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## Structure Reports

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**(Methyldiphenylphosphoranylidene)-ammonium chloride**Cintya Valerio-Cárdenas,<sup>a</sup> Luis Ortiz-Frade<sup>b\*</sup> and Jean-Michel Grévy M.<sup>a</sup><sup>a</sup>Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa Cuernavaca, Morelos 62210, Mexico, and<sup>b</sup>Electrochemistry Department, Centro de Investigación y Desarrollo Tecnológico en Electroquímica SC, Parque Tecnológico Querétaro, Sanfandila, Pedro de Escobedo, CP 76703, Querétaro, Mexico

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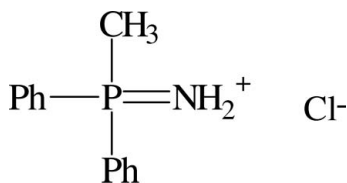
Received 28 May 2009; accepted 31 May 2009

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.089; data-to-parameter ratio = 14.6.

The title compound,  $\text{C}_{13}\text{H}_{15}\text{NP}^+\cdot\text{Cl}^-$ , was obtained by hydrolysis of the *N*-trimethylsilyl derivative of methyldiphenyl-iminophosphine. The dihedral angle between the phenyl rings in the cation is  $61.5(3)^\circ$ . In the crystal structure, intermolecular  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds links the two components, forming a centrosymmetric  $2 + 2$  aggregate.

**Related literature**

For iminophosphines, see: Appel & Hauss (1960); Hitchcock *et al.* (1999). For a related structure, see: Clegg & Bleasdale (1994).

**Experimental***Crystal data* $\text{C}_{13}\text{H}_{15}\text{NP}^+\cdot\text{Cl}^-$  $M_r = 251.68$ 

Monoclinic,  $P2_1/n$   
 $a = 9.4760(14)$  Å  
 $b = 11.8411(18)$  Å  
 $c = 11.8382(18)$  Å  
 $\beta = 107.773(2)^\circ$   
 $V = 1264.9(3)$  Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.4$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.54 \times 0.37 \times 0.28$  mm

*Data collection*

Brucker SMART 6000 CCD area-detector diffractometer  
 Absorption correction: none  
 7223 measured reflections

2226 independent reflections  
 2089 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.089$   
 $S = 1.14$   
 2226 reflections  
 152 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.48$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.25$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                                       | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{N1}-\text{H100}\cdots\text{Cl1}^{\text{i}}$  | 0.81 (3) | 2.37 (3)    | 3.181 (2)   | 176 (2)       |
| $\text{N1}-\text{H101}\cdots\text{Cl1}^{\text{ii}}$ | 0.84 (3) | 2.35 (3)    | 3.173 (2)   | 167 (2)       |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2426).

**References**

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**supplementary materials**

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## (Methyldiphenylphosphoranylidene)ammonium chloride

C. Valerio-Cárdenas, L. Ortiz-Frade and J.-M. Grévy M.

### Comment

The synthesis and coordination chemistry of iminophosphine ligands have attracted much interest during the past two decades owing to the potential applications of their complexes in catalysis (Hitchcock *et al.*, 1999). The procedures previously reported for the synthesis of  $[R_3PNH_2]^+$  cations involve the reaction of trialkylphosphines with hazardous chemicals such as chloramine (Appel & Hauss, 1960) or hydrogen azide (Clegg & Bleasdale, 1994). Here we report the structure of aminophosphonium salt, (I), obtained by reaction of the *N*-trimethylsilyl derivative of methyldiphenyliminophosphine with a mixture of  $MgCl_2$  and pyridine of technical grade.

The title compound,  $C_{13}H_{15}NPCl$ , is formed by cations  $[(C_6H_5)_2CH_3P=NH_2]^+$  and anions  $Cl^-$ . In this cation (Fig. 1) a pseudo-tetrahedral and a trigonal planar geometries are observed around the P atom and the N atom, respectively. In the crystal structure, intermolecular  $N-H\cdots Cl$  hydrogen bonds (Fig. 2) link two cations  $[(C_6H_5)_2CH_3P=NH_2]^+$  through two anions  $Cl^-$ , generating a distorted square arrangement along the *a* axis.

