P1—C7	1.821 (4)	C10—H10	0.9500
P1—C1 ⁱ	1.839 (4)	C11—C12	1.384 (6)
N1—C6	1.346 (5)	C11—H11	0.9500
N1—C2	1.348 (5)	C12—H12	0.9500
C1—C2	1.504 (6)	C13—C18	1.391 (6)
C1—P1 ⁱ	1.839 (4)	C13—C14	1.406 (6)
C1—H1A	0.9900	C14—C15	1.380 (6)
C1—H1B	0.9900	C14—H14	0.9500
C2—C3	1.390 (6)	C15—C16	1.376 (7)
C3—C4	1.389 (6)	C15—H15	0.9500
C3—H3	0.9500	C16—C17	1.390 (7)
C4—C5	1.380 (6)	C16—H16	0.9500
C4—H4	0.9500	C17—C18	1.387 (6)
C5—C6	1.374 (6)	C17—H17	0.9500
C5—H5	0.9500	C18—H18	0.9500
C6—H6	0.9500	N2—O3	1.222 (5)
C7—C8	1.383 (6)	N2—O2	1.239 (5)
C7—C12	1.399 (6)	N2—O1	1.273 (5)
N1—Ag1—O1	116.02 (13)	C12—C7—P1	121.4 (3)
N1—Ag1—P1	132.06 (9)	C7—C8—C9	120.4 (4)
O1—Ag1—P1	111.77 (10)	C7—C8—H8	119.8
N1—Ag1—Ag1 ⁱ	89.81 (9)	C9—C8—H8	119.8
O1—Ag1—Ag1 ⁱ	89.21 (11)	C10—C9—C8	120.1 (5)
P1—Ag1—Ag1 ⁱ	87.23 (3)	C10—C9—H9	119.9
C13—P1—C7	103.83 (18)	C8—C9—H9	119.9
C13—P1—C1 ⁱ	104.12 (18)	C11—C10—C9	119.6 (4)
C7—P1—C1 ⁱ	103.81 (19)	C11—C10—H10	120.2
C13—P1—Ag1	110.85 (13)	C9—C10—H10	120.2
C7—P1—Ag1	114.91 (15)	C10—C11—C12	120.7 (4)
C1 ⁱ —P1—Ag1	117.87 (13)	C10—C11—H11	119.7
C6—N1—C2	117.8 (3)	C12—C11—H11	119.7
C6—N1—Ag1	115.8 (3)	C11—C12—C7	119.8 (4)
C2—N1—Ag1	126.3 (3)	C11—C12—H12	120.1
C2—C1—P1 ⁱ	112.3 (3)	C7—C12—H12	120.1
C2—C1—H1A	109.1	C18—C13—C14	118.5 (4)
P1 ⁱ —C1—H1A	109.1	C18—C13—P1	125.1 (3)
C2—C1—H1B	109.1	C14—C13—P1	116.4 (3)
P1 ⁱ —C1—H1B	109.1	C15—C14—C13	120.4 (4)
H1A—C1—H1B	107.9	C15—C14—H14	119.8
N1—C2—C3	121.9 (4)	C13—C14—H14	119.8
N1—C2—C1	117.2 (3)	C16—C15—C14	120.9 (4)
C3—C2—C1	120.9 (4)	C16—C15—H15	119.6
C4—C3—C2	118.8 (4)	C14—C15—H15	119.6
C4—C3—H3	120.6	C15—C16—C17	119.4 (4)

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C2—C3—H3	120.6	C15—C16—H16	120.3
C5—C4—C3	119.6 (4)	C17—C16—H16	120.3
C5—C4—H4	120.2	C18—C17—C16	120.3 (4)
C3—C4—H4	120.2	C18—C17—H17	119.9
C6—C5—C4	118.0 (4)	C16—C17—H17	119.9
C6—C5—H5	121.0	C17—C18—C13	120.6 (4)
C4—C5—H5	121.0	C17—C18—H18	119.7
N1—C6—C5	123.9 (4)	C13—C18—H18	119.7
N1—C6—H6	118.1	O3—N2—O2	121.0 (4)
C5—C6—H6	118.1	O3—N2—O1	120.6 (4)
C8—C7—C12	119.3 (4)	O2—N2—O1	118.3 (4)
C8—C7—P1	119.3 (3)	N2—O1—Ag1	110.4 (3)

Symmetry codes: (i) $-x, -y, -z$.

Fig. 1

