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Bis(trichlorophosphine)iminium salts, $[Cl_3P{=}N{=}PCl_3]^+$, with transition metal halide counter-ions

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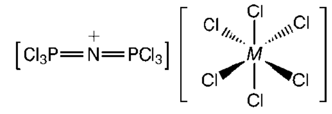
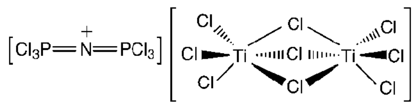
The structures of four bis(trichlorophosphine)iminium $\{[Cl_3P{=}N{=}PCl_3]^+$; systematic name: trichloro[(trichlorophosphoranylidene)iminio]phosphorus(V)$\}$ salts, namely bis(trichlorophosphine)iminium hexachloroniobate, $(Cl_6NP_2)[NbCl_6]$, (I), bis(trichlorophosphine)iminium hexachlorotantalate, $(Cl_6NP_2)[TaCl_6]$, (II), bis(trichlorophosphine)iminium tri-μ-chloro-bis[trichlorotitanium(IV)], $(Cl_6NP_2)[Ti_2Cl_9]$, (III), and bis[bis(trichlorophosphine)iminium] di-μ-chloro-bis[tetrachlorozirconium(IV)], $(Cl_6NP_2)_2[Zr_2Cl_{10}]$, (IV), have been determined. The P=N distances in the discrete $[Cl_3P{=}N{=}PCl_3]^+$ moieties in structures (I), (II) and (IV) range from 1.5460 (14) to 1.5554 (16) Å, and the P=N=P angles range from 136.8 (3) to 143.4 (4)°. The $[Cl_3P{=}N{=}PCl_3]^+$ cation in (III) is disordered and the calculated geometries for the cation are therefore less reliable. Compounds (I) and (II) are isostructural and the metal anions have slightly distorted octahedral geometries. The anion in compound (III) consists of two distorted octahedral Ti centres linked by three μ_2-Cl atoms, while in compound (IV), the dianion is derived from two distorted edge-shared $ZrCl_6$ octahedra.

Comment

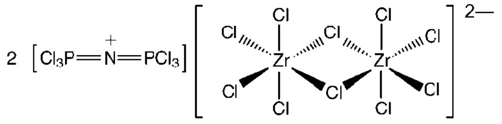
Bis(trichlorophosphine)iminium salts are commonly used precursors for the synthesis of inorganic heterocycles (Becke-Goehring & Müller, 1968; Dodge *et al.*, 1990). In addition, $[Cl_3P{=}N{=}PCl_3][PCl_6]$ is proposed as an intermediate in the formation of poly(dichlorophosphazene) *via* the living cationic polymerization of $Cl_3P{=}NSiMe_3$ with PCl_5 (Honeyman *et al.*, 1995). As part of our studies on the chemistry of boron-containing heterophosphazene ring systems (Gates *et al.*, 1998; McWilliams *et al.*, 2002), we discovered that the tetrachloroborate salt $[Cl_3P{=}N{=}PCl_3][BCl_4]$ reacted quickly with early transition metal halides in chlorinated solvents to produce BCl_3 gas and a series of new bis(trichlorophosphine)iminium salts with transition-metal-containing counter-ions, namely the title compounds (I)–(IV) (Figs. 1–4).



(I) M = Nb
(II) M = Ta



(III)



(IV)

Analysis of the resulting products was consistent with the absence of the $[BCl_4]^-$ anion, as no signals were detected in the ^{11}B NMR spectra. In addition, a signal at 22.2 p.p.m. was observed in the ^{31}P NMR spectra of salts (I)–(IV), indicative of the $[Cl_3P{=}N{=}PCl_3]^+$ cation (Faggiani *et al.*, 1980).

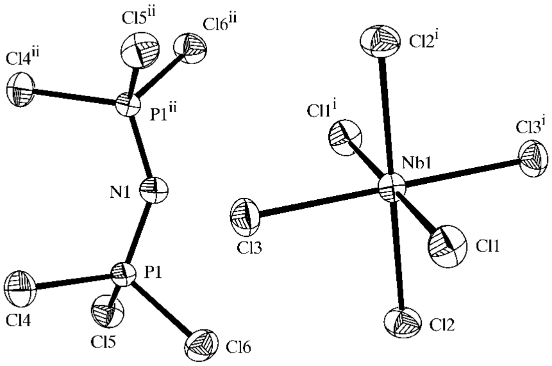


Figure 1
A view of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$.]

