Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

μ-1,2-Bis(diphenylphosphino)ethane-κ^2P:P-bis[trichloridogallium(III)]

Fei Cheng, Andrew L. Hector, William Levason, Gillian Reid, Michael Webster* and Wenjian Zhang

School of Chemistry, University of Southampton, Southampton SO17 1BJ, England
Correspondence e-mail: m.webster@soton.ac.uk

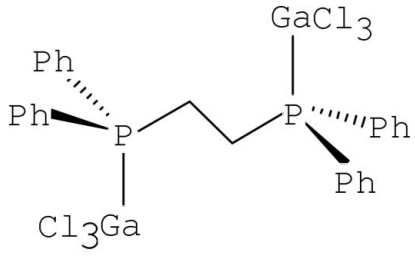
Received 12 May 2007; accepted 18 May 2007

Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.073; data-to-parameter ratio = 21.3.

The centrosymmetric molecule of the title compound, $[(GaCl_3)_2(C_{26}H_{24}P_2)]$ or $[(GaCl_3)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}]$, consists of two pseudo-tetrahedral Ga centres coordinated by three Cl atoms [Ga—Cl = 2.1608 (8)–2.1648 (8) Å] and bridged by the diphosphane ligand [Ga—P = 2.3854 (8) Å].

Related literature

For related literature, see: Baker *et al.* (1997); Brown *et al.* (1997); Cheng *et al.* (2007); Grant (1993); O'Brien & Pickett (2004).



Experimental

Crystal data

$[(GaCl_3)_2(C_{26}H_{24}P_2)]$
M_r = 750.53
Triclinic, $P\overline{1}$
a = 8.3586 (10) Å
b = 9.457 (2) Å
c = 11.644 (2) Å
α = 66.137 (8)°
β = 77.057 (10)°
γ = 65.540 (10)°
V = 764.4 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 2.41 mm^{-1}
T = 120 (2) K
0.20 × 0.20 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.645, T_{max} = 0.908
15738 measured reflections
3469 independent reflections
2672 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.073
S = 1.01
3469 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ga1—Cl1	2.1608 (8)	P1—C1	1.802 (2)
Ga1—Cl2	2.1648 (8)	P1—C7	1.804 (3)
Ga1—Cl3	2.1620 (8)	P1—C13	1.825 (3)
Ga1—P1	2.3854 (8)		
Cl1—Ga1—Cl2	114.33 (3)	Cl3—Ga1—P1	109.27 (3)
Cl1—Ga1—Cl3	112.70 (3)	C1—P1—C7	111.46 (12)
Cl3—Ga1—Cl2	110.48 (3)	C1—P1—C13	107.72 (12)
Cl1—Ga1—P1	103.11 (3)	C7—P1—C13	105.83 (11)
Cl2—Ga1—P1	106.38 (3)		

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank RCUK for support (grant No. EP/C006731/1).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2145).

References

Baker, L.-J., Kloo, L. A., Rickard, C. E. F. & Taylor, M. J. (1997). *J. Organomet. Chem.* **545–546**, 249–255.
Brown, M. A., Castro, J. A. & Tuck, D. G. (1997). *Can. J. Chem.* **75**, 333–341.
Cheng, F., Codgbrook, H. L., Hector, A. L., Levason, W., Reid, G., Webster, M. & Zhang, W. (2007). *Polyhedron* In the press. (DOI: 10.1016/j.poly.2007.05.008)
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Grant, R. (1993). *Chemistry of Aluminium, Gallium, Indium and Thallium*, edited by A. J. Downs, ch. 5. London: Blackie.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
O'Brien, P. & Pickett, N. L. (2004). *Comprehensive Coordination Chemistry II*, Vol. 9, edited by J. A. McCleverty & T. J. Meyer, pp. 1005–1063. Oxford: Elsevier.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.

supplementary materials

Acta Cryst. (2007). E**63**, m1761 [**doi:10.1107/S1600536807024592**]

μ-1,2-Bis(diphenylphosphino)ethane-κ^2P:P-bis[trichloridogallium(III)]

F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang

Comment

Gallium nitride, phosphide, and arsenide are compound semi-conductors (III-V materials) of key importance in the electronics industries; for example GaN, GaP and GaAs are used extensively in LED applications and GaAs is also widely used in integrated circuits, displays and solar cells (O'Brien & Pickett, 2004; Grant, 1993). Gallium halide and gallium alkyl complexes of organo-phosphorus or -arsenic ligands are precursors for the manufacture of GaP and GaAs (O'Brien & Pickett, 2004) and in the course of such an investigation, we obtained the title complex by combination of anhydrous $GaCl_3$ and $Ph_2P(CH_2)_2PPh_2$ in Et_2O.