### Experimental

The title compound was isolated from the reaction mixture of  $CH_3(Ph)_2P=N(SiMe_3)$  and  $MgCl_2$  in a 1:1 molar ratio in pyridine, and was crystallized from pyridine.

### Refinement

H atoms bound to N1 were located in a difference Fourier map and refined freely. Other atoms were positioned geometrically and refined as riding model, with  $C-H = 0.93$  or  $0.96$  Å, and with  $U_{iso}(H) = 1.2U_{eq}(C, \text{phenyl})$  or  $1.5U_{eq}(C, \text{methyl})$ .

### Figures

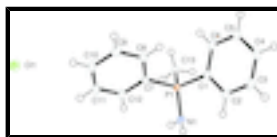


Fig. 1. The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

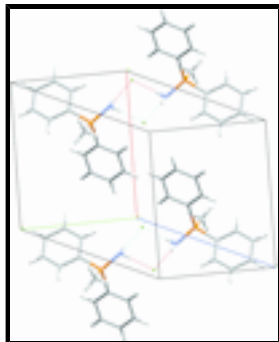


Fig. 2. A packing diagram of the title compound, showing molecules connected by N—H...Cl hydrogen bonds (dashed lines).

## (Methyldiphenylphosphoranylidene)ammonium chloride

### Crystal data

$C_{13}H_{15}NP^+ \cdot Cl^-$

$M_r = 251.68$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2yn$

$a = 9.4760$  (14) Å

$b = 11.8411$  (18) Å

$c = 11.8382$  (18) Å

$\beta = 107.773$  (2)°

$V = 1264.9$  (3) Å<sup>3</sup>

$Z = 4$

$F_{000} = 528$

$D_x = 1.322$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 7223 reflections

$\theta = 2.4$ – $25^\circ$

$\mu = 0.4$  mm<sup>-1</sup>

$T = 298$  K

Prism, colorless

$0.54 \times 0.37 \times 0.28$  mm

### Data collection

Brucker 6000 CCD area-detector diffractometer

Radiation source: sealed tube

Monochromator: graphite

$T = 298$  K

$\varphi$  and  $\omega$  scans

Absorption correction: none

7223 measured reflections

2226 independent reflections

2089 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 25^\circ$

$\theta_{min} = 2.4^\circ$

$h = -11 \rightarrow 7$

$k = -14 \rightarrow 14$

$l = -14 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.089$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.8702P]$

where  $P = (F_o^2 + 2F_c^2)/3$

|  |  |
|--|--|
| $S = 1.14$   | $(\Delta/\sigma)_{\max} < 0.001$                       |
| 2226 reflections   | $\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$  |
| 152 parameters   | $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$ |
| 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 ( $\text{\AA}^2$ )*