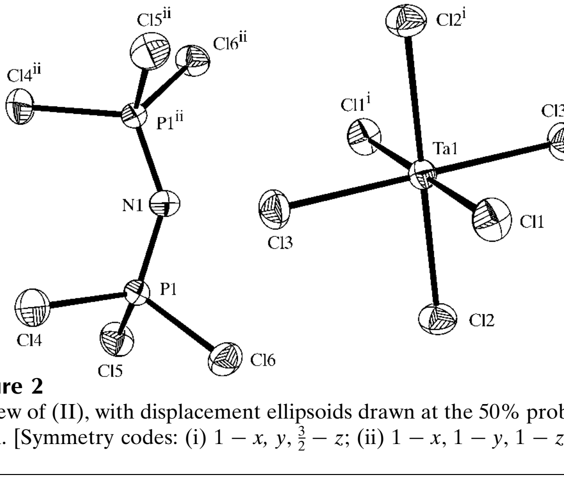


Figure 2
A view of (II), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$.]

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Salts (I)–(IV) crystallize as discrete cations and metal anions. The cation in (III) is disordered over two sites (see *Experimental*) and therefore its intramolecular geometry is not dicussed in detail. In the crystal structures of (I), (II) and (IV), the $[Cl_3P{=}N{=}PCl_3]^+$ cations lie on crystallographic twofold axes. The twofold axes pass through the central N atom and bisect the P=N=P angle. In (I), (II) and (IV), the $[Cl_3P{=}N{=}PCl_3]^+$ cations have P—N distances in the range 1.5460 (14)–1.5554 (16) Å. These values compare well with the P—N distances in the recently redetermined structure of $[Cl_3P{=}N{=}PCl_3][PCl_6]$ (Belaj, 1998), which vary from 1.556 (3) to 1.562 (3) Å. The P—N—P bond angles within the cations of (I), (II) and (IV) are in the range 136.8 (3)–143.4 (4)°, and are slightly larger than the angles observed in $[Cl_3P{=}N{=}PCl_3][PCl_6]$ [133.3 (2) and 135.8 (2)°]. The size of the P—N—P angle appears to depend on the nature of the anion and reflects the low energy required to deform the PNP unit (Faggiani *et al.*, 1980). Using the 'W' form of the Cl—P—N—P—Cl groupings for $[Cl_3P{=}N{=}PCl_3]^+$ [previously described by Belaj (1998)], the Cl—P—N—P torsion angles of (I) and (II) are −145.96 (6) and −146.05 (8)°, respectively. This is in contrast with the equivalent Cl—P—N—P torsion angles in $[Cl_3P{=}N{=}PCl_3][PCl_6]$, which are closer to 180°. The values in $[Cl_3P{=}N{=}PCl_3][PCl_6]$, however, are close to those found in compound (IV), which has a 'W'-form Cl—P—N—P torsion angle of −178.31 (6)°. In 1980, Belaj also found that the Cl—P—N angles in the cation were significantly smaller for the angle containing a Cl atom from the 'W' fragment [Cl6 for (I), (II) and (IV)] than the other Cl—P—N angles. This feature is also observed in each of (I), (II) and (IV) (see Tables 1, 2 and 4), despite the variation of the Cl—P—N—P torsion angle in (IV) from that in both (I) and (II).

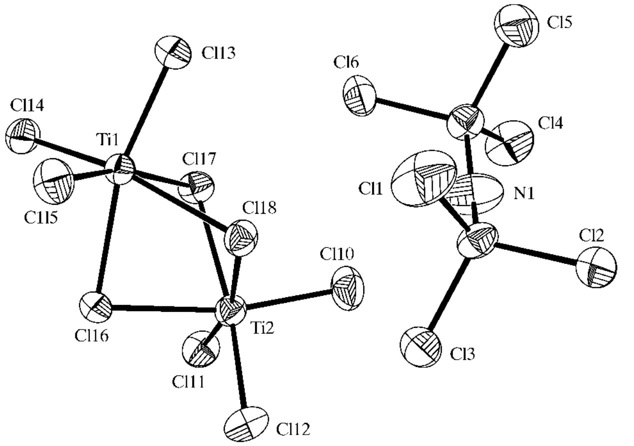

Figure 3
A view of (III), with displacement ellipsoids drawn at the 50% probability level. The disorder component has been omitted for clarity.

