

# [[*(N*-Methyl-*p*-toluidino)diphenylphosphoranylidene]methyl]*(N*-methyl-*p*-toluidino)diphenylphosphonium iodide

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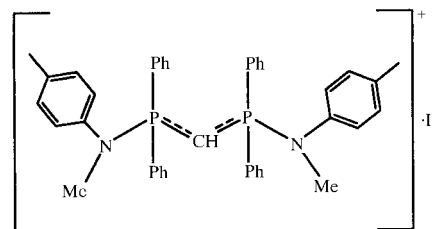
The cationic part of the homodifunctional aminophosphoranyl ligand,  $C_{41}H_{41}N_2P_2^+I^-$ , shows interesting features associated with the N–P–C–P–N skeleton. The P–C(H) bond distances [1.696 (3) and 1.697 (3) Å] possess partial double-bond characteristics. The nature of the P–C(H) and P–N bonds suggests that the positive charge is only distributed around the P–C–P atoms. The structure has near twofold symmetry through the central methylide-C atom.

## Comment

The amino [ $(R_2P-NXR')CR''$ ] and iminophosphoranyl ligands [ $(R_2P=NR')CXR''$ ] are essentially tautomeric forms, their basicity and reactivity altered by changing the groups at either phosphorus ( $R = Me, Ph$ ), nitrogen ( $X = H, Me$ ;  $R' = H, Me, Ph, C_6H_4Y-4$  where  $Y = Me, NO_2$ ) or methylide carbon ( $R'' = H, Me, SiMe_3$ ). The iminophosphoranyl ligands and their mono-anions are known to coordinate in various forms to electron-rich metals such as  $Rh^I$ ,  $Ir^I$ ,  $Pd^{II}$  and  $Pt^{II}$ . They donate one, two or four electrons to the metal centre, ligating *via* N and methylide-C atoms, producing chelating, ylid and terdentate species (Avis *et al.*, 1995; Imhoff *et al.*, 1991, 1995).

The title compound, (I), was unexpectedly synthesized in the reaction of  $[Rh\{CH(PPh_2=N-p\text{-tolyl})_2\}(COD)]$  with MeI, involving formation of  $[Rh(COD)I]_2$  and the transfer of Me groups to nitrogen. The formation of the discrete cation–anion pair, shown in Fig. 1, is distinct from a similar reaction of  $[Rh\{CH(PPh_2=N-p\text{-tolyl})_2\}(COD)]$  with HCl (Imhoff *et al.*, 1995) which resulted in protonation at one N and the methanide C atom. The cationic ligand (I) consists of two (*N*-methyl-*N*-*p*-tolylamino)diphenylphosphoranyl units attached *via* the phosphorus to a common methylide moiety. The P–N bond distances [1.656 (3) and 1.657 (3) Å] are typical of those found in aminophosphonium groups of metal complexes (Avis

*et al.*, 1995, 1997; Imhoff *et al.*, 1989, 1993), but are significantly longer than those found in iminophosphoranyl ligands such as  $(Ph_2P=NC_6H_4Me-4)_2CH_2$  (Imhoff *et al.*, 1990) and  $(Ph_2P=NC_6H_4Me-4)_2CHMe$  (Avis *et al.*, 1996). The P–N bond characteristics in these imino species were attributed to a  $p\pi(N)-d\pi(P)$  interaction. The N atoms in (I) are also  $sp^2$  hybridized but planar (nitrogen bond angles given in Table 1), producing little or no overlap between the nitrogen lone pair and the phosphorus *d* orbital. Both P atoms exhibit distorted tetrahedral geometries, with angles ranging from 103.96 (14)–114.01 (14)° around P1, and 103.84 (14)–114.40 (15)° for P2.



(I)

The N–C and P–C(Ph) bond distances are in good agreement with values observed in related systems. The P–C(H) distances of 1.696 (3) and 1.697 (3) Å are comparable to those found in the  $(Ph_3P=CH-PPh_3)^+$  cation (Carroll & Titus, 1977),  $Na(PhCHPPh_2CHPPh_2)$  (Schmidbauer *et al.*, 1980) and  $(MeSi)_2CPh_2-CHPPh_2CH(MeSi)_2$  (Appel *et al.*, 1984). These values lie between those expected for single and double P–C bonds, resulting in partial double-bond characteristics. The molecule possesses non-crystallographic  $C_2$  symmetry, considering the equivalence of bond lengths and bond angles around the N–P–C–P–N core. The puckering of the P–C–P component leads to a distorted trigonal geometry at C1,  $P1-C1-P2 = 133.6 (2)^\circ$ , and reduces the overall symmetry to  $C_1$ . The widening of this angle from the ideal  $120^\circ$  is possibly caused by steric repulsions between adjacent phenyl groups on the P atoms.

