Bis[μ-1,3-bis(diphenylphosphino)propane]-disilver(I) bis(tetrafluoroborate)

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.006 Å
R factor = 0.040
wR factor = 0.119
Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The dinuclear Ag^I phosphine complex $[Ag_2(dppp)_2]^{2+}$ [dppp = 1,3-bis(diphenylphosphino)propane] has been crystallized as the BF_4^- salt, *viz.* $[Ag_2(C_{27}H_{26}P_2)_2](BF_4)_2$, in order to reduce the effects of coordination by the anion. The dimeric complex consists of two-coordinate Ag^I centers bridged by dppp ligands. The P—Ag—P bond angle deviates significantly from linearity, with a value of 159.66 (3)°. The Ag—P bond distances are close to being equal, with values of 2.3935 (7) and 2.4016 (7) Å. The cation has a center of symmetry midway between the two Ag atoms.

Comment

The crystal structure of $[Ag_2(dppp)_2(NO_3)_2]$ has been reported (Tiekink, 1990). In this compound, short Ag—O interactions of 2.581 (3) and 2.674 (3) Å exist between the nitrate anions and the Ag^I cations. The effect of the complexation of the Ag^I cations by the nitrate anions has been evaluated by replacing nitrate with the more weakly coordinating anion, BF_4^-. In the structure detailed here, (I), short contacts between the $[Ag_2(dppp)_2]^{2+}$ complex and the BF_4^- anion are essentially absent, with the shortest Ag···F contacts being greater than 2.9 Å. Concomitant with the loss of complexation by the anion are significant changes in the geometry about the Ag center.

(I)
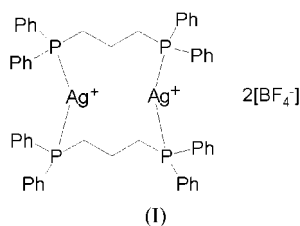
The Ag—P bond distances are remarkably similar between $[Ag_2(dppp)_2(NO_3)_2]$ and $[Ag_2(dppp)_2](BF_4)_2$, despite the removal of ion-pairing interactions, with values of 2.403 (1) and 2.426 (1) Å, and 2.3935 (7) and 2.4016 (7) Å being determined, respectively (Tiekink, 1990). The cation has a center of symmetry midway between the two Ag atoms. The most pronounced change between the nitrate complex and the tetrafluoroborate salt is noted in the P1—Ag1—P2 bond angle, which deviates significantly from linearity in (I), with a value of 159.66 (3)°. However, in $[Ag_2(dppp)_2(NO_3)_2]$, this distortion is even more pronounced, and here the angle is 152.2 (1)°. This increased bending can likely be ascribed to the effects of complexation by nitrate in $[Ag_2(dppp)_2(NO_3)_2]$. Not surprisingly, the tetrafluoroborate anion in (I) shows evidence of rotational disorder, as indicated by elongated displacement

ellipsoids for the F atoms and lack of regularity in the B—F bond lengths. Attempts to model the disorder by locating some or all of the F atoms over several partially occupied sites did not result in an improved model for the anion, so each of the sites has been treated as fully occupied.

Experimental

A crystal suitable for X-ray diffraction was obtained by slow evaporation of an acetone solution containing equimolar quantities of $AgBF_4$ (Alfa Aesar, 99%) and dppp (Strem, 98%).

Crystal data

$[Ag_2(C_{27}H_{26}P_2)_2](BF_4)_2$	$Z = 1$
$M_r = 1214.20$	$D_x = 1.558$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.6882$ (7) Å	Cell parameters from 9950
$b = 11.3911$ (7) Å	reflections
$c = 12.9037$ (8) Å	$\theta = 2.3–28.3°$
$\alpha = 90.908$ (2)°	$\mu = 0.95$ mm^{-1}
$\beta = 114.075$ (2)°	$T = 193$ (2) K
$\gamma = 112.741$ (2)°	Prism, colorless
$V = 1294.46$ (14) Å^3	$0.39 \times 0.19 \times 0.14$ mm

Data collection

Bruker SMART APEX diffractometer	6396 independent reflections
ω scans	5813 reflections with $I > 2\sigma(I)$
Absorption correction: analytical	$R_{int} = 0.020$
(*XPREP* in *SHELXTL*;	$\theta_{max} = 28.3°$
Sheldrick, 1997)	$h = -14 \rightarrow 14$
$T_{min} = 0.712$, $T_{max} = 0.877$	$k = -15 \rightarrow 15$
13475 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 1.0875P]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.028$
6396 reflections	$\Delta\rho_{max} = 1.61$ e Å^{-3}
340 parameters	$\Delta\rho_{min} = -1.05$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ag1—P2	2.3935 (7)	Ag1—P1	2.4016 (7)
P2—Ag1—P1	159.66 (3)		

H atoms were placed at calculated positions, refined using a riding model, and given U_{iso} parameters equal to $1.2U_{eq}$ of the parent C
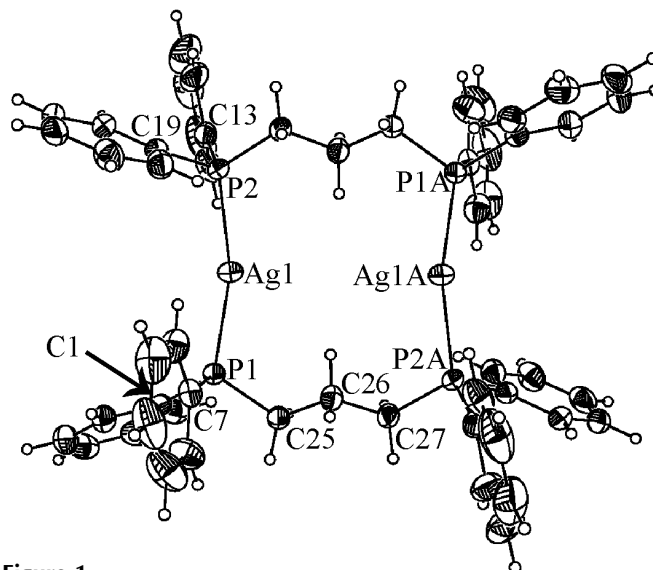

Figure 1
A view of the $[Ag_2(dppp)_2]^{2+}$ cation, with some of the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix A denotes an atom generated by inversion symmetry.

atom. C—H bond distances were constrained to 0.99 Å for C25, C26, and C27, and 0.95 Å for the aromatic H-atom positions. The highest peak was located 1.10 Å from F3 and the deepest hole was located 0.42 Å from F4.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART* and *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

References

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