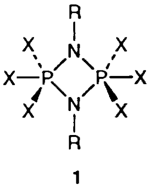
Simple Preparations of New Monomeric Trihalogenophosphine Imides†

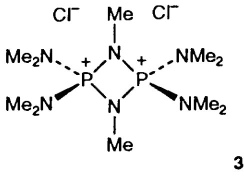
Neil Burford,*[a] Jason A. C. Clyburne,[a] Derek P. Gates,[a] Melbourne J. Schriver[a] and John F. Richardson*[b]

[a] *Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada*
[b] *Department of Chemistry, University of Louisville, Louisville, KY 40292, USA*

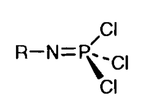
The oxidation of halogeno(2,4,6-tri-*tert*-butylphenylimino)phosphines [(2,4,6-$Bu^t_3C_6H_2$)NPX, X = Cl, Br or I] with dihalogens (Cl_2, Br_2 or I_2) resulted in the formation of trihalogeno(*N*-2,4,6-tri-*tert*-butylphenyl)phosphine imides. The imides (2,4,6-$Bu^t_3C_6H_2$)$NPCl_3$ and (2,4,6-$Bu^t_3C_6H_2$)$NPBr_3$ were obtained quantitatively from the corresponding halogenoiminophosphine with $PhICl_2$ and Br_2, respectively, and were crystallographically characterized [(2,4,6-$Bu^t_3C_6H_2$)$NPCl_3$: *Cm*, a = 11.960(3), b = 14.696(2), c = 5.954(2) Å, β = 97.71(2)°, Z = 2, R = 0.036, R' = 0.047; (2,4,6-$Bu^t_3C_6H_2$)$NPBr_3$: $P2_1/c$, a = 18.841(8), b = 9.480(4), c = 12.186(5) Å, β = 98.00(3)°, Z = 4, R = 0.068, R' = 0.074]. Reactions involving a halogenoiminophosphine and a different halogen are accompanied by halide exchange and give mixtures of products, most of which can be assigned and include the mixed trihalides, (2,4,6-$Bu^t_3C_6H_2$)NPX_2X'. No reaction is observed between (2,4,6-$Bu^t_3C_6H_2$)NPI and I_2, but one iodo derivative has been isolated and characterized spectroscopically and by X-ray crystallography as (2,4,6-$Bu^t_3C_6H_2$)$NPCl_2I$, which is formed in the disproportionation reaction of (2,4,6-$Bu^t_3C_6H_2$)NPCl and I_2. The trihalides are monomeric in the solid state and exhibit extremely short N–P bonds with large angles at the nitrogen centres.



1



2



3a R = C(Cl)(CCl_3)$_2$
3b R = C(CF_3)$_3$
3c R = 2, 4, 6-$Bu^t_3C_6H_2$

Chloro(organo)phosphine imide (chlorophosphazene) compounds typically adopt four-membered cyclic dimeric structures in the solid state. As such they are categorized as cyclodiphosphazanes, and may be covalent **1**[1,2] or ionic **2**.[3] Hundreds of derivatives have been reported,[4] however, only two examples of monomeric trichlorophosphine imides, **3a** and **3b**, have been confirmed.[5] The $[C(NPCl_3)_3]^+$ cation formally contains three monomeric phosphine imide units, however, we view it as a novelty and discount it from further discussion of the phosphine imide bond.[6] Recognizing compounds of this type as useful synthetic precursors by virtue of their potential for substitution, elimination or reduction, we have developed a simple procedure for the preparation of a series of monomeric trihalogenophosphine imides. Here we report the oxidative addition reactions of dihalogens to halogeno(2,4,6-tri-*tert*-butylphenylimino)phosphines [(2,4,6-$Bu^t_3C_6H_2$)NPX, X = Cl, Br or I].[7] Most of the new trihalides have been identified in solution by ^{31}P NMR spectroscopy, and the structures of three derivatives have been confirmed by X-ray crystallography.