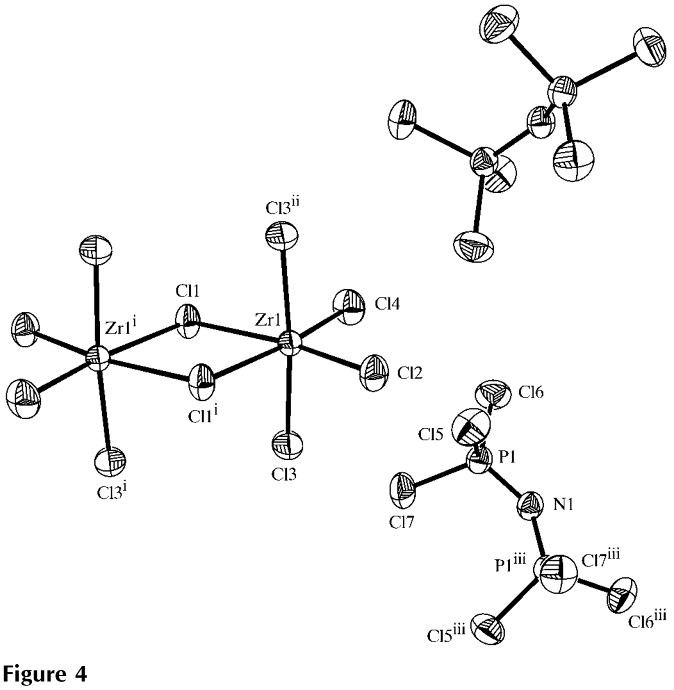

Figure 4
A view of (IV), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, y, z$; (iii) $\frac{1}{2}-x, y, \frac{3}{2}-z$.]

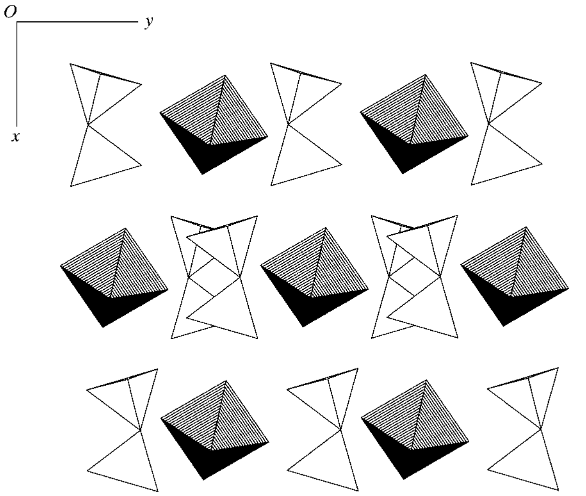

Figure 5
Polyhedral representation of the crystal packing of structures (I) and (II).

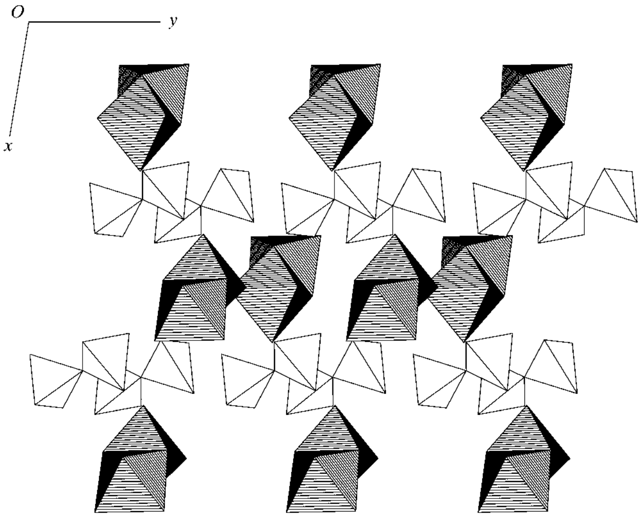

Figure 6
Polyhedral representation of the crystal packing of structure (III).

