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$P(C_6H_4CH_2NMe_2\text{-}2)_3$-stabilized mononuclear pentafluoropropionatosilver(I)

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The title complex, (pentafluoropropionato){tris[2-(dimethylaminomethyl)phenyl]phosphine}silver(I), $[P(C_6H_4CH_2NMe_2\text{-}2)_3]Ag[OC(O)CF_2CF_3]$ or $[Ag(C_3F_5O_2)(C_{27}H_{36}N_3P)]$, possesses a tetracoordinated silver(I) ion, with silver in a distorted tetrahedral environment. In the solid state, two independent molecules are found in the asymmetric unit. The $P(C_6H_4CH_2NMe_2\text{-}2)_3$ group acts as a tripodal ligand.

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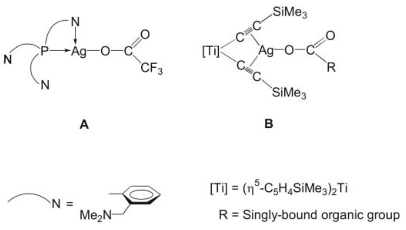
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.080
Data-to-parameter ratio = 20.3

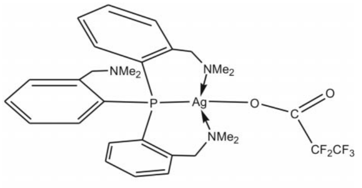
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Silver(I) carboxylates play an important role in the field of organic and organometallic synthesis (Housecroft, 1994), materials science (Schmidt *et al.*, 2002) and, for example, in homogeneous catalysis (Takeishi *et al.*, 1978). While the synthesis and reaction chemistry of such species is well understood, less is known about their molecular structure in solution and in the solid state (Lang *et al.*, 1998). This is based on the fact that they are light-sensitive and often insoluble in most common organic solvents. Only recently, the solid-state structures of mononuclear silver(I) carboxylates (A and B) were reported.



In type A, the silver(I) ion is tricoordinated by one O of the trifluoromethanesulfonate anion, the P atom and one of the three Me_2NCH_2 side-arms of the $P(C_6H_4CH_2NMe_2)_3$ ligand, forming a T-shaped structure with a linear P—Ag—O arrangement (Lang *et al.*, 1998). In structural type B molecules, the respective mononuclear $AgO_2C\mathit{R}$ moiety is stabilized by the chelating effect of the organometallic π-tweezer $[Ti](C{\equiv}CSiMe_3)_2$, which gives rise to a planar environment around silver(I) (Lang *et al.*, 1999).



(3)

To gain a deeper insight into structural aspects of silver(I) carboxylates, we report here the solid-state structure of the silver(I) pentafluoropropionate, $[(C_6H_4CH_2NMe_2)_3P]AgO_2CC_2F_5$, (3), which is easily accessible by the reaction of

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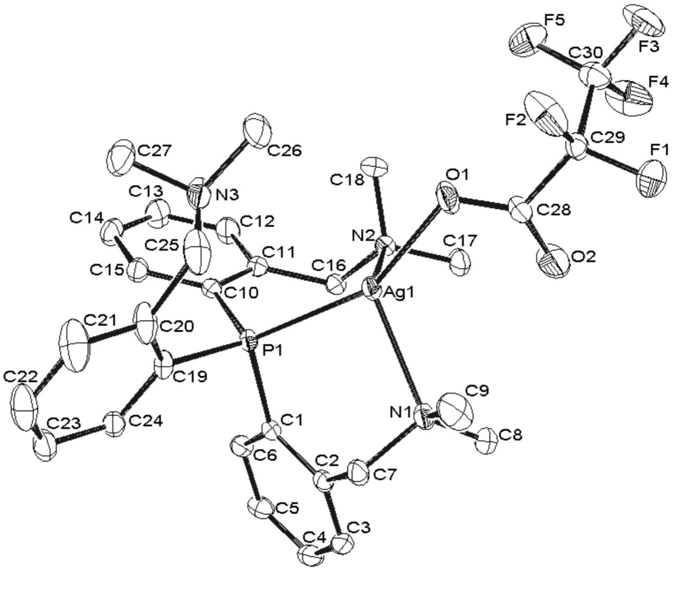

Figure 1
The molecular structure of (3) (only one of the two symmetrically independent molecules in the asymmetric unit is shown) in the solid state, with the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

aggregated [$AgO_2CC_2F_5$], (1), with one equivalent of $P(C_6H_4CH_2NMe_2\text{-}2)_3$, (2).