Experimental

Chlorine (Matheson) was obtained commercially and used without purification. Trimethylsilyl bromide (Aldrich) and trimethylsilyl iodide (Aldrich) were vacuum distilled, iodine (BDH) was sublimed and bromine (Fisher) and iodobenzene (Aldrich) were vacuum distilled from phosphorus(v) oxide. Methylene chloride, hexane, pentane and deuteriated solvents were dried over phosphorus(v) oxide and calcium hydride and stored in evacuated bulbs. Chloro-, bromo- and iodo-(2,4,6-tri-*tert*-butylphenylimino)phosphine[7] and (dichloroiodo)-benzene[8] were prepared according to the literature methods and were characterized by NMR spectroscopy. Solids were manipulated in a Vacuum/Atmospheres nitrogen-filled glovebox. Glass equipment was flame dried under vacuum before use. Reactions were performed in an evacuated (10^{-3} Torr ≈ 0.133 Pa) dual-compartment vessel.[9] Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. Infrared spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P spectrophotometer. NMR spectra were recorded on a Bruker AC250 spectrometer in 5 mm flame-sealed Pyrex tubes. Chemical shifts are reported in ppm relative to external standards (85% H_3PO_4 for ^{31}P, $SiMe_4$ for ^1H and ^{13}C), the multiplicity of each signal is presented after the chemical shift and relative signal integrations are given in parentheses.

Reactions of (2,4,6-$Bu^t_3C_6H_2$)NPCl.—(*a*) *With* Cl_2. Chlorine (1.00 mmol) was condensed onto a solution of (2,4,6-$Bu^t_3C_6H_2$)NPCl (0.33 g, 1.0 mmol) in CH_2Cl_2 (*ca.* 20 cm^3) and the mixture was stirred while warming to room temperature giving a clear yellow solution. Solvent was removed *in vacuo* and a small quantity (< 20 mg) of yellow crystalline solid was sublimed from the residue, and characterized (NMR see below) as (2,4,6-$Bu^t_3C_6H_2$)$NPCl_3$ (Found: C, 54.4; H, 7.3; N, 3.6; P, 7.8. Calc. for $C_{18}H_{29}Cl_3NP$: C, 54.5; H, 7.4; N, 3.5; P, 7.8%). ^{31}P NMR spectra of the reaction mixtures showed (2,4,6-$Bu^t_3C_6H_2$)$NPCl_3$ as a 35% component (by ^{31}P NMR signal integration) with more than five other unidentified phosphorus-containing compounds.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

(*b*) *With* PhICl$_2$. A solution of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl (0.33 g, 1.0 mmol) in CH$_2$Cl$_2$ (*ca.* 10 cm^3) was added to a slurry of PhICl$_2$ (0.32 g, 1.2 mmol) in CH$_2$Cl$_2$ (*ca.* 10 cm^3) over a period of 30 min. The solvent was removed *in vacuo* and the residue was recrystallized twice from hexane to give yellow crystals that were characterized as (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ (0.20 g, 50%) (Found: C, 54.4; H, 7.2; N, 3.5; Cl, 26.7. Calc. for C$_{18}$H$_{29}$Cl$_3$NP: C, 54.5; H, 7.4; N, 3.5; Cl, 26.8%). M.p. 148–149 °C. NMR: ^{31}P, δ −96; ^{1}H, δ 1.3 (s, 9 H), 1.46 (s, 18 H) and 7.3 (d, ^3J 3.0 Hz, 2 H); ^{13}C, δ 31.8 (s), 32.4 (s), 32.9 (s), 35.7 (s), 122.3 (s), 124.1 (s), 142.4 (d, ^1J 7.6) and 145 (d, ^1J 3.8 Hz). IR: 1605m, 1530s, 971w, 922w, 888w, 879m, 768m, 658m, 648m, 530s and 448m cm^{-1}. ^{31}P NMR spectra of the reaction mixtures contained a single signal at δ −96.

(*c*) *With* Br$_2$. Bromine (0.32 g, 2.0 mmol) in pentane (15 cm^3) was added to a solution of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl (0.52 g, 1.6 mmol) in pentane (*ca.* 15 cm^3). After stirring at room temperature for 12 h 50% of the solvent was removed *in vacuo* and the solid that formed was warmed back into solution. Slow cooling to room temperature resulted in the formation of orange-red crystals which were characterized as a mixture of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$, (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_2$Cl and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBrCl$_2$. Total recovered mass 0.62 g [Found: C, 43.2; H, 5.7. Calc. based on the integrated ratios observed in the ^{31}P NMR spectrum, δ −236 (40), −183 (50) and −136 (10): C, 43.3; H, 5.9%]. M.p. 172–184 °C.

(*d*) *With* I$_2$. A slurry of I$_2$ (0.28 g, 1.1 mmol) in pentane (30 cm^3) was added to a solution of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl (0.70 g, 2.2 mmol) in pentane (*ca.* 20 cm^3). After stirring overnight at room temperature slow removal of the solvent *in vacuo* resulted in the precipitation of orange-red needle-like crystals which were isolated in very low yield and characterized as (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_2$I (Found: C, 44.6; H, 5.9; N, 2.7. Calc. for C$_{18}$H$_{29}$Cl$_2$INP: C, 44.3; H, 6.0; N, 2.9%). M.p. 124–130 °C (sublimes). NMR: ^{31}P (pentane), δ −211; ^{1}H and ^{13}C, identical spectra to those of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$. IR: 1598s, 1476s, 924w, 880m, 527s, 507m, 480s and 431m cm^{-1}.

