Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Redetermination of an acyclic triphosphenium tetrachloroaluminate salt at 173 K

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Received 12 July 2006
Accepted 13 July 2006

At 173 K, the structure of the acyclic 'triphosphenium' salt 1,1,1,3,3,3-hexaphenyltriphosphenium tetrachloroaluminate dichloromethane hemisolvate, $[(Ph_3P)_2P][AlCl_4]\cdot 0.5CH_2Cl_2$, contains two cations, two anions and one solvent molecule in the asymmetric unit. There are no unusually short anion–cation distances and the structures of the ions are comparable to those that have been reported previously.

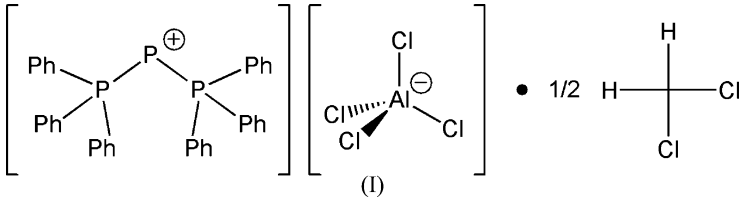
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.006 Å
R factor = 0.049
wR factor = 0.131
Data-to-parameter ratio = 20.4

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

Comment

The acyclic triphosphenium (I) was synthesized from the reaction of PCl_3, $AlCl_3$ and PPh_3 in dichloromethane following the procedure described by Schmidpeter *et al.* (1985). Although some of the information pertaining to the crystal structure of (I) collected at room temperature was reported in the original communication (Schmidpeter *et al.*, 1985), geometrical parameters and other structural details for this compound are not available in the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002). This compound contains the only reported structurally characterized acyclic triphosphenium cation and continues to be of fundamental interest to synthetic and theoretical main group inorganic chemists (see, for example, Ellis & Macdonald, 2006). To rectify the omission, we now report the crystal structure of (I) obtained at low temperature.



(I)

The asymmetric unit of (I) consists of two crystallographically independent ion pairs and a molecule of dichloromethane. All of the atoms sit in general positions and the contents of the asymmetric unit are depicted in Fig. 1.

Both cations exhibit strongly bent geometries with respect to the P—P—P angles (Table 1). The P—P bond distances are significantly shorter than typical single P—P bonds. The metrical parameters are similar to those originally reported for the room-temperature structure. The anions are slightly distorted tetrahedra, in which the Cl—Al—Cl angles range from 107.87 (8) to 110.93 (7)° and the Al—Cl bond lengths vary from 2.1181 (16) to 2.1367 (16) Å.

The closest cation–anion contacts observed in the crystal structure of (I), although not unusually short, are listed in Table 2.

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Experimental

The salt (I) was synthesized using the method described in the literature (Schmidpeter *et al.*, 1985). Suitable crystals were obtained by cooling a saturated dichloromethane solution of the salt to 243 K.

Crystal data

$(C_{36}H_{30}P_3)[AlCl_4]\cdot 0.5CH_2Cl_2$
M_r = 766.76
Orthorhombic, $Pna2_1$
a = 33.283 (5) Å
b = 9.2443 (13) Å
c = 23.979 (4) Å
V = 7378 (2) Å^3
Z = 8
D_x = 1.381 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.57 mm^{-1}
T = 173 (2) K
Prism, colorless
0.50 × 0.40 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.652, T_{max} = 0.795
79631 measured reflections
16737 independent reflections
14199 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.131
S = 1.07
16737 reflections
821 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 1.5731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}
Absolute structure: Flack (1983), 8081 Friedel pairs
Flack parameter: −0.01 (4)

Table 1
Selected geometric parameters (Å, °).

P1—P2	2.1301 (12)	Cl3—Al1	2.1294 (17)
P2—P3	2.1249 (12)	Cl4—Al1	2.1367 (16)
P4—P5	2.1337 (12)	Cl5—Al2	2.1322 (15)
P5—P6	2.1312 (12)	Cl6—Al2	2.1304 (16)
Cl1—Al1	2.1228 (16)	Cl7—Al2	2.1344 (17)
Cl2—Al1	2.1250 (16)	Cl8—Al2	2.1181 (16)
P3—P2—P1	102.16 (5)	P6—P5—P4	102.25 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···P2	0.95	2.58	3.152 (4)	119
C42—H42···Cl3^{i}	0.95	2.82	3.716 (4)	157
C42—H42···P2	0.95	2.61	3.165 (4)	118
C76—H76···P5	0.95	2.60	3.166 (4)	118
C102—H102···P5	0.95	2.60	3.157 (4)	118
C105—H105···Cl9^{ii}	0.95	2.82	3.623 (6)	143
C123—H123···Cl4^{iii}	0.95	2.79	3.589 (6)	143

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y, z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{3}{2}, z+\frac{1}{2}$.

H atoms were placed in calculated positions with a C–H distance of 0.95 Å for the atoms attached to C atoms in the phenyl groups or a C–H distance of 0.99 Å for the atoms attached to the methylene C atom. These atoms were included in the refinement using the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$. The U^{ij} components of the Cl atoms in the solvent were restrained to be similar to each other. The only peak in the final difference Fourier map greater than 1.0 e Å^{-3} is located at a distance of 1.03 Å from Cl10.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT-Plus* (Bruker, 1997); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*, *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

The funding that has enabled this work has been provided by the Natural Sciences and Engineering Research Council (Canada), the Canada Foundation for Innovation, the Ontario Innovation Trust and the Ontario Research and Development Challenge Fund (University of Windsor Centre for Catalysis and Materials Research).

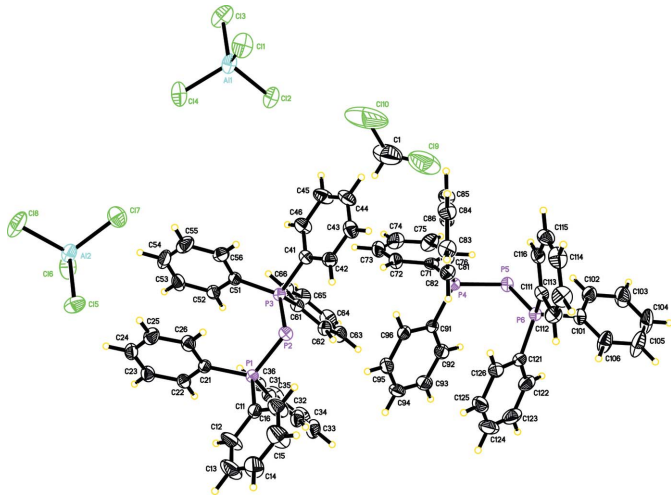

Figure 1
View of the asymmetric unit of (I). Displacement ellipsoids are depicted at the 50% probability level.

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