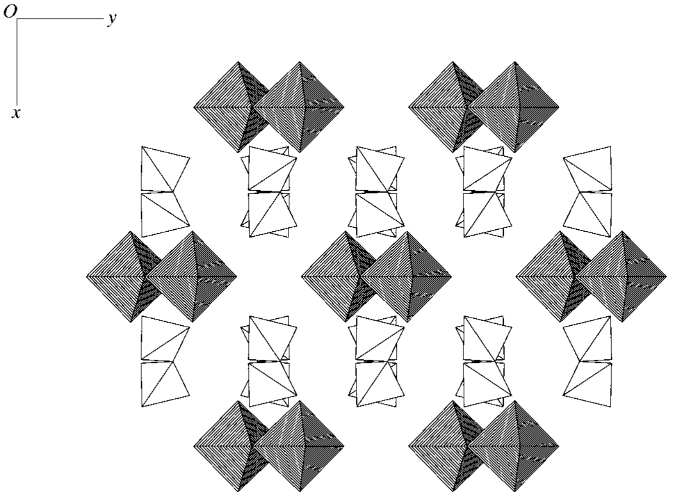

Figure 7
Polyhedral representation of the crystal packing of structure (IV).

Compounds (I) and (II) are isostructural in space group $C2/c$, with $Z = 4$. A Ta atom in (II) replaces the Nb atom in (I). In these two structures, the $[NbCl_6]^-$ or $[TaCl_6]^-$ ion has a slightly distorted octahedral geometry, with the metal atom located on a crystallographic inversion centre. Due to the Nb and Ta atoms being similar in size, the M—Cl (M = Nb or Ta) distances within these anions are also similar, *viz.* 2.3457 (7)–2.3613 (7) Å in $[NbCl_6]^-$ and 2.3428 (11)–2.3559 (9) Å in $[TaCl_6]^-$. The inversion symmetry in the anions of (I) and (II) restricts the *trans* Cl—M—Cl angles to exactly 180°, while the *cis* angles are in the range 89.36 (3)–90.64 (3)° for (I) and 89.37 (4)–90.63 (4)° for (II). Fig. 5 shows a polyhedral representation of the crystal packing in structures (I) and (II), viewed perpendicular to the xy plane. The figure shows alternate layers (superimposed in the xy plane) of anion octahedra and cations packing in the z direction.

In compound (III), both the cation and the anion are on general positions, but the cation is disordered over two sites (see *Experimental*). The $[Ti_2Cl_9]^-$ anion of (III) consists of two distorted octahedral Ti centres linked by three μ_2-Cl atoms. The Ti—μ_2-Cl—Ti angles range from 86.39 (3) to 87.45 (3)° and, consequently, the bridging Ti—Cl bond lengths [2.4548 (9)–2.5127 (8) Å] are longer than the terminal Ti—Cl bond lengths [2.2036 (10)–2.2319 (10) Å]. The *trans* Cl—Ti—Cl angles in (III) vary from 164.15 (4) to 166.69 (4)°, while the *cis* angles have values in the range 76.94 (3)–99.91 (4)°. The crystal structue of (III), as viewed in Fig. 6, shows layers of anions (face-shared octahedra) alternating with cations in the x direction.

The remaining compound, (IV), crystallized as the 2:1 salt $[Cl_3P{=}N{=}PCl_3]_2[Zr_2Cl_{10}]$ containing the unusual decachlorodizirconate dianion (derived from two edge-shared $ZrCl_6$ octahedra). The $[Zr_2Cl_{10}]^{2-}$ dianion has crystallographic $2/m$ symmetry, with a mirror plane running through the two Zr atoms and the six equatorial Cl atoms, while a twofold axis (perpendicular to the mirror plane) is located at the centre of the four-membered ring formed by the two Zr atoms and the two bridging Cl atoms. Again, a distorted octahedral geometry is observed about the transition metal atom, with a symmetry-unique bridging Zr—Cl—Zr angle of 101.92 (4)° and two elongated bridging Zr—Cl bonds of 2.6106 (11) and 2.6354 (12) Å. The shortened terminal Zr—Cl bonds are in the range 2.3640 (12)–2.4266 (9) Å. The *trans* Cl—Zr—Cl angles range from 167.20 (4) to 174.74 (5)°, while the *cis* angles range from 78.08 (4) to 100.04 (5)°. Fig. 7 illustrates the packing in the crystal structure of (IV), which consists of alternating layers of $[Zr_2Cl_{10}]^{2-}$ anions (edge-shared octahedra) and $[Cl_3P{=}N{=}PCl_3]^+$ cations in the x direction.