Reaction of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr *with* Br$_2$.—Bromine (0.15 g, 0.93 mmol) in hexane (*ca.* 5 cm^3) was added to a solution of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr (0.33 g, 0.91 mmol) in hexane (*ca.* 5 cm^3). After stirring at room temperature for 5 min the solvent was removed *in vacuo* and the solid was recrystallized from a minimum of warm hexane giving orange-red crystals which were characterized as (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$ (0.34 g, 71%) (Found: C, 41.1; H, 5.7; N, 2.6. Calc. for C$_{18}$H$_{29}$Br$_3$NP: C, 40.8; H, 5.5; N, 2.6%). M.p. 161.5–163 °C. NMR: ^{31}P, δ −236; ^{1}H and ^{13}C, identical spectra to those of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$. IR: 1601m, 1504s, 923w, 881w, 513s, 487m, 446s and 425m cm^{-1}. ^{31}P NMR spectra of the reaction mixture showed a single signal at δ −236.

NMR Studies.—The reactions listed below were examined by combining the reactants in equimolar amounts in pentane and obtaining a ^{31}P NMR spectrum of the reaction mixture. The results are presented as the chemical shifts of the observed signals with their relative integration given as percentages in parentheses followed by our assignment for each signal.

(2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl. With Br$_2$, δ −236 (40), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$; −213 (minor), PCl$_x$Br$_{3-x}$; −183 (40), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_2$Cl; −162 (minor); −136 (10), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBrCl$_2$; and −96 (1), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$; with I$_2$, δ −211, (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_2$I and 200–160 (dependent upon the stoichiometry, δ 200 with an excess of I$_2$), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPI, average signal due to exchange.

(2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr. With PhICl$_2$, δ −96 (10), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$; −135 (70), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBrCl$_2$; and −183 (20), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_2$Cl; with I$_2$, δ 177 (>90), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPI, average signal due to exchange; with (2,4,6-Bu$^t_3$C$_6$H$_2$)NPI, δ 159 (100), average signal due to exchange.

Table 1 Crystal data for (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$

	(2,4,6-Bu$^t_3$C$_6$H$_2$)-NPCl$_3$	(2,4,6-Bu$^t_3$C$_6$H$_2$)-NPBr$_3$
Formula	C$_{18}$H$_{29}$Cl$_3$NP	C$_{18}$H$_{29}$Br$_3$NP
M	396.77	530.14
Crystal system	Monoclinic	Monoclinic
Space group	*Cm*	*P*2$_1$/*c*
a/Å	11.960(3)	18.841(8)
b/Å	14.696(2)	9.480(4)
c/Å	5.954(2)	12.186(5)
β/°	97.71(2)	98.00(3)
U/Å^3	1037.1	2155.3
Z	2	4
D$_c$/Mg m^{-3}	1.27	1.63
F(000)	420	1056
Crystal size/mm	0.20 × 0.36 × 0.45	0.20 × 0.20 × 0.20
μ/cm^{-1}	5.2	56.4
Absorption correction, maximum, minimum	1.00, 0.95	1.328, 0.751
Range of *h,k,l*	±15, +19, +7	±20, −10, +13
2θ$_{max}$/°	60	46
Reflections measured	1837	2639
Unique observed reflections [$I > 3\sigma(I)$]	1511	1639
Parameters refined	130	195
p, *q*, where $w = [\sigma(F_o)^2 + (pF_o)^2 + q]^{-1}$	0.030, 0.4	0.005, 0.8
R	0.036	0.068
R'	0.047	0.074
Goodness of fit	1.03	1.101
Largest feature in final difference map/e Å^{-3}	0.33	0.79

(2,4,6-Bu$^t_3$C$_6$H$_2$)NPI. With PhICl$_2$, δ 220 (1), PCl$_3$; 158 (40), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPI, average signal due to exchange; −96 (10), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$; and −211 (40), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_2$I; with Br$_2$, δ 227 (100) PBr$_3$; with I$_2$, no reaction.

(2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$. With (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$, no reaction.