The presence of two coincident Ga—Cl vibrations in the IR and Raman spectra and the ^{71}Ga NMR chemical shift of δ = 267 are consistent with the presence of *pseudo*-tetrahedral gallium centres (Cl_3P donor sets) (Cheng *et al.*, 2007; Baker *et al.*, 1997). Colourless crystals of the title compound were obtained from CH_2Cl_2/n-hexane, and the structure determination confirms the deduction from the spectroscopic data.

The molecule (Figure 1) has a centre of symmetry which places the $GaCl_3$ groups in an *anti* arrangement. Comparison with the structure of $[(I_3Ga)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}]$ reported previously (Brown *et al.*, 1997) shows a very similar conformation, although in this case not determined by symmetry. The d(Ga—P) in the present chloro-complex of 2.3854 (8) Å) is shorter than the d(Ga—P) in the corresponding iodo-complex (2.404 (9), 2.410 (9) Å) consistent with weaker Lewis acidity of GaI_3.

Similar trends in bond lengths are observed in the $[GaX_3(PPh_3)]$ (X = Cl or I) complexes (Cheng *et al.*, 2007; Baker *et al.*, 1997).

Experimental

A solution of $Ph_2P(CH_2)_2PPh_2$ (0.156 g, 0.39 mmol) in anhydrous Et_2O (5 cm^3) was added dropwise to a stirred solution of $GaCl_3$ (0.137 g, 0.78 mmol) in Et_2O (4 cm^3). After stirring at room temperature for 15 h, the resultant white precipitate was filtered off, washed with Et_2O and dried *in vacuo*. Yield: 63%. Required for $C_{26}H_{24}Cl_6Ga_2P_2$: C, 41.6; H, 3.1. Found: C, 41.6; H, 3.3%. ^{1}H NMR ($CDCl_3$): δ = 7.71–7.44 (m, [20H], Ph), 2.92 (d, [4H], CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −7.6 (relative to external 85% H_3PO_4). ^{71}Ga NMR: δ = 267 (relative to $[Ga(H_2O)_6]^{3+}$ in water). IR (Nujol): ν(Ga—Cl) = 390(*s*), 351(*m*) cm^{-1}; Raman: ν(Ga—Cl) = 389(*m*), 352(*s*) cm^{-1}.

Crystals were obtained by vapour diffusion of n-hexane into a CH_2Cl_2 solution of the complex.

Refinement

H atoms were placed in calculated positions (C—H = 0.95 (aromatic), 0.99 Å (CH_2)) and refined as riding; U_{iso}(H) was set equal to 1.2U_{eq}(C).

Figures

Fig. 1. Molecular structure of $[(GaCl_3)_2\{Ph_2P(CH_2)_2PPh_2\}]$, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: (*a*) −*x*, 1 − *y*, −*z*.

μ-1,2-Bis(diphenylphosphino)ethane-bis[trichloridogallium(III)]