In the structures of (I)–(IV), there are intermolecular Cl···Cl distances which are shorter than the sum of the van der Waals radii of 3.50 Å (Bondi, 1964). The shortest Cl···Cl distance, for each compound, ranges from 3.184 (6) Å for Cl17···Cl1A(x, $-1 + y$, z) in (III) to 3.3908 (13) Å for Cl7···Cl3($-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$) in (IV). In all four title structures, the closest intermolecular Cl···Cl distances are between a Cl atom of a cation and a Cl atom of an anion. In the structure of $[Cl_3P{=}N{=}PCl_3][PCl_6]$, the shortest intermolecular Cl···Cl distances [3.182 (2) and 3.194 (2) Å] are between two Cl atoms belonging to anions, and these close contacts have been explained (Belaj, 1998). This anion–anion close contact is not present, however, in structures (I)–(IV).

Experimental

All manipulations of reagents and products were conducted under strictly anhydrous and anaerobic conditions. The metal-containing salts were prepared by the reaction of $[Cl_3P{=}N{=}PCl_3][BCl_4]$ (Binder & Fluck, 1971) with one or two equivalents of metal halide at room temperature for 12 h in dichloromethane. Gas evolution (BCl_3) was observed during the reaction, and removal of the volatiles *in vacuo* afforded white solids (80–95% yields). Recrystallization from dichloromethane (243 K, 12 h) gave yellow (I) or colourless (II)–(IV) crystals suitable for single-crystal X-ray diffraction studies. Data for (I)–(IV), ^{31}P NMR ($CDCl_3$): 22.1 (*s*) p.p.m., ^{11}B NMR ($CDCl_3$): no signal detected; IR (ν, cm^{-1}): 1378 (*s*), 1267 (*w*), 835 (*m*), 665 (*m*) and 632 (*s*); elemental analysis calculated for (II) ($Cl_{12}NP_2Ta$, M_r = 682.30): N 2.05%; found: N 2.19%.

Compound (I)

Crystal data

$(Cl_6NP_2)[NbCl_6]$
$M_r = 594.26$
Monoclinic, $C2/c$
$a = 13.4095 (7)$ Å
$b = 8.5268 (6)$ Å
$c = 15.0432 (9)$ Å
$\beta = 103.928 (4)^\circ$
$V = 1669.47 (18)$ Å^3
$Z = 4$

$D_x = 2.364$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 033 reflections
$\theta = 2.5$–27.5°
$\mu = 2.81$ mm^{-1}
$T = 150 (1)$ K
Block, yellow
0.23 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.531$, $T_{max} = 0.568$
6672 measured reflections

1908 independent reflections
1676 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5^\circ$
$h = -17 \rightarrow 17$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 18$

i116 Eric Rivard et al. • $(Cl_6NP_2)[NbCl_6]$, $(Cl_6NP_2)[TaCl_6]$, $(Cl_6NP_2)[Ti_2Cl_9]$ and $(Cl_6NP_2)_2[Zr_2Cl_{10}]$ Acta Cryst. (2002). C58, i114–i118

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.082$
$S = 1.08$
1908 reflections
76 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 2.7251P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.95$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0010 (2)

Table 1
Selected geometric parameters (Å, °) for (I).