X-Ray Data Collection, Solution and Refinement.—Crystals of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ were obtained by vacuum sublimation at 50 °C onto a water-cooled finger. Crystals of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$ and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_2$I* were obtained from CH$_2$Cl$_2$ solution. Crystals were mounted in thin-walled Pyrex capillaries under an atmosphere of N$_2$ in the dry-box. Unit-cell parameters were obtained from the setting angles of 25 accurately centred reflections. The choice of space groups was based on systematically absent reflections and confirmed by the program TRACER[10] and the successful solution and refinement of the structures. All pertinent crystallographic data are summarized in Table 1. Data were collected at room temperature (23 °C) on an Enraf-Nonius CAD-4 diffractometer (Mo-Kα, λ = 0.710 73 Å, graphite monochromator) using the ω–2θ scan technique. The stability of the crystals was monitored every 60 min using three standard reflections and no significant decay was observed. Data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied based on a series of psi scans [(2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$] or DIFABS[11] [(2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$]. Scattering factors

---

* The data set was collected on a poor quality crystal [*P*2$_1$/*n*, *a* = 9.903(3), *b* = 11.638(3), *c* = 19.734(5) Å, β = 103.34(2)°, *U* = 2213.0 Å^3, *Z* = 4, *D*$_c$ = 1.47 Mg m^{-3}]. The structure was solved and confirmed to be (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_2$I, but severe rotational disorder of the PCl$_2$I group prevented a satisfactory refinement of the model (*R* = 0.084, *R'* = 0.102, goodness of fit = 4.86).

were taken from Cromer and Waber[12a] and anomalous dispersion effects[12b] were included in F_c.

The structures were solved using direct methods to find the heavier elements and the remaining non-hydrogen atoms were located from a series of Fourier-difference maps. All crystallographic programs used were part of the MOLEN package.[13] Hydrogen atoms were included in ideal positions as fixed contributions ($B_{iso} = 1.3B$ of the bonded atom) to the structure factors. The unique butyl group in (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ had rotational as well as positional disorder in the mirror plane. The model consisted of two tertiary carbon atoms in the plane of the mirror [C(9a) and C(9b)] and four carbon atoms representing the methyl groups. In projection the model presents a ring of methyl groups perpendicular to the C(4)–C(9) bond. The butyl group at C(4) was found to be disordered in the structure of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$. The model consisted of two sets of three methyl groups rotated with respect to each other, with occupancies of 70:30.

The models were refined using full-matrix least-squares techniques based on F, minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where the weight was defined as $w = [\sigma(F)^2 + (pF)^2 + q]^{-1}$ (Table 1).[14] Positional parameters for the non-hydrogen atoms are given in Tables 2 and 3, and selected bond lengths and angles are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Preparation of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ *and* (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$.—The stability of the halogenoiminophosphines, (2,4,6-Bu$^t_3$C$_6$H$_2$)NPX (X = Cl, Br or I), is dependent upon a steric shield provided by the 2,4,6-tri-*tert*-butylphenyl substituent.[7] These compounds are being exploited as synthons,[15] and we have now made use of them as obvious precursors to the corresponding trihalogenophosphine imides. Oxidation of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl with chlorine gives the trichloride (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ **3c** in about 35% yield together with a number of unassigned products, while reaction with the milder reagent (dichloroiodo)benzene (PhICl$_2$) proceeds quantitatively (as shown by the ^{31}P NMR spectrum of the reaction mixture). Compound **3c** can be easily purified by vacuum sublimation, and itself represents a useful inorganic synthon. In contrast, ^{31}P NMR studies revealed that (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ is not formed by the Kirsanov reaction [(2,4,6-Bu$^t_3$C$_6$H$_2$)NH$_2$ + PCl$_5$].[16]

The bromination of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr generated (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$ quantitatively, however, no reaction is observed between (2,4,6-Bu$^t_3$C$_6$H$_2$)NPI and I$_2$, reflecting the decreasing oxidizing power of the halogens with increasing atomic number. Both (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$ have been isolated and comprehensively characterized.

Reactions of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPX (X = Cl, Br *or* I) *with* PhICl$_2$, Br$_2$ *or* I$_2$.—Reactions involving the monohalides (2,4,6-Bu$^t_3$C$_6$H$_2$)NPX (X = Cl, Br or I) with halogens other than X [*e.g.* (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl with Br$_2$] have been examined by ^{31}P NMR spectroscopy for all possible combinations. In general, these reactions seem to produce most trihalide combinations for the corresponding starting materials. For example, the reaction mixture of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl with Br$_2$ exhibits ^{31}P NMR signals assigned to (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ (δ −96), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBrCl$_2$ (δ −136), (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_2$Cl (δ −183) and (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$ (δ −236). The three bromine-containing compounds co-crystallize and it has not been possible to separate them on a bulk scale. However, we have isolated a single crystal of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$ (shown by X-ray crystallography) from the mixture, indicating that the mixture contains individual crystals of each component.