|      | $x$          | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| P1   | 0.20314 (5)  | 0.33420 (4)  | 0.71372 (4)  | 0.01414 (15)                     |
| N1   | 0.06353 (19) | 0.39343 (16) | 0.61815 (16) | 0.0187 (4)                       |
| Cl1  | 0.91197 (5)  | 0.62714 (4)  | 0.64308 (4)  | 0.02031 (15)                     |
| C1   | 0.1596 (2)   | 0.31208 (16) | 0.84887 (17) | 0.0162 (4)                       |
| C2   | 0.0407 (2)   | 0.36780 (17) | 0.86978 (19) | 0.0212 (5)                       |
| H2   | -0.0166      | 0.4178       | 0.8138       | 0.025*                           |
| C3   | 0.0086 (3)   | 0.34818 (18) | 0.97476 (19) | 0.0249 (5)                       |
| H3   | -0.0703      | 0.3858       | 0.9893       | 0.03*                            |
| C4   | 0.0922 (2)   | 0.27361 (18) | 1.05784 (18) | 0.0224 (5)                       |
| H4   | 0.0693       | 0.2606       | 1.1277       | 0.027*                           |
| C5   | 0.2106 (2)   | 0.21799 (18) | 1.03713 (18) | 0.0232 (5)                       |
| H5   | 0.2672       | 0.1678       | 1.0932       | 0.028*                           |
| C6   | 0.2447 (2)   | 0.23704 (17) | 0.93316 (18) | 0.0205 (4)                       |
| H6   | 0.3244       | 0.1998       | 0.9195       | 0.025*                           |
| C7   | 0.3717 (2)   | 0.41427 (15) | 0.74335 (17) | 0.0153 (4)                       |
| C8   | 0.4749 (2)   | 0.42223 (17) | 0.85534 (17) | 0.0184 (4)                       |
| H8   | 0.4571       | 0.387        | 0.9199       | 0.022*                           |
| C9   | 0.6046 (2)   | 0.48279 (17) | 0.87060 (18) | 0.0213 (5)                       |
| H9   | 0.6731       | 0.489        | 0.9457       | 0.026*                           |
| C10  | 0.6325 (2)   | 0.53406 (17) | 0.77462 (19) | 0.0219 (5)                       |
| H10  | 0.7204       | 0.5737       | 0.7851       | 0.026*                           |
| C11  | 0.5301 (2)   | 0.52647 (18) | 0.66312 (19) | 0.0243 (5)                       |
| H11  | 0.5491       | 0.5611       | 0.5988       | 0.029*                           |
| C12  | 0.3994 (2)   | 0.46749 (18) | 0.64691 (18) | 0.0214 (5)                       |
| H12  | 0.33         | 0.4633       | 0.572        | 0.026*                           |
| C13  | 0.2304 (2)   | 0.20247 (16) | 0.65085 (18) | 0.0190 (4)                       |
| H13A | 0.3207       | 0.1686       | 0.6992       | 0.029*                           |

