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1,1,3,3-Tetraphenyl-1,2,3-triphosphenium tetrachloroaluminate dichloromethane solvate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.075
Data-to-parameter ratio = 23.5

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

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The title compound, $(C_{27}H_{26}P_3)[AlCl_4]\cdot CH_2Cl_2$, was isolated from a mixture containing the triphosphenium ion and its protonated derivative. The central cation ring is non-planar, as in the analogous hexachlorostannate (though the structures are not isomorphous), and the P—P distances are intermediate between those typical for single and double bonds.

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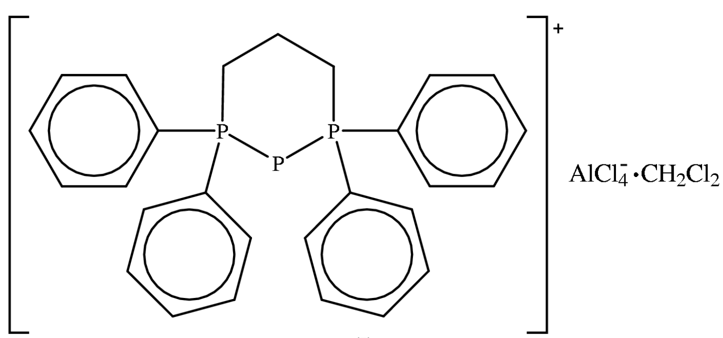
Comment

The cyclic triphosphenium cation was formed as its chloride salt by a reaction between 1,3-bis(diphenylphosphino)propane (dppp) and PCl_3 as shown below:

$$3Ph_2P(CH_2)_3PPh_2 + 2PCl_3 \rightarrow 2[C_{17}H_{26}P_3]^+\cdot Cl^- + [Ph_2P(Cl)(CH_2)_3P(Cl)Ph_2]^{2+}\cdot 2Cl^-$$

A 2:1 mixture of $AlCl_3$ and ^{t}BuCl was then added, both to protonate the cation and to complex the Cl^- ion as the tetrachloroaluminate(III) (Lochschmidt & Schmidpeter, 1985; Schmidpeter *et al.*, 1985; Burton *et al.*, 2005). While clear NMR evidence for protonation was obtained, the crystals isolated from the solution were found to be from the title compound, (I), *i.e.* the unprotonated ring cation as its tetrachloroaluminate(III) salt. This cation has been structurally characterized previously using X-ray crystallography as the hexachlorostannate(IV) salt (Boon *et al.*, 2000). Selected bond distances and angles for the cations in the two structures are listed in Table 2.



(I)

Despite the close relationship between the hexachlorostannate(IV) and (I), the structures reported are very different, with the former in the space group $I4/m$ and the tetrachloroaluminate in $P\bar{1}$.

In both the hexachlorostannate(IV) salt and (I) (Fig. 1), the six-membered cyclic triphosphenium ring is non-planar, as expected. However, in the hexachlorostannate, both P—P bond lengths are identical at 2.132 (1) Å since the cation