Table 2 Positional parameters for (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$

Atom	*x*	*y*	*z*	Occupancy
Cl(1)	0.339	0.000	−0.095	0.5
Cl(2)	0.277 01(9)	−0.104 48(6)	0.323 0(2)	1.0
P	0.222 58(8)	0.000	0.121 1(2)	0.5
N	0.102 6(3)	0.000	0.028 0(6)	0.5
C(1)	0.003 4(3)	0.000	−0.129 3(6)	0.5
C(2)	−0.047 3(2)	0.083 6(2)	−0.204 7(4)	1.0
C(3)	−0.145 5(2)	0.080 6(2)	−0.358 5(5)	1.0
C(4)	−0.196 4(3)	0.000	−0.438 5(7)	0.5
C(5)	−0.001 0(2)	0.177 1(2)	−0.118 9(5)	1.0
C(6)	−0.001 3(3)	0.182 4(2)	0.137 9(6)	1.0
C(7)	−0.115 8(2)	0.194 8(2)	−0.186 6(6)	1.0
C(8)	−0.074 4(3)	0.256 0(2)	−0.224 6(8)	1.0
C(9a)	−0.312 4(5)	0.000	−0.586(1)	0.30
C(9b)	−0.297 1(7)	0.000	−0.628(2)	0.20
C(10)	−0.399 7(6)	0.039 5(8)	−0.481(2)	0.45
C(11)	−0.375(3)	0.092(3)	−0.587(7)	0.25
C(12)	−0.338 1(7)	0.090 7(6)	−0.706(2)	0.40
C(13)	−0.290 8(8)	−0.060(1)	−0.812(2)	0.40

Table 3 Positional parameters for (2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$

Atom	*x*	*y*	*z*
Br(1)	0.8306(1)	0.1522(2)	0.2959(2)
Br(2)	0.9280(1)	0.1901(2)	0.0863(2)
Br(3)	0.9478(1)	0.4143(3)	0.2969(2)
P	0.8642(2)	0.3122(4)	0.1872(3)
N	0.8089(5)	0.406(1)	0.1318(8)
C(1)	0.7632(6)	0.478(1)	0.0436(9)
C(2)	0.6965(7)	0.415(1)	0.0013(9)
C(3)	0.6540(6)	0.493(2)	−0.080(1)
C(4)	0.6735(7)	0.623(1)	−0.119(1)
C(5)	0.7381(6)	0.674(1)	−0.076(1)
C(6)	0.7848(6)	0.609(1)	0.007(1)
C(7)	0.6684(7)	0.276(1)	0.041(1)
C(8)	0.6614(8)	0.288(2)	0.166(1)
C(9)	0.5935(8)	0.237(2)	−0.018(1)
C(10)	0.7170(8)	0.156(1)	0.018(1)
C(11)	0.6213(7)	0.704(2)	−0.206(1)
C(12a)	0.595(2)	0.832(3)	−0.153(2)
C(13a)	0.554(1)	0.617(3)	−0.250(2)
C(14a)	0.659(1)	0.748(3)	−0.306(2)
C(12b)	0.552(4)	0.724(7)	−0.157(5)
C(13b)	0.597(3)	0.608(5)	−0.310(4)
C(14b)	0.659(3)	0.851(6)	−0.246(4)
C(15)	0.8553(6)	0.684(1)	0.052(1)
C(16)	0.8627(7)	0.827(1)	−0.002(1)
C(17)	0.8572(7)	0.713(1)	0.176(1)
C(18)	0.9209(7)	0.599(2)	0.028(1)

Table 4 Selected bond lengths (Å) and angles (°)

(2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$		(2,4,6-Bu$^t_3$C$_6$H$_2$)NPBr$_3$	
P–N	1.467(4)	P–N	1.46(1)
P–Cl(1)	2.017(1)	P–Br(1)	2.165(4)
P–Cl(2)	2.004(1)	P–Br(2)	2.171(4)
		P–Br(3)	2.148(4)
N–C(1)	1.410(4)	N–C(1)	1.45(1)
C(1)–N–P	160.9(3)	C(1)–N–P	160.1(9)
Cl(1)–P–Cl(2)	100.71(5)	Br(1)–P–Br(2)	101.8(2)
		Br(1)–P–Br(3)	100.8(2)
		Br(2)–P–Br(3)	100.2(2)
N–P–Cl(1)	118.9(2)	N–P–Br(1)	117.2(5)
N–P–Cl(2)	116.69(9)	N–P–Br(2)	118.5(4)
		N–P–Br(3)	115.4(4)

The chemical analyses of the co-crystallized (recrystallized) sample are consistent with a mixture in the relative ratios revealed in the ^{31}P NMR spectrum of the sample. The formation of (2,4,6-Bu$^t_3$C$_6$H$_2$)NPCl$_3$ as a minor product and (2,4,6-

Bu$^t{}_3$C$_6$H$_2$)NPBrCl$_2$ in about 10% yield (by ^{31}P NMR integration) indicates that the reaction involves a halogen-exchange process.