Nb1—Cl1	2.3457 (7)	Nb1—Cl2	2.3613 (7)
Nb1—Cl3	2.3517 (7)	P1—N1	1.5460 (14)
Cl1—Nb1—Cl3	89.36 (3)	N1—P1—Cl4	113.76 (13)
N1—P1—Cl6	110.34 (12)	Cl6—P1—Cl4	107.58 (5)
N1—P1—Cl5	112.37 (5)	Cl5—P1—Cl4	106.57 (5)
Cl6—P1—Cl5	105.78 (5)	P1—N1—P1$^{\rm i}$	143.1 (3)
Cl6—P1—N1—P1$^{\rm i}$	−145.96 (6)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Compound (II)

Crystal data

$(Cl_6NP_2)[TaCl_6]$
$M_r = 682.30$
Monoclinic, *C*2/*c*
$a = 13.3957$ (5) Å
$b = 8.5165$ (4) Å
$c = 15.0937$ (5) Å
$\beta = 103.855$ (3)°
$V = 1671.86$ (11) Å^3
$Z = 4$

$D_x = 2.711$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 10 506 reflections
$\theta = 2.5$–27.5°
$\mu = 8.66$ mm^{-1}
$T = 150$ (1) K
Needle, colourless
0.21 × 0.17 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.200$, $T_{\max} = 0.271$
6759 measured reflections

1917 independent reflections
1675 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 1.08$
1917 reflections
76 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 1.5713P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.29$ e Å^{-3}
$\Delta\rho_{\min} = -1.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00092 (12)

Table 2
Selected geometric parameters (Å, °) for (II).

Ta1—Cl1	2.3428 (11)	Ta1—Cl2	2.3559 (9)
Ta1—Cl3	2.3484 (10)	P1—N1	1.546 (2)
Cl1—Ta1—Cl3	89.37 (4)	N1—P1—Cl4	113.59 (18)
N1—P1—Cl6	110.14 (17)	Cl6—P1—Cl4	107.76 (7)
N1—P1—Cl5	112.33 (7)	Cl5—P1—Cl4	106.74 (7)
Cl6—P1—Cl5	105.88 (6)	P1—N1—P1$^{\rm i}$	143.3 (4)
Cl6—P1—N1—P1$^{\rm i}$	−146.05 (8)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Compound (III)

Crystal data

$(Cl_6NP_2)[Ti_2Cl_9]$
$M_r = 703.50$
Triclinic, $P\overline{1}$
$a = 8.9436$ (4) Å
$b = 9.0892$ (4) Å
$c = 14.2963$ (6) Å
$\alpha = 91.770$ (2)°
$\beta = 105.714$ (3)°
$\gamma = 107.973$ (2)°
$V = 1055.78$ (8) Å^3

$Z = 2$
$D_x = 2.213$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 12 979 reflections
$\theta = 4.3$–26.3°
$\mu = 2.79$ mm^{-1}
$T = 250$ (1) K
Needle, colourless
0.25 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.526$, $T_{\max} = 0.660$
12 979 measured reflections

4258 independent reflections
3346 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 26.3°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 10$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.099$
$S = 1.02$
4258 reflections
248 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

Ti1—Cl15	2.2036 (10)	Ti2—Cl17	2.4548 (9)
Ti1—Cl17	2.4941 (9)	Ti2—Cl16	2.4832 (9)
Ti1—Cl18	2.5047 (9)	Ti2—Cl18	2.4930 (9)
Ti1—Cl16	2.5127 (8)	N1—P1	1.519 (3)
Ti2—Cl12	2.2319 (10)	N1—P2	1.530 (3)
Cl13—Ti1—Cl14	99.31 (4)	N1—P1—Cl2	112.55 (19)
Cl15—Ti1—Cl17	165.71 (4)	Cl1—P1—Cl2	107.08 (10)
Cl14—Ti1—Cl18	164.15 (4)	N1—P1—Cl3	111.23 (19)
Cl13—Ti1—Cl16	165.03 (4)	Cl1—P1—Cl3	106.92 (9)
Cl18—Ti1—Cl16	76.94 (3)	Cl2—P1—Cl3	105.66 (9)
Cl12—Ti2—Cl17	166.69 (4)	N1—P2—Cl4	110.3 (2)
Cl11—Ti2—Cl18	166.04 (4)	N1—P2—Cl6	111.82 (18)
Ti2—Cl16—Ti1	86.43 (3)	Cl4—P2—Cl6	107.47 (8)
Ti2—Cl17—Ti1	87.45 (3)	N1—P2—Cl5	113.88 (18)
Ti2—Cl18—Ti1	86.39 (3)	Cl4—P2—Cl5	107.10 (8)
P1—N1—P2	154.3 (3)	Cl6—P2—Cl5	105.92 (10)
N1—P1—Cl1	113.0 (2)		
P2—N1—P1—Cl3	143.8 (7)	P1—N1—P2—Cl4	155.0 (7)