On prolonged exposure of (3) to light, it slowly decomposes to give elemental silver along with free $P(C_6H_4CH_2NMe_2\text{-}2)_3$. The X-ray diffraction study confirms the composition of (3) found on the basis of elemental analysis, NMR (^1H, ^{13}C {1H} and ^{31}P {1H}) and IR studies (Fig. 1).

In the asymmetric unit, two independent molecules (molecules 3*a* and 3*b*) are present, which show identical metal–ligand dimensions.

The silver(I) ion in molecules 3*a* (Ag1) and 3*b* (Ag2) is tetracoordinated by a datively bound phosphorus (molecule 3*a*: P1; molecule 3*b*: P2) and two N atoms (3*a*: N1, N2; 3*b*: N4, N5) and one s-bound O atom (3*a:* O1; 3*b*: O3); one of the three Me_2NCH_2 units remains uncoordinated. However, in solution dynamic processes are observed for the three amino side chains (Lang *et al.*, 1998). Due to this coordination mode, a distorted tetrahedral environment is found for Ag1 and Ag2 (Fig. 1).

The Ag—P, Ag—O and Ag—N separations are in the range of bond distances typical for this type of complex (Lang *et al.*, 1998). Similar values are found in {[$P(C_6H_4CH_2N\text{-}Me_2\text{-}2)_3$]AgOC(O)$CF_3$} (type A molecule). The somewhat longer bond distance in A is attributed to the different coordination sphere around silver, and hence to the different electron density at Ag^I. The Ag1—N1, Ag1—N2, Ag2—N4 and Ag—N5 separations are between 2.4433 (16) and 2.4592 (15) Å, while in A, Ag—N dimensions of 2.478 (2) Å are found (Lang *et al.*, 1998). The Ag—O bonds of 3a and 3*b* are longer than that typical for A [2.183 (2) Å; Lang *et al.*, 1998], which can be explained, as stated earlier, by the different coordination spheres around silver(I).

The differences in the coordination mode of the $P(C_6H_4CH_2NMe_2\text{-}2)_3$ ligand in (3) (P, N, N, O type) and in type A molecules (P, N, O type) can also be concluded from ^{31}P {1H} NMR spectroscopic studies. The ^{31}P {1H} NMR resonance signal for (3) is found at −30.0 p.p.m., while for A a signal at −31.9 p.p.m. is observed. This shift is typical of going from tetra- to tricoordinated silver(I) ions in silver–phosphane chemistry with $P(C_6H_4CH_2NMe_2\text{-}2)_3$ as auxiliary phosphane ligand (Lang *et al.*, 1998). Due to the silver isotopes ^{107}Ag and ^{109}Ag, two doublets are observed, the coupling constants being $J^{107}Ag^{31}P$ = 578 Hz and $J^{109}Ag^{31}P$ = 642 Hz.

The interatomic bond distances and angles for the $P(C_6H_4CH_2NMe_2\text{-}2)_3$ and $OCCF_2CF_3$ ligands are as expected and are in agreement with the well known experimental data found for other complexes, *e.g.* molecules of type A (Lang *et al.*, 1998).

As expected, the angles around the *sp*^{2}-hybridized C atom C28 (3*a*) or C58 (3*b*) show a trigonal-planar environment. As found by IR spectroscopic studies, also in the solid state, only one of the two O atoms of the carboxylate group is σ-bound to the silver(I) ion. This is indicated by the Ag1—O2 and Ag2—O4 distances, which are far out of range of typical Ag—O bonding interactions (Bowmaker *et al.*, 1995).