Other combinations of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPX and dihalogens reveal similar product mixtures which are the result of halogen exchange. However, reactions involving iodine are apparently restricted to monoiodo-phosphine imide and -iminophosphine products. Independent of the stoichiometry, the reaction between (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl and I$_2$ forms (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_2$I (δ −211), which has been isolated in very low yield. The remainder of the disproportionation is an exchanging mixture of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl and (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPI whose chemical shift is dependent upon the stoichiometry. A trace of I$_2$ results in a signal *ca.* δ 150 close to that of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl (δ 139 in C$_6$D$_6$),[7] while excess of I$_2$ gives a signal at *ca.* δ 200 close to that of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPI (δ 218 in C$_6$D$_6$).[7] Mixtures of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr and (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPI also show an average signal indicating an exchange process which presumably takes place *via* the iminophosphenium cation, [(2,4,6-Bu$^t{}_3$C$_6$H$_2$)NP]$^+$,[7,17] and is possibly promoted by trihalide anion formation X'$_2$X$^-$. In contrast, mixtures of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ and (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$ show no sign of halide exchange. On this basis, we envisage the formation of mixed halides to occur by means of halide exchange at the monohalide followed by oxidation of the resulting monohalides by the now mixed dihalogens, as illustrated in equations (1)–(4). A process of this

$$(2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX} + \text{X}'_2 \longrightarrow (2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX}' + \text{XX}' \quad (1)$$

$$(2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX}' + \text{X}_2 \longrightarrow (2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX}'\text{X}_2 \quad (2)$$

$$(2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX} + \text{XX}' \longrightarrow (2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX}'\text{X}_2 \quad (3)$$

$$(2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPX} + \text{X}'_2 \longrightarrow (2,4,6\text{-Bu}^t{}_3\text{C}_6\text{H}_2)\text{NPXX}'_2 \quad (4)$$

nature accounts for the formation of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_2$I from the reaction of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl + I$_2$. The reluctance to form diiodo or triiodo trihalides in such reactions may be due to either the low reduction potential (+0.536 V, *cf.* Br +1.066 V, Cl +1.358 V)[18] of the iodo dihalogen, or more likely the steric restriction of an interaction between an iodo mixed dihalogen and the phosphorus centre.

Structural Features.—The solid-state structures of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ and (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$ have been determined by X-ray crystallography and views of the compounds are presented in Figs. 1 and 2. The crystal structure of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_2$I has also been determined and confirms the covalent monomeric arrangement, however, the disorder in the structure prevents accurate assessment of bond lengths and angles. No significant intermolecular contacts are observed in the structures of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ or (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$, and therefore the distorted tetrahedral four-co-ordinate environment for phosphorus is perhaps expected. Nevertheless, it is worth noting that McAuliffe and co-workers have recently shown that diiodo-[20] and dibromo-phosphoranes[21] adopt linear 'spoke' structures **4** in the solid state involving four-co-ordinate phosphorus centres rather than the expected five-co-ordinate arrangement. We conclude that for the trihalogenophosphine imides, four-co-ordination for phosphorus is a more dominant feature than the linear 'spoke' arrangement for the halogens, which would require a three-co-ordinate trigonal geometry for phosphorus.

The molecules exhibit unusually large angles at the nitrogen centre [(2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ 160.9(3)°, (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$ 160.1(9)°]. For comparison, monomeric arylphosphazenes (RNPR$_3$) have geometries at the nitrogen centre, which may be considered consistent with the valence-shell electron-pair repulsion (VSEPR) model [PhNPPh$_3$, C–N–P 130.4(3)°;[22] C$_5$H$_4$NNPPh$_3$, 128.6(3)°;[23] NC(NMe$_2$)CN(Cl)NCNPPh$_3$, 121°[24]], and this is general for other phosphine imide derivatives.[25] Transition-metal complexes of the R$_3$PN$^-$ ligand exhibit a wide range of angles for the metal-bound nitrogen centre (130–177°),[26] and the wide angles are rationalized in terms of N–P and N–M π interactions and sp hydridization at the nitrogen centre.[27]