## supplementary materials

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|      |           |           |           |        |
|------|-----------|-----------|-----------|--------|
| H13B | 0.2365    | 0.2146    | 0.5723    | 0.029* |
| H13C | 0.1487    | 0.1532    | 0.6472    | 0.029* |
| H100 | 0.068 (3) | 0.391 (2) | 0.550 (2) | 0.029* |
| H101 | 0.033 (3) | 0.456 (2) | 0.637 (2) | 0.029* |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$      | $U^{13}$    | $U^{23}$      |
|-----|-------------|-------------|-------------|---------------|-------------|---------------|
| P1  | 0.0128 (3)  | 0.0156 (3)  | 0.0142 (3)  | -0.00095 (19) | 0.0046 (2)  | -0.00070 (18) |
| N1  | 0.0175 (9)  | 0.0236 (9)  | 0.0157 (9)  | 0.0019 (7)    | 0.0059 (7)  | 0.0003 (7)    |
| C11 | 0.0202 (3)  | 0.0240 (3)  | 0.0178 (3)  | 0.0003 (2)    | 0.0075 (2)  | -0.00091 (19) |
| C1  | 0.0158 (10) | 0.0173 (10) | 0.0159 (10) | -0.0044 (8)   | 0.0053 (8)  | -0.0025 (8)   |
| C2  | 0.0194 (11) | 0.0199 (10) | 0.0253 (11) | 0.0020 (8)    | 0.0082 (9)  | 0.0014 (8)    |
| C3  | 0.0240 (12) | 0.0271 (11) | 0.0285 (12) | 0.0021 (9)    | 0.0154 (10) | -0.0013 (9)   |
| C4  | 0.0244 (12) | 0.0281 (11) | 0.0184 (10) | -0.0092 (9)   | 0.0123 (9)  | -0.0037 (8)   |
| C5  | 0.0217 (11) | 0.0292 (11) | 0.0174 (10) | -0.0005 (9)   | 0.0039 (8)  | 0.0047 (9)    |
| C6  | 0.0170 (11) | 0.0247 (11) | 0.0211 (10) | 0.0004 (9)    | 0.0075 (8)  | 0.0003 (8)    |
| C7  | 0.0141 (10) | 0.0135 (9)  | 0.0186 (10) | 0.0007 (8)    | 0.0056 (8)  | -0.0021 (7)   |
| C8  | 0.0176 (10) | 0.0206 (10) | 0.0177 (10) | -0.0002 (8)   | 0.0065 (8)  | 0.0012 (8)    |
| C9  | 0.0173 (11) | 0.0237 (11) | 0.0204 (10) | -0.0021 (8)   | 0.0024 (8)  | -0.0032 (8)   |
| C10 | 0.0178 (11) | 0.0211 (10) | 0.0289 (11) | -0.0060 (8)   | 0.0101 (9)  | -0.0050 (9)   |
| C11 | 0.0286 (12) | 0.0259 (11) | 0.0218 (11) | -0.0067 (9)   | 0.0127 (9)  | 0.0011 (9)    |
| C12 | 0.0212 (11) | 0.0249 (11) | 0.0171 (10) | -0.0045 (9)   | 0.0044 (8)  | -0.0011 (8)   |
| C13 | 0.0202 (11) | 0.0180 (10) | 0.0202 (10) | -0.0006 (8)   | 0.0083 (8)  | -0.0034 (8)   |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|           |             |           |             |
|-----------|-------------|-----------|-------------|
| P1—N1     | 1.6150 (18) | C6—H6     | 0.93        |
| P1—C13    | 1.781 (2)   | C7—C8     | 1.390 (3)   |
| P1—C1     | 1.789 (2)   | C7—C12    | 1.397 (3)   |
| P1—C7     | 1.798 (2)   | C8—C9     | 1.386 (3)   |
| N1—H100   | 0.81 (3)    | C8—H8     | 0.93        |
| N1—H101   | 0.84 (3)    | C9—C10    | 1.383 (3)   |
| C1—C2     | 1.391 (3)   | C9—H9     | 0.93        |
| C1—C6     | 1.395 (3)   | C10—C11   | 1.382 (3)   |
| C2—C3     | 1.387 (3)   | C10—H10   | 0.93        |
| C2—H2     | 0.93        | C11—C12   | 1.384 (3)   |
| C3—C4     | 1.378 (3)   | C11—H11   | 0.93        |
| C3—H3     | 0.93        | C12—H12   | 0.93        |
| C4—C5     | 1.386 (3)   | C13—H13A  | 0.96        |
| C4—H4     | 0.93        | C13—H13B  | 0.96        |
| C5—C6     | 1.383 (3)   | C13—H13C  | 0.96        |
| C5—H5     | 0.93        |           |             |
| N1—P1—C13 | 106.26 (10) | C1—C6—H6  | 120         |
| N1—P1—C1  | 109.06 (10) | C8—C7—C12 | 119.72 (18) |
| C13—P1—C1 | 110.36 (9)  | C8—C7—P1  | 123.15 (15) |
| N1—P1—C7  | 113.38 (9)  | C12—C7—P1 | 117.10 (14) |
| C13—P1—C7 | 108.05 (9)  | C9—C8—C7  | 119.82 (19) |