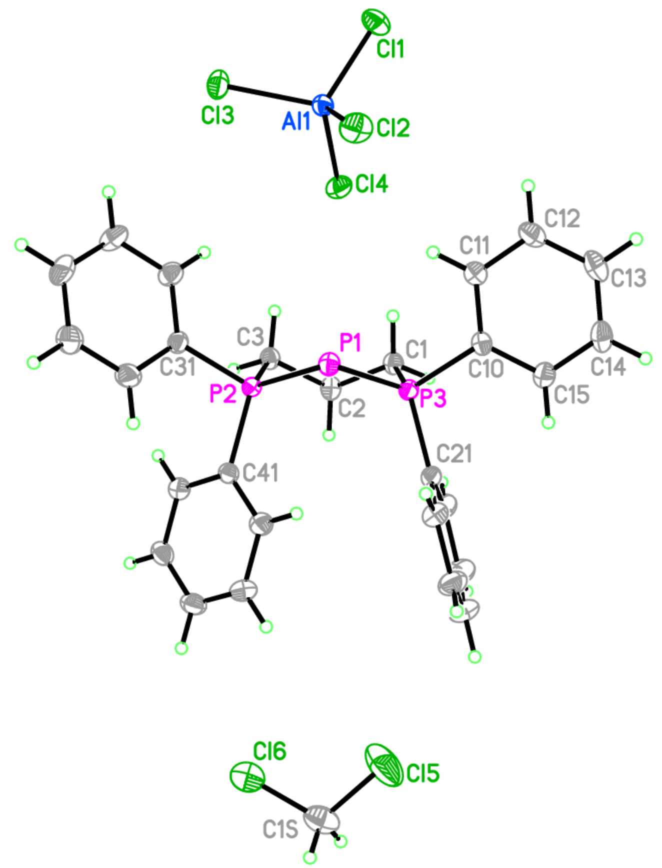


Figure 1
View of (I) with selected atoms labelled. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

occupies a position on a mirror plane, whereas in (I) there is a slight asymmetry in these distances [P1—P2 = 2.1259 (5) Å and P1—P3 = 2.1310 (5) Å]. In both structures, the P—P distance is clearly intermediate between the normal values for P—P single (2.20–2.25 Å) and P═P double bonds (2.00–2.05 Å; Schmidpeter *et al.*, 1983). These P—P bond lengths are comparable to those in the analogous five-membered ring compound [2.122 (1) and 2.128 (2) Å; Schmidpeter *et al.*, 1982], to those in the related (planar) five-membered ring with a benzene backbone [2.124 (1) and 2.122 (1) Å; Barnham *et al.*, 2001] and to those in a neutral six-membered ring compound containing three linked phosphorus atoms [2.134 (1) Å; Karsch *et al.*, 1995]. The P2—P1—P3 bond angle is slightly smaller in (I) at 95.58 (2)° compared with 96.44 (6)° in the hexachlorostannate, possibly reflecting crystal packing effects.

In (I), the charge is balanced by an isolated tetrahedral $[AlCl_4]^-$ anion, with Al—Cl distances between 2.1299 (5) and 2.1446 (5) Å [average 2.1361 (5) Å], and bond angles around the central Al atom between 108.22 (2) and 110.98 (2)° [average 109.47 (2)°]. There is also a dichloromethane solvent molecule in the structure, which is ordered and fully occupied (as is the $[AlCl_4]^-$), which is presumably due to the presence of weak C—H···Cl and Cl···Cl interactions (Table 1), though the magnitude of the anisotropic displacement parameters indicates that there is slightly increased motion compared with the rest of the structure.

Experimental

1,3-Bis(diphenylphosphino)propane (dppp) (0.503 g, 1.22 mmol) was dissolved in CH_2Cl_2 and PCl_3 (0.11 ml, 1.26 mmol) was added. The solution was stirred overnight; its ^{31}P NMR spectrum then showed that the six-membered ring cyclic triphosphenium cation had formed as its chloride salt [δ ^{31}P 23.1 (*d*, (2P), −209.4 (*t*, 1P; $^1J_{PP}$ = 424.8 Hz) (Burton *et al.*, 2005)]. $AlCl_3$ (0.344 g, 2.58 mmol) and ^{t}BuCl (0.14 ml, 1.29 mmol) were placed in a Schlenk tube, and the above solution was added to the mixture, with stirring. After overnight stirring, the ^{31}P{^{1}H} NMR spectrum showed formation of the protonated derivative [δ ^{31}P 13.8 (*d*, 2P), −156.1 (*t*, 1P; $^1J_{PP}$ = 226.0 Hz) (Burton *et al.*, 2005)]. This was confirmed by recording the proton-coupled spectrum, enabling $^1J_{PH}$ to be evaluated as 223.0 Hz. After filtration, the solution still showed the presence of the unprotonated ring cation. On cooling in a refrigerator, crystals of the title compound appeared after four weeks; the unprotonated ring was still present in the ^{31}P NMR spectrum of the filtrate.

