metal-organic papers

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Key indicators

Single-crystal X-ray study T = 293 K Mean σ (C–C) = 0.007 Å R factor = 0.045 wR factor = 0.126 Data-to-parameter ratio = 21.5

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

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Di-µ-acetato-bis[(tri-p-tolylphosphine)silver(I)]

In the title compound, $[Ag_2(O_2C_2H_3)_2(C_{21}H_{21}P)_2]$, the acetate groups function as bridging ligands to form a dimeric structure with approximate trigonal–planar geometry at the Ag^I atoms.

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Comment

The chemistry of supramolecular network structures, nanostructures and coordination polymers has attracted intense research interest in recent years. The architecture of these structures is strongly influenced by the nature of the mediating metal and ligand, the reaction stoichiometry and the counterions, and in a subtle way by the solvent molecule, intermolecular forces and π - π stacking interactions. Among the metals, silver and gold are of particular interest on account of the potential of their compounds as biologically active agents (Berners-Price et al., 1999), catalysts (Ohkouchi et al., 2001) and luminescent materials (Sun et al., 2002). The bulk of the work to date on the supramolecular chemistry of silver has utilized N-, O- or S-donor bridging ligands (Leininger et al., 2000; Blake et al., 1999; Caulder & Raymond, 1999). Here, we report the structure of the title compound, (I), an example of a silver complex utilizing acetate as an O,O-bridging ligand.



In complex (I), two acetate anions act as bridging ligands, linking two tri-*p*-tolylphosphinesilver(I) units to form a dimer. Although the anions might be termed bidentate, the bridging is quite unsymmetrical; the two Ag–O distances differ by 0.13 Å, with the angles around the O atoms also showing significant differences. Likewise, although the geometry around the Ag atom may be thought of as being approximately trigonal-planar, the angular deviations from a trigonal planar geometry, together with the differing Ag–O distances, are rather large. This is the second reported structure of a silver dimer bridged by acetate groups (Cambridge Structural Database, Version 5.27, January 2006 update; Allen, 2002), although a small number of these dimers have been reported with bridging perfluoroacetates.

Efforts to study the solution behaviour of $[L_nAgX]$ complexes were initiated by Muetterties & Alegranti (1972). A series of $[AgX{P(4-MeC_6H_4)_3}_n]$ complexes, where n = 2-4



Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. For the C atoms, the first digit indicates the ring number and the second indicates the position of the atom in the ring.

and X included a wide range of counteranions, was studied by ³¹P NMR spectroscopy. The ligands were labile in all the complexes studied, so that the first-order P–Ag coupling was not resolved above *ca* 203 K. Rapid ligand-exchange reactions have been reported for all ³¹P NMR investigations of ionic Ag^I monodentate phosphine complexes, thus making NMR spectroscopy of limited use for this type of complex.

Experimental

Silver acetate (0.100 mg, 0.60 mmol) was added to a solution of tri-*p*-tolylphosphine (182 mg, 0.60 mmol) in acetonitrile (5.0 ml). Upon heating and stirring all solids dissolved. Crystals of the title compound formed in quantitative yield on allowing the solution to cool and stand.

Crystal data

| $[Ag_2(C_2H_3O_2)_2(C_{14}H_{21}P)]$ |
|--------------------------------------|
| $M_r = 942.52$ |
| Monoclinic, $P2/c$ |
| a = 18.621 (5) Å |
| b = 10.254 (5) Å |
| c = 23.481 (5) Å |
| $\beta = 105.456 \ (5)^{\circ}$ |
| $V = 4321 (3) \text{ Å}^3$ |

Data collection

Bruker SMART CCD 1K areadetector diffractometer φ and ω scans Absorption correction: multi-scan (*SADABS*; Bruker, 1998) $T_{\rm min} = 0.704, T_{\rm max} = 0.887$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.126$ S = 1.0010655 reflections 495 parameters H-atom parameters constrained Z = 4 $D_x = 1.449 \text{ Mg m}^{-3}$ Mo K\alpha radiation $\mu = 1.02 \text{ mm}^{-1}$ T = 293 (2) KBlock, colourless $0.37 \times 0.36 \times 0.12 \text{ mm}$