|              |              |                |              |
|--------------|--------------|----------------|--------------|
| C1—P1—C7     | 109.67 (9)   | C9—C8—H8       | 120.1        |
| P1—N1—H100   | 113.4 (18)   | C7—C8—H8       | 120.1        |
| P1—N1—H101   | 117.9 (17)   | C10—C9—C8      | 120.29 (19)  |
| H100—N1—H101 | 114 (2)      | C10—C9—H9      | 119.9        |
| C2—C1—C6     | 119.87 (18)  | C8—C9—H9       | 119.9        |
| C2—C1—P1     | 120.66 (15)  | C11—C10—C9     | 120.08 (19)  |
| C6—C1—P1     | 119.46 (15)  | C11—C10—H10    | 120          |
| C3—C2—C1     | 119.44 (19)  | C9—C10—H10     | 120          |
| C3—C2—H2     | 120.3        | C10—C11—C12    | 120.23 (19)  |
| C1—C2—H2     | 120.3        | C10—C11—H11    | 119.9        |
| C4—C3—C2     | 120.7 (2)    | C12—C11—H11    | 119.9        |
| C4—C3—H3     | 119.6        | C11—C12—C7     | 119.85 (18)  |
| C2—C3—H3     | 119.6        | C11—C12—H12    | 120.1        |
| C3—C4—C5     | 119.91 (19)  | C7—C12—H12     | 120.1        |
| C3—C4—H4     | 120          | P1—C13—H13A    | 109.5        |
| C5—C4—H4     | 120          | P1—C13—H13B    | 109.5        |
| C6—C5—C4     | 120.11 (19)  | H13A—C13—H13B  | 109.5        |
| C6—C5—H5     | 119.9        | P1—C13—H13C    | 109.5        |
| C4—C5—H5     | 119.9        | H13A—C13—H13C  | 109.5        |
| C5—C6—C1     | 119.94 (19)  | H13B—C13—H13C  | 109.5        |
| C5—C6—H6     | 120          |                |              |
| N1—P1—C1—C2  | -15.77 (19)  | N1—P1—C7—C8    | 142.46 (17)  |
| C13—P1—C1—C2 | -132.14 (17) | C13—P1—C7—C8   | -100.05 (18) |
| C7—P1—C1—C2  | 108.93 (17)  | C1—P1—C7—C8    | 20.29 (19)   |
| N1—P1—C1—C6  | 163.41 (16)  | N1—P1—C7—C12   | -39.42 (19)  |
| C13—P1—C1—C6 | 47.04 (19)   | C13—P1—C7—C12  | 78.07 (17)   |
| C7—P1—C1—C6  | -71.89 (18)  | C1—P1—C7—C12   | -161.59 (15) |
| C6—C1—C2—C3  | 0.2 (3)      | C12—C7—C8—C9   | 0.0 (3)      |
| P1—C1—C2—C3  | 179.35 (16)  | P1—C7—C8—C9    | 178.04 (15)  |
| C1—C2—C3—C4  | -0.5 (3)     | C7—C8—C9—C10   | -0.9 (3)     |
| C2—C3—C4—C5  | 0.5 (3)      | C8—C9—C10—C11  | 0.9 (3)      |
| C3—C4—C5—C6  | -0.1 (3)     | C9—C10—C11—C12 | -0.1 (3)     |
| C4—C5—C6—C1  | -0.2 (3)     | C10—C11—C12—C7 | -0.8 (3)     |
| C2—C1—C6—C5  | 0.2 (3)      | C8—C7—C12—C11  | 0.9 (3)      |
| P1—C1—C6—C5  | -179.01 (16) | P1—C7—C12—C11  | -177.32 (16) |

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D-H\cdots A$                      | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| N1—H100 $\cdots$ C11 <sup>i</sup>  | 0.81 (3) | 2.37 (3)    | 3.181 (2)   | 176 (2)       |
| N1—H101 $\cdots$ C11 <sup>ii</sup> | 0.84 (3) | 2.35 (3)    | 3.173 (2)   | 167 (2)       |

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

Fig. 1

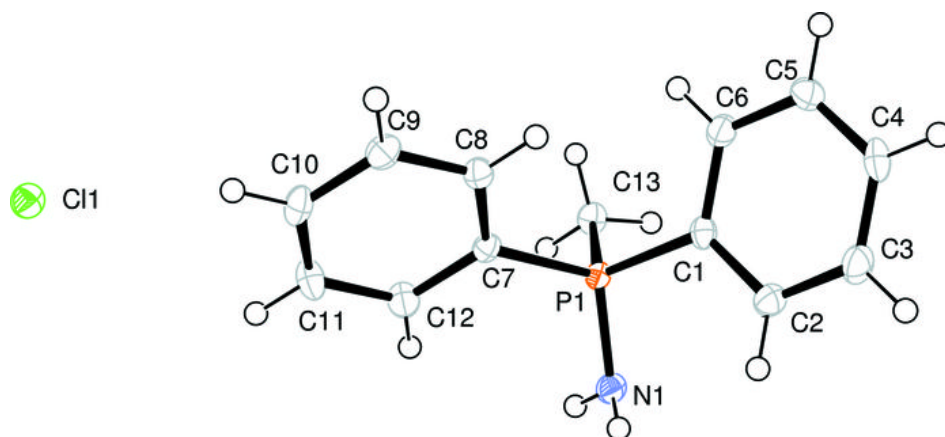


Fig. 2