Crystal data

$[(GaCl_3)_2(C_{26}H_{24}P_2)]$	Z = 1
M_r = 750.53	F_{000} = 374
Triclinic, $P\overline{1}$	D_x = 1.630 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 8.3586 (10) Å	Cell parameters from 3379 reflections
b = 9.457 (2) Å	θ = 2.9–27.5º
c = 11.644 (2) Å	μ = 2.41 mm^{-1}
α = 66.137 (8)º	T = 120 (2) K
β = 77.057 (10)º	Plate, colourless
γ = 65.540 (10)º	0.20 × 0.20 × 0.04 mm
V = 764.4 (2) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	3469 independent reflections
Radiation source: Nonius rotating anode	2672 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.046
T = 120(2) K	θ_{max} = 27.5º
φ and ω scans	θ_{min} = 3.2º
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	h = −10→10
T_{min} = 0.645, T_{max} = 0.908	k = −12→12
15738 measured reflections	l = −15→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.073$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.6686P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
3469 reflections	$\Delta\rho_{max} = 0.56$ e Å^{-3}
163 parameters	$\Delta\rho_{min} = -0.64$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ga1	0.32216 (4)	0.20961 (3)	0.22313 (3)	0.01933 (9)
Cl1	0.35788 (9)	−0.00419 (9)	0.39476 (7)	0.03122 (18)
Cl2	0.48454 (9)	0.15689 (9)	0.06153 (7)	0.03109 (17)
Cl3	0.35063 (9)	0.41397 (9)	0.24547 (8)	0.03397 (18)
P1	0.02504 (8)	0.28638 (8)	0.18155 (6)	0.01615 (15)
C1	−0.1279 (3)	0.3960 (3)	0.2806 (2)	0.0173 (5)
C2	−0.0817 (3)	0.3569 (3)	0.4008 (2)	0.0221 (6)
H2	0.0249	0.2687	0.4314	0.026*
C3	−0.1914 (4)	0.4470 (3)	0.4752 (3)	0.0256 (6)
H3	−0.1605	0.4198	0.5573	0.031*
C4	−0.3461 (3)	0.5766 (3)	0.4307 (3)	0.0219 (6)
H4	−0.4199	0.6392	0.4818	0.026*
C5	−0.3935 (3)	0.6153 (3)	0.3124 (3)	0.0231 (6)
H5	−0.4998	0.7043	0.2822	0.028*
C6	−0.2857 (3)	0.5241 (3)	0.2372 (2)	0.0195 (6)
H6	−0.3195	0.5491	0.1565	0.023*
C7	−0.0119 (3)	0.1020 (3)	0.2033 (2)	0.0176 (5)
C8	0.1053 (4)	−0.0017 (3)	0.1387 (3)	0.0226 (6)

H8	0.1985	0.0274	0.0839	0.027*
C9	0.0850 (4)	−0.1466 (3)	0.1550 (3)	0.0258 (6)
H9	0.1638	−0.2170	0.1109	0.031*
C10	−0.0500 (4)	−0.1892 (3)	0.2357 (3)	0.0248 (6)
H10	−0.0640	−0.2887	0.2467	0.030*
C11	−0.1646 (3)	−0.0873 (3)	0.3003 (3)	0.0254 (6)
H11	−0.2563	−0.1178	0.3561	0.030*
C12	−0.1467 (3)	0.0590 (3)	0.2843 (3)	0.0211 (6)
H12	−0.2261	0.1291	0.3285	0.025*
C13	−0.0181 (3)	0.4203 (3)	0.0182 (2)	0.0174 (5)
H13A	0.0569	0.3586	−0.0378	0.021*
H13B	−0.1426	0.4498	0.0052	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.02001 (16)	0.01879 (16)	0.02054 (17)	−0.00612 (12)	0.00056 (11)	−0.01015 (12)
Cl1	0.0287 (4)	0.0259 (4)	0.0247 (4)	−0.0010 (3)	−0.0019 (3)	−0.0043 (3)
Cl2	0.0270 (4)	0.0394 (4)	0.0267 (4)	−0.0085 (3)	0.0062 (3)	−0.0193 (3)
Cl3	0.0343 (4)	0.0321 (4)	0.0482 (5)	−0.0150 (3)	−0.0018 (3)	−0.0239 (4)
P1	0.0197 (3)	0.0142 (3)	0.0162 (3)	−0.0075 (3)	0.0014 (3)	−0.0069 (3)
C1	0.0207 (13)	0.0138 (12)	0.0190 (13)	−0.0077 (10)	0.0024 (10)	−0.0078 (10)
C2	0.0219 (14)	0.0201 (14)	0.0185 (14)	−0.0032 (11)	−0.0017 (11)	−0.0057 (11)
C3	0.0323 (16)	0.0272 (15)	0.0186 (14)	−0.0092 (12)	0.0008 (12)	−0.0122 (12)
C4	0.0221 (14)	0.0204 (14)	0.0255 (15)	−0.0093 (11)	0.0078 (11)	−0.0134 (12)
C5	0.0172 (13)	0.0197 (14)	0.0296 (16)	−0.0048 (11)	0.0013 (11)	−0.0096 (12)
C6	0.0204 (13)	0.0213 (14)	0.0183 (14)	−0.0094 (11)	−0.0022 (10)	−0.0060 (11)
C7	0.0203 (13)	0.0138 (12)	0.0174 (13)	−0.0061 (10)	−0.0048 (10)	−0.0025 (10)
C8	0.0264 (14)	0.0216 (14)	0.0219 (14)	−0.0125 (11)	0.0042 (11)	−0.0088 (12)
C9	0.0348 (16)	0.0199 (14)	0.0248 (15)	−0.0095 (12)	0.0005 (12)	−0.0117 (12)
C10	0.0310 (15)	0.0177 (14)	0.0283 (16)	−0.0120 (12)	−0.0078 (12)	−0.0043 (12)
C11	0.0214 (14)	0.0207 (14)	0.0329 (16)	−0.0116 (11)	0.0011 (12)	−0.0059 (12)
C12	0.0202 (13)	0.0154 (13)	0.0259 (15)	−0.0049 (10)	−0.0006 (11)	−0.0078 (11)
C13	0.0223 (13)	0.0185 (13)	0.0132 (13)	−0.0081 (11)	0.0004 (10)	−0.0073 (11)