Crystal data

$(C_{27}H_{26}P_3)[AlCl_4]\cdot CH_2Cl_2$
M_r = 697.09
Triclinic, $P\bar{1}$
a = 9.4446 (1) Å
b = 12.4158 (1) Å
c = 15.0802 (2) Å
α = 72.645 (1)°
β = 78.207 (1)°
γ = 77.390 (1)°
V = 1628.61 (3) Å^3
Z = 2
D_x = 1.422 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5459 reflections
θ = 2.5–28.3°
μ = 0.72 mm^{-1}
T = 120 (2) K
Block, colourless
0.20 × 0.11 × 0.07 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP*/*SHELXTL*; Sheldrick, 1997*a*)
T_{min} = 0.869, T_{max} = 0.951
15853 measured reflections
8053 independent reflections
7277 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 28.3°
h = −11 → 12
k = −16 → 16
l = −20 → 17

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.03
8053 reflections
343 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.9727P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···Cl4	0.99	2.89	3.8275 (14)	158
C3—H3*A*···Cl3^{i}	0.99	2.90	3.6609 (14)	134
C3—H3*B*···Cl4	0.99	2.90	3.8317 (14)	158
C36—H36···Cl1^{ii}	0.95	2.85	3.7275 (16)	155
C1S—H1*SA*···Cl1^{iii}	0.99	2.85	3.702 (2)	145

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, y - 1, z$; (iii) $x - 1, y - 1, z$.

Table 2
Comparison of selected bond distances (Å) and angles (°) for the cation in the title compound as its $[SnCl_6]^{2-}$ (Boon *et al.*, 2000) and $[AlCl_4]^{-}$salts.

	$[SnCl_6]^{2-}$	$[AlCl_4]^{-}$
P1—P2	2.132 (1)	2.1259 (5)
P1—P3	2.132 (1)	2.1310 (5)
P2—C3	1.815 (3)	1.8146 (13)
P3—C1	1.815 (3)	1.8143 (13)
C1—C2	1.535 (4)	1.5356 (18)
C2—C3	1.535 (4)	1.5362 (18)
P2—C31	1.810 (3)	1.8025 (13)
P2—C41	1.815 (3)	1.8109 (13)
P3—C10	1.815 (3)	1.8063 (13)
P3—C21	1.810 (3)	1.8060 (14)
P2—P1—P3	96.44(6)	95.579 (18)
P1—P2—C3	113.2 (1)	113.68 (4)
P2—C3—C2	113.4 (2)	112.69 (9)
C3—C2—C1	113.5 (4)	113.29 (11)
C31—P2—C41	105.9 (1)	107.16 (6)
C41—P2—C3	110.2 (1)	106.01 (6)
C31—P2—P1	103.4 (1)	104.73 (5)
C21—P3—C1	110.2 (1)	108.17 (6)
C10—P3—P1	103.4 (1)	104.71 (5)
C21—P3—C10	105.9 (1)	107.44 (6)

All H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined using a riding model, with $U_{iso} = 1.2U_{eq}(C)$. The largest residual electron-density peak is located 0.88 Å from atom Cl5, as is the deepest hole.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Sheldrick, 1997*a*); software used to prepare material for publication: *SHELXTL*.

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References

Barnham, R. J., Deng, R. M. K., Dillon, K. B., Goeta, A. E., Howard, J. A. K. & Puschmann, H. (2001). *Heteroatom Chem.* **12**, 501–510.
Boon, J. A., Byers, H. L., Dillon, K. B., Goeta, A. E. & Longbottom, D. A. (2000). *Heteroatom Chem.* **11**, 226–231.
Bruker (1998). *SMART-NT* (Version 5.0) and *SAINT-NT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Burton, J. D., Deng, R. M. K., Dillon, K. B., Monks, P. K. & Olivey, R. J. (2005). *Heteroatom Chem.* Submitted.
Karsch, H. H., Witt, E., Schneider, A. & Herdtweck, E. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 557–560.
Lochschmidt, S. & Schmidpeter, A. (1985). *Z. Naturforsch. Teil B*, **40**, 765–773.
Schmidpeter, A., Lochschmidt, S., Burget, G. & Sheldrick, W. S. (1983). *Phosphorus Sulfur*, **18**, 23–26.
Schmidpeter, A., Lochschmidt, S., Karaghiosoff, K. & Sheldrick, W. S. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1447–1448.
Schmidpeter, A., Lochschmidt, S. & Sheldrick, W. S. (1982). *Angew. Chem. Int. Ed. Engl.* **21**, 63–64.
Sheldrick, G. M. (1997*a*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*b*). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.