The N–P bonds are dramatically shorter [(2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ 1.467(4) Å, (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$, 1.46(1) Å] than typically observed [*cf.* arylphosphazenes, PhNPPh$_3$, 1.602(3) Å;[22] C$_5$H$_4$NNPPh$_3$, 1.574(2) Å;[23] NC(NMe$_2$)NC(Cl)NC-NPPh$_3$, 1.622(5) Å[24]], with the bond in (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ representing one of the shortest N–P bonds reported to date. The iminophosphenium cation [(2,4,6-Bu$^t{}_3$C$_6$H$_2$)NP]$^+$, which is considered to contain a triple NP bond,[28,29] has a similar length of 1.475(8) Å.[7] Although the phosphorus centres in (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ and (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$ are distorted from a tetrahedral geometry, they exhibit close to C_{3v} symmetry with the narrow angle for X–P–X of 100° (*cf.* OPCl$_3$, Cl–P–Cl 103.3°).[30]

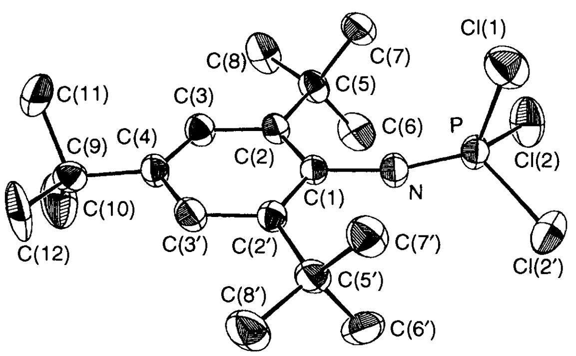


Fig. 1 An ORTEP[19] view of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPCl$_3$ showing one of the butyl groups in the disorder model

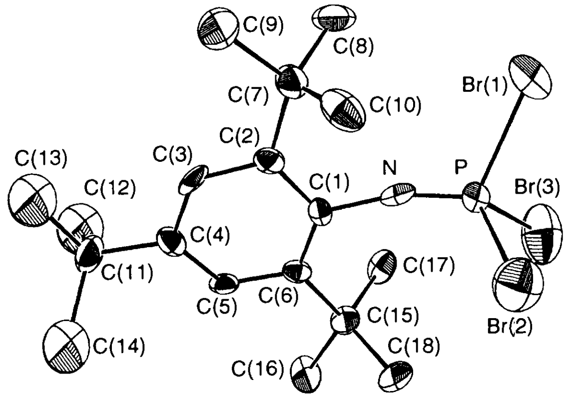
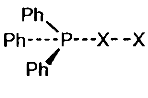
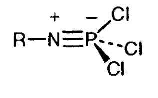


Fig. 2 An ORTEP[19] view of (2,4,6-Bu$^t{}_3$C$_6$H$_2$)NPBr$_3$ showing one of the butyl groups in the disorder model



4



5

Steric and Electronic Control of Geometries at Nitrogen.—The dominating steric influence of the 2,4,6-tri-*tert*-butylphenyl substituent is now well established and has been exploited to enable the isolation of monomeric units that would otherwise dimerize or oligomerize [*e.g.* (2,4,6-Bu$^t{}_3$C$_6$H$_2$)P=P(2,4,6-

$Bu^t{}_3C_6H_2)$[31] and $(2,4,6\text{-}Bu^t{}_3C_6H_2)OAl(Bu^t)_2$[32]]. Inhibition of dimerization is further demonstrated in the three monomeric $(2,4,6\text{-}Bu^t{}_3C_6H_2)NPX_3$ derivatives presented here.

Steric stresses are evident within each molecule in terms of severe bond angle distortions, but most noteworthy are the critically short N–P bonds and extreme (large) angles at nitrogen. In $(2,4,6\text{-}Bu^t{}_3C_6H_2)NPCl_3$ **3c** the N–P bond is significantly shorter and the C–N–P angle is substantially larger than those in the directly related monomeric trichlorides **3a** [1.504(2) Å and 144.6(2)°] and **3b** [1.505(3) Å and 142.9(3)°]. Although the electronic effects of the $C(CF_3)_3$ and $CCl(CCl_3)_2$ substituents are dramatically different from those of $(2,4,6\text{-}Bu^t{}_3C_6H_2)$, we consider the greater steric bulk provided by the latter to be most important in terms of the angle imposed at the nitrogen centre.

The short N–P bond and large C–N–P angle in **3c** implies sp hybridization at the nitrogen centre and suggests that the triple N–P bond model **5** is a significant resonance contributor to the electronic structure. We speculate that the non-VSEPR geometry is associated with a relative shortening of the N–P bond, whether a function of steric stress or electronic factors. The potential for enhancement of the N–P π interaction is greater in the presence of electronegative substituents.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society (N. B.) and the Killam Trust (M. J. S.) for financial support and the Atlantic Region Magnetic Resonance Centre for obtaining the NMR spectra.