Geometric parameters (Å, °)

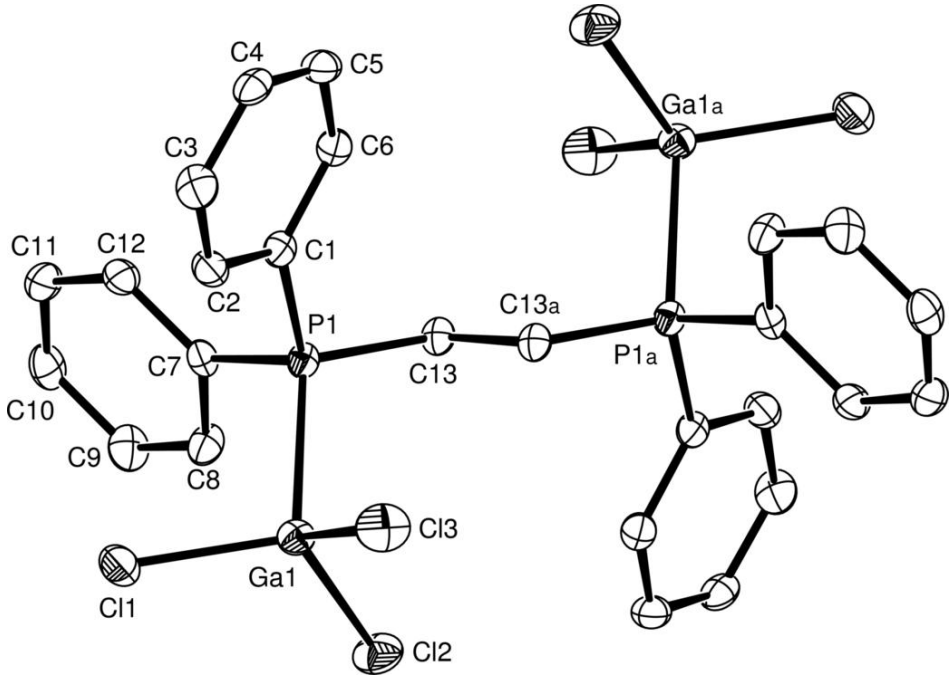
Ga1—Cl1	2.1608 (8)	C5—H5	0.9500
Ga1—Cl2	2.1648 (8)	C6—H6	0.9500
Ga1—Cl3	2.1620 (8)	C7—C12	1.385 (4)
Ga1—P1	2.3854 (8)	C7—C8	1.399 (4)
P1—C1	1.802 (2)	C8—C9	1.383 (4)
P1—C7	1.804 (3)	C8—H8	0.9500
P1—C13	1.825 (3)	C9—C10	1.383 (4)
C1—C2	1.396 (4)	C9—H9	0.9500
C1—C6	1.394 (3)	C10—C11	1.383 (4)
C2—C3	1.382 (4)	C10—H10	0.9500
C2—H2	0.9500	C11—C12	1.386 (4)
C3—C4	1.385 (4)	C11—H11	0.9500