Experimental

$P(C_6H_4CH_2NMe_2\text{-}2)_3$, (1) (0.88 g, 2.0 mmol), dissolved in 20 ml of dichloromethane, was added dropwise to [$AgO_2CC_2F_5$], (2) (0.54 g, 2.0 mmol), suspended in 20 ml of dichloromethane, at 273 K. After 2 h of stirring at this temperature in the dark, the reaction mixture was filtered through a pad of celite. Evaporation of all volatile materials from the filtrate in an oil-pump vacuum afforded a brown solid. Crystallization from dichloromethane/*n*-pentane (ratio 1:1) at 298 K gave colourless crystals of (3). Yield: 2.69 g (8.27 mmol, 83% based on [$AgO_2CC_2F_5$]). M.p.: 439–441 K (decomposition). Elemental analysis calculated for $C_{30}H_{36}AgF_5N_3O_2P$ (704.47): C 51.15, H 5.15, N 5.96%; found: C 50.87, H 5.09, N 5.76%. IR (KBr) ν (cm^{-1}): 3054 (*w*), 2940 (*m*), 2857 (*m*), 2816 (*s*), 2769 (*s*), 2707 (*w*), 1686 (*vs*) (CO, *asym.*), 1459 (*s*) (CO, *sym.*), 1404 (*m*), 1364 (*m*), 1324 (*m*), 1207 (*s*) (CF_3, *str.*), 1165 (*vs*), 1025 (*s*), 965 (*w*), 841 (*s*), 813 (*m*), 755 (*s*), 733 (*s*), 620 (*w*), 501 (*m*), 462 (*m*). ^1H NMR ($CDCl_3$): δ 2.17 (*s*, 18H, CH_3), 3.35 (*d*, $^2J_{HH}$ = 12.3 Hz, 3H, CH_2), 3.68 (*d*, $^2J_{HH}$ = 12.3 Hz, 3H, CH_2), 6.83 (*dd*, $^3J_{HH}$ = 7.93 Hz, $^4J_{PH}$ = 7.93 Hz, 3H, C_6H_4), 7.15–7.39 (*m*, 9H, C_6H_4). ^{13}C {1H} NMR ($CDCl_3$): δ 46.4 (CH_3), 65.2 (*d*, $^3J_{PC}$ = 9.1 Hz, CH_2), 119.6 (*qt*, $^2J_{FC}$ = 321.5 Hz, $^3J_{FC}$ = 52.6 Hz, CF_3), 108.3 (*qt*, $^2J_{FC}$ = 334.5 Hz, $^3J_{FC}$ = 37.0 Hz, CF_2), 128.6 (*d*, J_{PC} = 4.2 Hz, C_6H_4), 130.4 (C_6H_4), 132.2 (*d*, J_{PC} = 20.1 Hz, C_6H_4), 133.1 (*d*, J_{PC} = 8.4 Hz, C_6H_4), 134.5 (C_6H_4), 142.20 (*d*, J_{PC} = 18.6 Hz, ^{i}C/ C_6H_4), 168.52 (*t*, J_{FC} = 24.3, $O_2CCF_2CF_3$). ^{31}P{1H} NMR ($CDCl_3$): δ −30.0 (*dd*, $^1J_{107Ag\text{-}P}$ = 578 Hz, $^1J_{109Ag\text{-}P}$ = 642 Hz).

Crystal data

[$Ag(C_3F_5O_2)(C_{27}H_{36}N_3P)$]
M_r = 704.46
Monoclinic, $P2_1/c$
a = 16.8535 (7) Å
b = 14.8719 (6) Å
c = 26.0014 (11) Å
β = 106.567 (1)°
V = 6246.5 (4) Å^3
Z = 8

D_x = 1.498 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8602 reflections
θ = 2.2–31.2°
μ = 0.76 mm^{-1}
T = 173 (2) K
Irregular, colourless
0.50 × 0.28 × 0.25 mm

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Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\rm min} = 0.775$, $T_{\rm max} = 0.827$
105 617 measured reflections
21 437 independent reflections
17 914 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 32.0°$
$h = -25 \rightarrow 24$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 38$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.080$
$S = 1.09$
21 437 reflections
1054 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 6.2345P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 1.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Ag1—O1	2.2789 (13)	Ag2—O3	2.2383 (13)
Ag1—P1	2.4145 (4)	Ag2—P2	2.3892 (4)
Ag1—N2	2.4360 (16)	Ag2—N4	2.4270 (16)
Ag1—N1	2.4433 (16)	Ag2—N5	2.4592 (15)

The H-atom positions have been taken from a difference Fourier map and refined freely, as were U(H) values.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXL*97.

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References

Bowmaker, G. A., Effendy, Hanna, J. V., Healy, P. C., Millar, G. J., Skelton, B. W. & White, A. H. (1995). *J. Phys. Chem.* **99**, 3909–3917.

Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Housecroft, C. E. (1994). *Coord. Chem. Rev.* **131**, 1–34.

Lang, H., Koehler, K., Rheinwald, G., Zsolnai, L., Buechner, M., Driess, A., Huttner, G. & Straehle, J. (1999). *Organometallics*, **18**, 598–605.

Lang, H., Leschke, M., Rheinwald, G. & Melter, M. (1998). *Inorg. Chem. Commun.* **1**, 254–256.

Schmidt, H., Shen, Y., Leschke, M., Haase, Th., Kohse-Höinghaus, K., Lang, H. (2003). *J. Organomet. Chem.* **669**, 25–31.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Takeishi, M., Fujii, S., Niino, S. & Hayama, S. (1978). *Tetrahedron Lett.* **36**, 3361–3364.

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