29517 measured reflections 10655 independent reflections 5873 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.044$ $\theta_{\text{max}} = 28.3^{\circ}$

$$\begin{split} w &= 1/[\sigma^2(F_o^2) + (0.0509P)^2 \\ &+ 2.6206P] \\ \text{where } P &= (F_o^2 + 2F_c^2)/3 \\ (\Delta/\sigma)_{\text{max}} &= 0.003 \\ \Delta\rho_{\text{max}} &= 1.81 \text{ e } \text{ Å}^{-3} \\ \Delta\rho_{\text{min}} &= -0.70 \text{ e } \text{ Å}^{-3} \end{split}$$

| Table 1 | |
|---------|--|
|---------|--|

Selected geometric parameters (Å, °).

| O1-Ag2 | 2.371 (3) | P1-Ag1 | 2.3485 (15) |
|--------------|------------|--------------|-------------|
| O2-Ag1 | 2.235 (3) | P2-Ag2 | 2.3372 (12) |
| O3-Ag1 | 2.366 (3) | Ag1-Ag2 | 3.1507 (9) |
| O4-Ag2 | 2.237 (3) | 0 0 | |
| C1-O1-Ag2 | 122.4 (3) | O2-Ag1-O3 | 91.17 (12) |
| C1-O2-Ag1 | 105.2 (3) | P1-Ag1-O3 | 115.59 (9) |
| C3-O3-Ag1 | 125.2 (3) | O4-Ag2-P2 | 142.53 (9) |
| C3-O4-Ag2 | 105.6 (3) | O4-Ag2-O1 | 94.15 (12) |
| O2-Ag1-P1 | 152.43 (9) | P2-Ag2-O1 | 112.64 (9) |
| | | | |
| O2-C1-O1-Ag2 | -66.6(5) | C1-O2-Ag1-P1 | -101.4(3) |
| C2-C1-O1-Ag2 | 115.1 (4) | C1-O2-Ag1-O3 | 92.1 (3) |
| O1-C1-O2-Ag1 | 1.0 (5) | C3-O3-Ag1-O2 | -14.7(5) |
| C2-C1-O2-Ag1 | 179.3 (3) | C3-O3-Ag1-P1 | 172.2 (4) |
| O4-C3-O3-Ag1 | -68.9(6) | C3-O4-Ag2-P2 | -134.7(2) |
| C4-C3-O3-Ag1 | 112.1 (5) | C3-O4-Ag2-O1 | 88.5 (3) |
| O3-C3-O4-Ag2 | 3.8 (5) | C1-O1-Ag2-O4 | -14.6(4) |
| C4-C3-O4-Ag2 | -177.1 (4) | C1-O1-Ag2-P2 | -167.8 (3) |
| | | | |

Table 2Hydrogen-bond geometry (Å, $^{\circ}$).

| $D - H \cdots A$ | D-H | $H \cdots A$ | $D \cdots A$ | $D - \mathbf{H} \cdots A$ |
|---------------------------|---------------|--------------|--------------|---------------------------|
| C22−H22···O4 ⁱ | 0.93 | 2.44 | 3.291 (6) | 153 |
| C32−H32···O3 | 0.93 | 2.49 | 3.388 (6) | 163 |
| Symmetry code: (i) x | $v \pm 1 \pi$ | | | |

Symmetry code: (i) x, y + 1, z.

H atoms were positioned geometrically and refined using a riding model, with fixed C–H distances of 0.93 Å (CH) $[U_{iso}(H) = 1.2U_{eq}]$ and 0.96 Å (CH₃) $[U_{iso}(H) = 1.5U_{eq}]$. The highest residual electron-density peak is located 2.33 Å from atom H57*C*.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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