References

1 A. Schmidpeter, in *The Chemistry of Inorganic Homo- and Heterocycles*, eds. I. Haiduc and D. B. Sowerby, Academic Press, New York, 1987, vol. II, p. 617.

2 D. E. C. Corbridge, *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, 1990, ch. 5.

3 A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, I. E. Boldeskul, A. P. Marchenko and A. M. Pinchuk, *J. Struct. Chem. (Engl. Transl.)*, 1987, **28**, 274.

4 M. Bermann, *Top. Phosphorus Chem.*, 1972, **7**, 311.

5 M. Y. Antipin, Y. T. Struchkov, V. M. Yurchenko and E. S. Kozlov, *J. Struct. Chem. (Engl. Transl.)*, 1982, **23**, 227; M. Y. Antipin, Y. T. Struchkov and E. S. Kozlov, *J. Struct. Chem. (Engl. Transl.)*, 1986, **26**, 575.

6 U. Muller, *Z. Anorg. Allg. Chem.*, 1980, **463**, 117.

7 E. Niecke, M. Nieger and F. Reichert, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1715.

8 L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, 1967, vol. 1.

9 N. Burford, J. Muller and T. M. Parks, *J. Chem. Educ.*, in the press.

10 S. L. Lawson and R. A. Jacobsen, Ames Laboratory Report IS-1141, USABC, Iowa State University, Ames, IA, 1965.

11 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 159.

12 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, (*a*) Table 2.2B; (*b*) Table 2.3.1 (Present distributor: Kluwer Academic Publishers, Dordrecht and Boston).

13 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, 1990.

14 R. C. G. Killean and J. L. Lawrence, *Acta Crystallogr., Sect. B*, 1969, **25**, 1750.

15 G. David, E. Niecke, M. Nieger, V. von der Gonna and W. W. Schoeller, *Chem. Ber.*, 1993, **126**, 1513; E. Niecke and D. Gudat, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 217; R. Detsch, E. Niecke, M. Nieger and F. Reichert, *Chem. Ber.*, 1992, **125**, 321; J. Hein, C. Gartner-Winkhaus, M. Nieger and E. Niecke, *Heteroatom Chem.*, 1991, **2**, 409; E. Niecke, R. Detsch and M. Nieger, *Chem. Ber.*, 1990, **123**, 797; E. Niecke, M. Nieger, C. Gartner-Winkhaus and B. Kramer, *Chem. Ber.*, 1990, **123**, 477; E. Niecke, J. Hein and M. Nieger, *Organometallics*, 1989, **8**, 2290.

16 See, for example, H. R. Allcock, *Phosphorus-Nitrogen Compounds*, Academic Press, New York, 1972, p. 113.

17 N. Burford, J. A. C. Clyburne, P. K. Bakshi and T. S. Cameron, *J. Am. Chem. Soc.*, 1993, **115**, 8823.

18 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.

19 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

20 S. M. Godfrey, D. G. Kelly, C. A. McAuliffe, A. G. Mackie, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101.

21 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355.

22 E. Bohm, K. Dehnicke, A. Maurer and D. Fenske, *Z. Naturforsch., Teil B*, 1988, **43**, 138.

23 S. Kulpe, I. Seidel, J. Bodeker and P. Kockritz, *Cryst. Res. Technol.*, 1984, **19**, 649.

24 T. S. Cameron, K. Mannan, M. Biddlestone and R. A. Shaw, *Z. Naturforsch., Teil B*, 1975, **30**, 973.

25 See, for example, T. Mohan, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1992, **31**, 2271, Table IV.

26 K. Dehnicke and J. Strahle, *Polyhedron*, 1989, **8**, 707.

27 F. L. Phillips and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1976, 1448.

28 R. Glaser, C. J. Horan and P. E. Haney, *J. Phys. Chem.*, 1993, **97**, 1835; R. Glaser, C. J. Horan, G. S.-C. Choy and B. L. Harris, *J. Phys. Chem.*, 1992, **96**, 3689.

29 R. D. Curtis, M. J. Schriver and R. E. Wasylishen, *J. Am. Chem. Soc.*, 1991, **113**, 1493.

30 T. Moritani, K. Kuchitsu and Y. Morino, *Inorg. Chem.*, 1971, **10**, 344.

31 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587.

32 M. A. Petrie, M. M. Olmstead and P. Power, *J. Am. Chem. Soc.*, 1991, **113**, 8704.

Received 6th *September* 1993; *Paper* 3/05333D