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[(2*E*)-2-Benzylidenehydrazino]tricyclohexylphosphonium chloride

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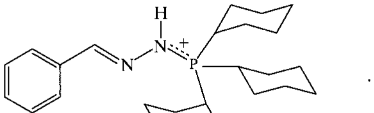
In the title compound, $C_{25}H_{40}N_2P^+\cdot Cl^-$, the cation structure (at 150 K) is intermediate between those of the iminophosphorane and the ylide, consistent with delocalization of the positive charge between the P and the adjacent N atoms. The cation and anion are linked by a strong N—H⋯Cl hydrogen bond.

Comment

The character of the P═N bond in iminophosphoranes is usually described by the resonance of two canonical forms, the ylide $R_3P^+—N^-X$ and the iminophosphorane proper $R_3P═NX$. The relative contributions of the two, *i.e.* the multiplicity of the bond, are easily affected by the nature of the substituents, the overall molecular charge, hydrogen bonds and weak intermolecular interactions. Thus, diffraction studies of iminotriphenylphosphorane, (I), revealed two different, but similar, polymorphs with significantly different P═N bond lengths of 1.524 (3) (Grün *et al.*, 1996) and 1.582 (2) Å (Davidson *et al.*, 1998). The exact nature of the π component of the bond and the role in it of the *d* orbitals of the P atom remain a subject of controversy (Johnson, 1993). We report herein the structure of the title salt, (II), obtained as an incidental by-product in the synthesis of a ruthenium carbene complex, which can add useful data to the discussion.



(II)

The asymmetric unit of (II) comprises one cation and one chloride anion (Fig. 1), linked by a strong hydrogen bond (Table 2). It is noteworthy that there are no hydrogen bonds involving the NH group in the crystal structure of either polymorph of (I).

The P—N1—N2—C7—C1 moiety is approximately planar, and the displacements of these atoms from their mean plane do not exceed 0.1 Å. The non-weighted mean plane makes a dihedral angle of 25.1 (1)° with the plane of the adjacent phenyl ring. The N2═C7 bond distance [1.285 (2) Å] is close to the standard double-bond value, 1.279 (8) Å (Allen *et al.*, 1987). The N1—N2 distance [1.399 (1) Å] is similar to that of the single bond in N-protonated benzalazine (Noltemeyer *et al.*, 1983), 1.402 (8) Å, which also has a *transoid* conformation. Thus, the resonance is restricted mainly to the two canonical forms with the positive charge localized on either the P or the N1 atoms, *viz.* $Cy_3P^+—NH—N═CHPh$ or $Cy_3P═NH^+—N═CHPh$ (where Cy is cyclohexyl). The P═N distance of 1.651 (1) Å in (II) indicates a considerable shift towards the ylide structure compared to (I), although it is still a long way shorter than the purely single P—N bond of 1.769 Å (Bart *et al.*, 1982). Protonation of an iminophosphorane molecule is known to produce such a shift: compare P═N of 1.603 Å in Ph_3PNPh (Böhm *et al.*, 1988) to 1.624–1.628 Å in Ph_3PN^+HPh (Böhm *et al.*, 1988; Llamas-Saiz *et al.*, 1992). The only previously studied cation with a PN(H)N chain, $Ph_3P^+—NH—NMe_2$ (Stoldt & Kreher, 1978), displays the bond distances P—N = 1.640 (3) Å and N—N = 1.425 (4) Å.

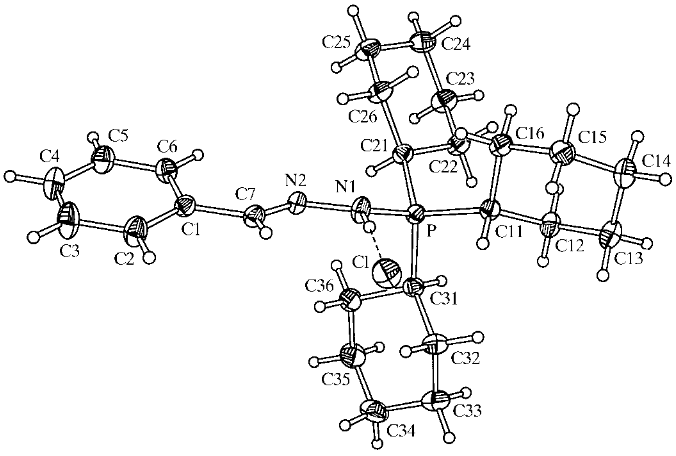


Figure 1
The molecular structure of (II) showing 50% probability displacement ellipsoids.

Experimental

A solution of phenyldiazomethane (2 equivalents) in dichloromethane was added to a mixture of $[\eta^6\text{-}(p\text{-cymene})RuCl]_2$ (1 equivalent) and tricyclohexyl phosphine (2 equivalents), also in dichloromethane, at 195 K under nitrogen. The mixture was then allowed to warm slowly to room temperature, the solvent was removed under vacuum and the remaining solid (the target ruthenium complex) was washed with ether. The ether wash, kept at *ca* 248 K (in a freezer) for several weeks, yielded crystals of (II).

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Crystal data

$C_{25}H_{40}N_2P^+\cdot Cl^-$
$M_r = 435.01$
Monoclinic, $P2_1/n$
$a = 12.106$ (3) Å
$b = 13.187$ (3) Å
$c = 15.819$ (4) Å
$\beta = 99.62$ (2)°
$V = 2490$ (1) Å^3
$Z = 4$

$D_x = 1.160$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 512 reflections
$\theta = 12.0$–27.5°
$\mu = 0.231$ mm^{-1}
$T = 150$ (2) K
Ellipsoid, yellow
0.40 × 0.30 × 0.30 mm

Data collection

SMART 1 K CCD area-detector diffractometer
ω scans
18481 measured reflections
6546 independent reflections
5420 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.03$
$\theta_{\rm max} = 29°$
$h = -16 \rightarrow 15$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 1.078$
6546 reflections
422 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 1.0707P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—N1	1.6506 (11)	N1—N2	1.3992 (14)
P—C31	1.8207 (13)	N2—C7	1.2845 (16)
P—C11	1.8225 (13)	C1—C7	1.4689 (17)
P—C21	1.8235 (13)		
N1—P—C31	112.33 (6)	C11—P—C21	116.77 (6)
N1—P—C11	101.20 (6)	N2—N1—P	120.13 (8)
C31—P—C11	108.56 (6)	P—N1—H1	117.5 (12)
N1—P—C21	109.58 (6)	C7—N2—N1	114.14 (10)
C31—P—C21	108.36 (6)		

All H atoms were refined in an isotropic approximation; Csp^2—H bond distances ranged from 0.91 (2) to 0.99 (2) Å and Csp^3—H distances ranged from 0.96 (2) to 1.01 (2) Å.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl	0.876 (18)	2.165 (18)	3.0406 (12)	177.0 (16)

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1122). Services for accessing these data are described at the back of the journal.

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