Compound (IV)

Crystal data

$(Cl_6NP_2)_2[Zr_2Cl_{10}]$
$M_r = 1114.24$
Orthorhombic, *Cmca*
$a = 18.0456$ (4) Å
$b = 11.4295$ (6) Å
$c = 15.7039$ (5) Å
$V = 3239.0$ (2) Å^3
$Z = 4$
$D_x = 2.285$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 7047 reflections
$\theta = 3.3$–26.5°
$\mu = 2.66$ mm^{-1}
$T = 250$ (1) K
Needle, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.498$, $T_{\max} = 0.769$
7407 measured reflections
1725 independent reflections
1386 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\max} = 26.5°$
$h = -22 \rightarrow 22$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 0$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.074$
$S = 1.06$
1725 reflections
76 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 3.2260P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00067 (9)

Table 4
Selected geometric parameters (Å, °) for (IV).

Zr1—Cl4	2.3640 (12)	Zr1—Cl1$^{\rm i}$	2.6354 (12)
Zr1—Cl3	2.4266 (9)	P1—N1	1.5554 (16)
Zr1—Cl1	2.6106 (11)		
Cl4—Zr1—Cl2	100.04 (5)	Zr1—Cl1—Zr1$^{\rm i}$	101.92 (4)
Cl3—Zr1—Cl3$^{\rm ii}$	174.74 (5)	N1—P1—Cl6	109.86 (14)
Cl2—Zr1—Cl1	167.20 (4)	N1—P1—Cl5	113.57 (8)
Cl4—Zr1—Cl1$^{\rm i}$	170.84 (4)	N1—P1—Cl7	113.29 (9)
Cl1—Zr1—Cl1$^{\rm i}$	78.08 (4)	P1—N1—P1$^{\rm iii}$	136.8 (3)
Cl6—P1—N1—P1$^{\rm iii}$	−178.31 (6)	Cl7—P1—N1—P1$^{\rm iii}$	−59.83 (7)
Cl5—P1—N1—P1$^{\rm iii}$	61.88 (7)		

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

During the refinement of (III), the anisotropic displacement parameters of the central N atom of the $[Cl_3P{=}N{=}PCl_3]^+$ cation refined to an unusually large value, compared with the values for the atoms in the anion. In addition to this feature, difference Fourier maps showed several residual electron-density peaks, of approximately 1 e Å^{-3}, close to the anisotropic Cl atoms in the cation. This suggested that the $[Cl_3P{=}N{=}PCl_3]^+$ moiety was disordered over two sites. In the final cycles of refinement, the cation was refined with two disorder components of equal geometry [using the *SAME* command in *SHELXTL*/*PC* (Sheldrick, 1999)], with all atoms occupying two independent sites. The minor-occupany disorder component is an equivalent $[Cl_3P{=}N{=}PCl_3]^+$ moiety in which the central N atom is shifted by about 0.7 Å and the rest of the molecule is, in turn, displaced by this shift. The final value for the occupancy was 0.852 (6) for the major component and 0.148 (2) for the minor component. The N, P and Cl atoms with major occupancy and the Cl atoms with minor occupancy were refined with anisotropic displacement parameters, while the minor-occupany P and N atoms were refined with isotropic displacement parameters. The final $R[I > 2\sigma(I)]$ value improved from 0.042 for the ordered anisotropic model to 0.036 for the refinement using a disordered model. The final model of the cation gave values for the P—N distances and P—N—P angles that were unusual (see Table 3) compared with compounds (I), (II) and (IV), and the values in other previously determined salts containing $[Cl_3P{=}N{=}PCl_3]^+$ cations (Belaj, 1998; Müller *et al.*, 1988). Although the values in (III) appear unusual, least-squares refinements performed using geometric restraints (using previously determined geometries for $[Cl_3P{=}N{=}PCl_3]^+$ cations) caused the refinement to become unstable.

For all four title compounds, data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1999); program(s) used to refine structure: *SHELXTL*/*PC*; molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1570). Services for accessing these data are described at the back of the journal.

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