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(Trifluoroacetato-*O*,*O*′)bis(triphenylphosphine-*P*)silver(I)

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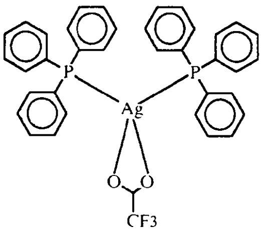
Abstract

The Ag atom in the title complex, $[Ag(C_2F_3O_2)(C_{18}H_{15}P)_2]$, is bonded to two triphenylphosphine ligands and a chelating trifluoroacetate anion in a distorted tetrahedral geometry.

Comment

Silver(I) acetate reacts with triphenylphosphine to form dimeric bis[acetato(triphenylphosphine)silver(I)], as well as monomeric acetatobis(triphenylphosphine)silver(I). The latter crystallizes with two independent molecules, *A* and *B*, in the unit cell. The Ag atoms in the monomeric compound show a distorted tetrahedral coordination: the acetate anion chelates in an isobidentate manner in molecule *A* [Ag—P = 2.433 (1) and 2.448 (1) Å; Ag—O = 2.420 (2) and 2.438 (2) Å], but in an anisobidentate manner in molecule *B* [Ag—P = 2.426 (1) and 2.461 (1) Å; Ag—O = 2.379 (3) and 2.510 (3) Å] (Ng & Hamid Othman, 1997). The Ag atom in the (trifluoroacetato-*O*,*O*′)bis(triphenylphosphine-*P*)silver(I) analog, (I), is carboxylate-chelated in a distorted tetrahedral geometry, but whereas the silver–phosphorus distances [Ag—P = 2.423 (1) and 2.445 (1) Å] are similar to those in molecule *A* of acetatobis(triphenylphosphine)silver(I), the silver–oxygen distances [Ag—O = 2.526 (3) and 2.542 (4) Å] are significantly longer, in agreement with the observation that the trifluoroacetato ion is a weaker Lewis base than the acetato ion.



(I)

An analysis of the structural features of several acetates and trifluoroacetates has found that the O—C—O angles of trifluoroacetates exceed those of acetates (Brown, 1980); this feature is also observed for the (trifluoroacetato-*O*,*O*′)bis(triphenyl-

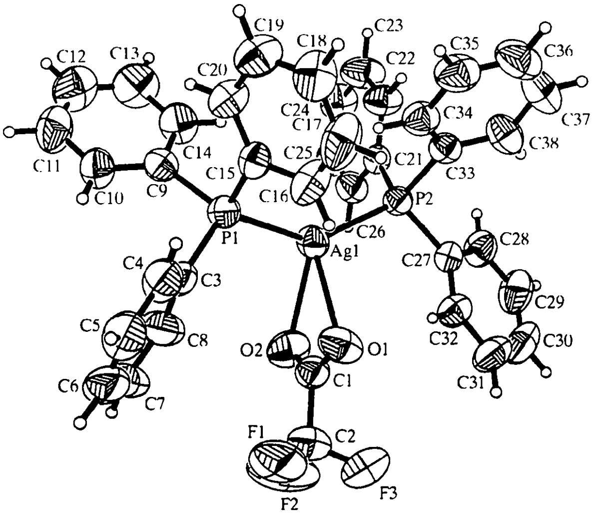


Fig. 1. *ORTEP*II (Johnson, 1976) plot at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

phosphine-*P*)silver(I) [127.8 (4)°] and acetatobis(triphenylphosphine)silver(I) [molecule *A*, 123.1 (3)°] pair. This angle is somewhat smaller than the value of 130.1 (8)° found in the parent Lewis acid, which exists as dimeric bis[(trifluoroacetato)silver(I)]. In this compound, the Ag atom shows linear coordination arising from the bridging mode of the carboxylato anion [Ag—O = 2.232 (6) and 2.249 (6) Å; O—Ag—O = 157.9 (2)°; Griffin *et al.*, 1972]. The P—Ag—P angle [142.18 (4)°] in (trifluoroacetato-*O,O'*)bis(triphenylphosphine-*P*)silver(I) is unusually large, exceeding those in acetatobis(triphenylphosphine)silver(I) and its sesquihydrate (Ng & Hamid Othman, 1997), as well as that in nitratobis(triphenylphosphine)silver(I) [138.2 (1)°; Barron *et al.*, 1986], whose Ag atom also shows a distorted tetrahedral coordination.

Experimental

To synthesize the tetrakis(triphenylphosphine)silver(I) salt of the bis(trifluoroacetato)triphenylstannate ion [whose existence has been verified in the tetramethylammonium salt (Ng & Kumar Das, 1997)], triphenyltin trifluoroacetate (Ford & Sams, 1971), prepared *in situ* by condensing triphenyltin hydroxide with trifluoroacetic acid (1:1 molar ratio) in ethanol, was treated with an ethanol solution of one molar equivalent of silver(I) trifluoroacetate and four molar equivalents of triphenylphosphine. The reactants were briefly heated; slow cooling of the filtered solution yielded two types of colorless crystals. One, which contains a heavy atom, is rhombohedral [a = 16.453 (1) and c = 52.645 (4) Å], but its structure has resisted solution by several direct-methods and heavy-atom suites. The title complex was isolated along with the rhombohedral crystals. The reaction between silver(I) trifluoroacetate and triphenylphosphine in either ethanol or toluene did not furnish a crystalline material.

Crystal data

$[Ag(C_2F_3O_2)(C_{18}H_{15}P)_2]$
$M_r = 745.43$
Orthorhombic
Pbca
$a = 16.964 (3)$ Å
$b = 18.972 (4)$ Å
$c = 21.063 (3)$ Å
$V = 6779 (2)$ Å^3
$Z = 8$
$D_x = 1.461$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 300 reflections
$\theta = 1.5–30.0°$
$\mu = 0.738$ mm^{-1}
$T = 298 (2)$ K
Block
0.20 × 0.20 × 0.20 mm
Colorless

Data collection

Siemens CCD diffractometer
Hemisphere scan
Absorption correction: empirical (Sheldrick, 1995)
$T_{min} = 0.747$, $T_{max} = 0.863$
40 260 measured reflections
8316 independent reflections

7192 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 28.32°$
$h = -22 \rightarrow 19$
$k = -25 \rightarrow 24$
$l = -27 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.133$
$S = 1.334$
8316 reflections
442 parameters
H atoms: riding model, $U(H) = 1.5U_{eq}(C)$

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 9.3434P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.343$ e Å^{-3}
$\Delta\rho_{min} = -0.623$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ag1—P1	2.445 (1)	Ag1—O1	2.526 (3)
Ag1—P2	2.423 (1)	Ag1—O2	2.542 (4)
P1—Ag1—P2	142.18 (4)	C3—P1—Ag1	115.9 (1)
P1—Ag1—O1	97.13 (9)	C9—P1—Ag1	118.9 (1)
P1—Ag1—O2	104.78 (9)	C15—P1—Ag1	107.8 (1)
P2—Ag1—O1	111.00 (9)	C21—P2—Ag1	114.3 (1)
P2—Ag1—O2	112.41 (9)	C27—P2—Ag1	114.1 (1)
O1—Ag1—O2	51.6 (1)	C33—P2—Ag1	113.0 (1)

The CF_3 group, disordered over two positions, was refined with C—F = 1.33±0.01 and F···F = 2.17±0.02 Å.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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