C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.381 (4)	C13—C13^{i}	1.532 (5)
C4—H4	0.9500	C13—H13A	0.9900
C5—C6	1.391 (4)	C13—H13B	0.9900
Cl1—Ga1—Cl2	114.33 (3)	C5—C6—C1	119.8 (2)
Cl1—Ga1—Cl3	112.70 (3)	C5—C6—H6	120.1
Cl3—Ga1—Cl2	110.48 (3)	C1—C6—H6	120.1
Cl1—Ga1—P1	103.11 (3)	C12—C7—C8	120.2 (2)
Cl2—Ga1—P1	106.38 (3)	C12—C7—P1	122.0 (2)
Cl3—Ga1—P1	109.27 (3)	C8—C7—P1	117.67 (19)
C1—P1—C7	111.46 (12)	C9—C8—C7	119.7 (2)
C1—P1—C13	107.72 (12)	C9—C8—H8	120.1
C7—P1—C13	105.83 (11)	C7—C8—H8	120.1
C1—P1—Ga1	111.15 (9)	C8—C9—C10	120.0 (3)
C7—P1—Ga1	108.80 (8)	C8—C9—H9	120.0
C13—P1—Ga1	111.78 (9)	C10—C9—H9	120.0
C2—C1—C6	119.7 (2)	C11—C10—C9	120.2 (2)
C2—C1—P1	118.82 (19)	C11—C10—H10	119.9
C6—C1—P1	121.4 (2)	C9—C10—H10	119.9
C3—C2—C1	119.9 (2)	C10—C11—C12	120.6 (2)
C3—C2—H2	120.1	C10—C11—H11	119.7
C1—C2—H2	120.1	C12—C11—H11	119.7
C4—C3—C2	120.3 (3)	C7—C12—C11	119.3 (2)
C4—C3—H3	119.9	C7—C12—H12	120.3
C2—C3—H3	119.9	C11—C12—H12	120.3
C3—C4—C5	120.3 (2)	C13^{i}—C13—P1	112.4 (2)
C3—C4—H4	119.9	C13^{i}—C13—H13A	109.1
C5—C4—H4	119.9	P1—C13—H13A	109.1
C4—C5—C6	120.1 (2)	C13^{i}—C13—H13B	109.1
C4—C5—H5	120.0	P1—C13—H13B	109.1
C6—C5—H5	120.0	H13A—C13—H13B	107.8
Cl1—Ga1—P1—C1	77.84 (9)	C4—C5—C6—C1	−1.4 (4)
Cl3—Ga1—P1—C1	−42.24 (9)	C2—C1—C6—C5	1.9 (4)
Cl2—Ga1—P1—C1	−161.53 (9)	P1—C1—C6—C5	−174.51 (19)
Cl1—Ga1—P1—C7	−45.25 (9)	C1—P1—C7—C12	2.0 (3)
Cl3—Ga1—P1—C7	−165.34 (9)	C13—P1—C7—C12	−114.9 (2)
Cl2—Ga1—P1—C7	75.37 (9)	Ga1—P1—C7—C12	124.9 (2)
Cl1—Ga1—P1—C13	−161.76 (9)	C1—P1—C7—C8	−175.6 (2)
Cl3—Ga1—P1—C13	78.15 (9)	C13—P1—C7—C8	67.5 (2)
Cl2—Ga1—P1—C13	−41.14 (9)	Ga1—P1—C7—C8	−52.7 (2)
C7—P1—C1—C2	90.2 (2)	C12—C7—C8—C9	0.7 (4)
C13—P1—C1—C2	−154.1 (2)	P1—C7—C8—C9	178.3 (2)
Ga1—P1—C1—C2	−31.3 (2)	C7—C8—C9—C10	−0.5 (4)
C7—P1—C1—C6	−93.3 (2)	C8—C9—C10—C11	−0.1 (4)
C13—P1—C1—C6	22.3 (2)	C9—C10—C11—C12	0.6 (4)
Ga1—P1—C1—C6	145.10 (18)	C8—C7—C12—C11	−0.2 (4)
C6—C1—C2—C3	−0.9 (4)	P1—C7—C12—C11	−177.8 (2)
P1—C1—C2—C3	175.6 (2)	C10—C11—C12—C7	−0.4 (4)

C1—C2—C3—C4	−0.6 (4)	C1—P1—C13—C13^{i}	64.0 (3)
C2—C3—C4—C5	1.0 (4)	C7—P1—C13—C13^{i}	−176.6 (2)
C3—C4—C5—C6	−0.1 (4)	Ga1—P1—C13—C13^{i}	−58.4 (3)

Symmetry codes: (i) −*x*, −*y*+1, −*z*.

Fig. 1


C4
C5
Ga1a
C3
C6
C11
C12
C1
C2
C13a
P1
C7
C13
P1a
C10
C9
C8
Cl3
Ga1
Cl1
Cl2