Only the P–C(H)–P distances have non-integral bond orders so presumably the charge is localized within the P–

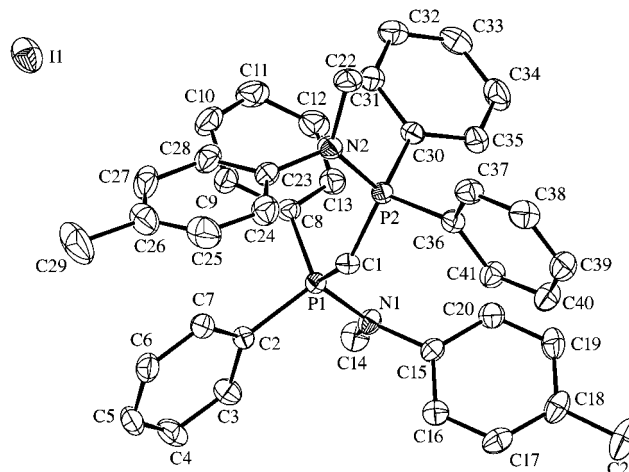


Figure 1

Plot of (I) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

C—P component, as depicted by the mesomeric structure in the chemical scheme. Further delocalization over the whole N—P—C—P—N skeleton is precluded because of the non-planar arrangement of the atoms. The diffuse nature of the positive charge, and possibly steric hindrance, isolates the iodide anion from the cation. The shortest contacts between the iodide and adjacent aminophosphoranyl molecules involve interactions with methyl- or phenyl-H atoms:  $I1 \cdots H14C^i$  (3.15 Å),  $I1 \cdots H37^{ii}$  (3.20 Å) and  $I1 \cdots H10$  of 3.22 Å [symmetry codes: (i)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ].

## Experimental

Compound (I) was obtained from the reaction of  $[Rh\{CH(PPh_2)=N-p\text{-tolyl}\}_2](COD)$  with about 10 equivalents of MeI in benzene (Imhoff *et al.*, 1995). Brown crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a room-temperature solution of the compound in benzene–dichloromethane (1:1).

### Crystal data

$C_{41}H_{41}N_2P_2^+I^-$	$D_x = 1.385 \text{ Mg m}^{-3}$
$M_r = 750.60$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 13.3126$ (5) Å	$\theta = 14.0\text{--}18.0^\circ$
$b = 14.3251$ (5) Å	$\mu = 1.010 \text{ mm}^{-1}$
$c = 18.9767$ (7) Å	$T = 295$ (2) K
$\beta = 95.819$ (3) $^\circ$	Block, brown
$V = 3600.3$ (2) Å <sup>3</sup>	$0.40 \times 0.30 \times 0.13 \text{ mm}$
$Z = 4$	

### Data collection

Enraf–Nonius CAD-4F diffractometer	5992 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$\theta_{\max} = 28^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -17 \rightarrow 17$
$T_{\min} = 0.788, T_{\max} = 0.877$	$k = -18 \rightarrow 0$
8582 measured reflections	$l = 0 \rightarrow 24$
8582 independent reflections	3 standard reflections
	frequency: 60 min
	intensity decay: 1%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 3.4354P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.121$	$(\Delta/\sigma)_{\max} = 0.003$
$S = 1.031$	$\Delta\rho_{\max} = 1.35 \text{ e } \text{Å}^{-3}$
8582 reflections	$\Delta\rho_{\min} = -0.97 \text{ e } \text{Å}^{-3}$
423 parameters	
H atoms treated by a mixture of independent and constrained refinement	

X-ray data were collected with a sufficiently large collimator tube to ensure a homogeneous X-ray beam at the crystal by use of a Zr  $\beta$ -filter rather than a graphite monochromator (Alexander & Smith, 1962).

All H atoms, with the exception of H1 on C1, were constrained and allowed to ride on their C atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl})$ . Methyl-H atoms were refined as rigid groups which allow for rotation around the C—C bonds, whilst maintaining a tetrahedral geometry at the C atom. H1 was located from a difference Fourier map and its coordinates allowed to refine with the isotropic displacement parameter constrained to  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C1})$ ; the C1—H1 bond length refined to 0.98 (3) Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction:

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

P1—N1	1.656 (3)	P2—C30	1.801 (3)
P1—C1	1.696 (3)	P2—C36	1.816 (3)
P1—C8	1.806 (3)	N1—C15	1.441 (4)
P1—C2	1.820 (3)	N1—C14	1.477 (4)
P2—N2	1.658 (3)	N2—C23	1.440 (4)
P2—C1	1.697 (3)	N2—C22	1.477 (4)
N1—P1—C1	113.99 (14)	C1—P2—C36	106.21 (15)
N1—P1—C8	103.94 (14)	C30—P2—C36	108.60 (14)
C1—P1—C8	113.95 (14)	C15—N1—C14	113.7 (2)
N1—P1—C2	109.26 (14)	C15—N1—P1	123.1 (2)
C1—P1—C2	106.43 (14)	C14—N1—P1	123.0 (2)
C8—P1—C2	109.20 (14)	C23—N2—C22	113.7 (2)
N2—P2—C1	113.96 (14)	C23—N2—P2	122.8 (2)
N2—P2—C30	103.81 (14)	C22—N2—P2	122.9 (2)
C1—P2—C30	114.43 (14)	P1—C1—P2	133.64 (19)
N2—P2—C36	109.75 (14)		

*HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF* (Beurskens, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1596). Services for accessing these data are described at the back of the journal.

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