Sequential dehydrochloride coupling of trichlorophosphine with 2,6-di-isopropylaniline: aminophosphine precursors to phosphetidines

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Abstract: Various stoichiometric combinations of PCl_3 with $DippNH_2$ (Dipp = 2,6-di-isopropylphenyl) have been examined using ^{31}P NMR spectroscopy. The dehydrochloride coupling reaction is mediated by the moderate steric bulk of the Dipp substituent. Isolation procedures and characterization data are reported for the aminodichlorophosphine (**1**), the aminotetrachlorodiphosphine (**4**), and the dichlorophosphetidine (**7**). The observations offer new appreciation of dehydrochloride coupling products of halophosphines with primary amines.

Key words: phosphorus, nitrogen, phosphazanes, phosphetidines, iminophosphine.

Résumé : Faisant appel à la spectroscopie RMN du ^{31}P, on a étudié diverses combinaisons stoechiométriques de PCl_3 avec de la $DippNH_2$ ($DippNH_2$ = 2,6-di-isopropylphényle). La réaction de couplage avec déshydrochloruration est favorisée par l'empêchement stérique modéré du substituant Dipp. On rapporte les méthodes d'isolement et les données de caractérisation de l'aminodichlorophosphine (**1**), de l'aminotétrachlorodiphosphine (**4**), et de la dichlorophosphétidine (**7**). Les faits observés offrent une nouvelle appréciation sur la nature des produits de couplage avec déshydrochloruration d'halophosphines avec des amines primaires.

Mots clés : phosphore, azote, phosphazanes, phosphétidines, iminophosphine.

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Introduction

The established structural diversity of nitrogen-phosphorus compounds is a manifestation of the strong and versatile N—P bond. A variety of N—P coupling reactions have been employed, but elimination of hydrogen chloride is prototypical and is responsible for the formation of mono-, bis-, and tris-aminophosphines from appropriate stoichiometric combinations of PCl_3 and a secondary amine (1). In comparison, reactions of PCl_3 with primary amines offer a more diverse array of structural options because of the possibility of P-N-P linkages, as illustrated in Fig. 1. In spite of ring strain, the four-membered, dimeric phosphetidine (phosphazane) frameworks **7** and **9** (2–7) are routinely isolated for conventional derivatives (R = Me, Et, Ph) (8). Less common are reports of the sequential (intermediate) metathesis products **1** (8), **2** (8), **3** (5), **4** (5), and **5** (9), and examples of the higher order chain **6** have not been reported (10–14).

Primary amines bearing 'bulky' substituents are predictably restricted from multi-dehydrochloride coupling reactions. In the case of R = 2,4,6-tri-tert-butylphenyl (Mes*), intramolecular hydrogen chloride elimination occurs to produce the iminophosphine Mes*N=PCl (15). We now show how both phosphetidine formation and intramolecular elimination are impeded by the presence of the 2,6-di-isopropylphenyl (Dipp) substituent, which provides intermediate steric influence on the thermodynamic and kinetic factors governing the coupling reaction. ^{31}P NMR spectroscopic studies of a series of stoichiometric combinations of PCl_3 and $DippNH_2$ reveal many of the sequential dehydrochloride coupling products, and assignments of ^{31}P chemical shifts have been confirmed for isolated samples of **1**, **4**, **7**, and **9** (3).

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Experimental procedures (16)

General

Diethylether was obtained from ACP Chemicals Inc. and hexane from Anachemia. All other chemicals and reagents were obtained from Aldrich Chemical Company. All solvents were degassed and stored in evacuated bulbs. Solids were handled in a nitrogen-filled glove-box. Sample

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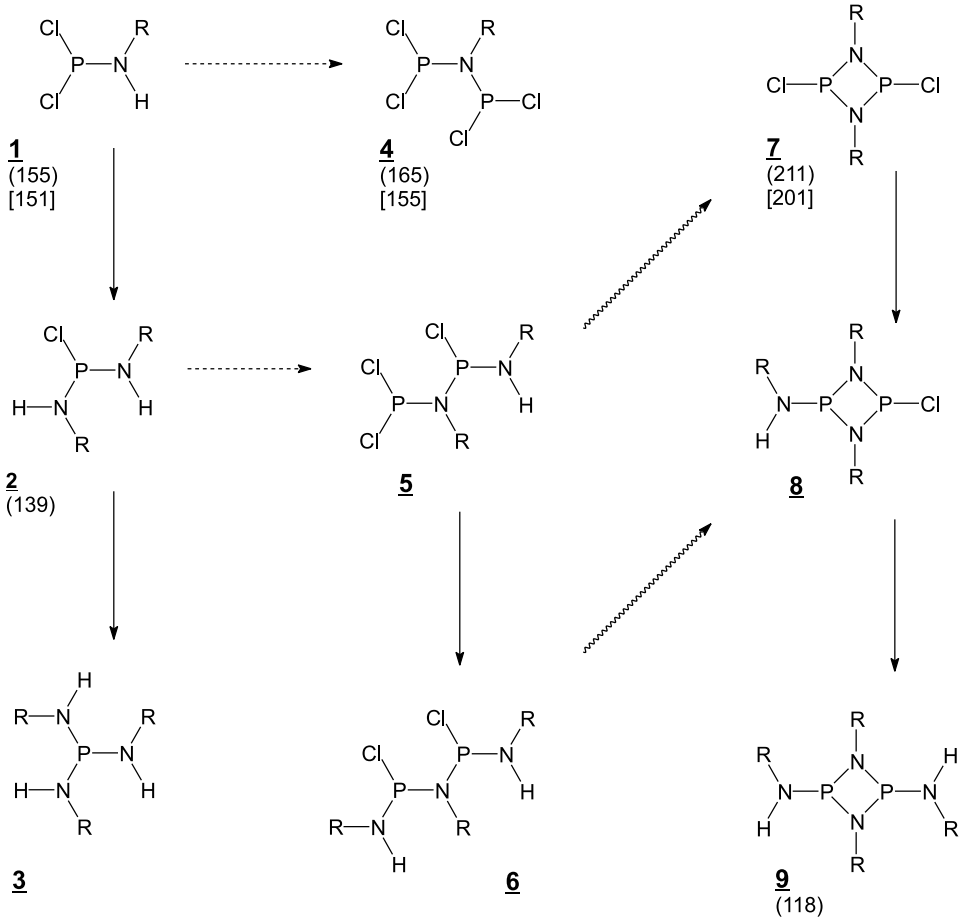
Fig. 1 Potential products of sequential dehydrochloride metathesis from PCl_3 and RNH_2. Solid arrows represent addition of amine with loss of HCl, dashed arrows represent addition of phosphine with loss of HCl, and wavy arrows represent cyclisation with HCl elimination. ^{31}P NMR chemical shift assignments (ppm) are given in parentheses for *R* = Dipp, and in square brackets for *R* = Ph.



handling and reactions were performed under oxygen and moisture-free conditions. 2,6-Di-isopropylaniline ($DippNH_2$) was used as received. Dichloromethane was dried at reflux over CaH_2, P_4O_{10}, and CaH_2; hexane, toluene, and benzene were dried over potassium; and diethylether was dried over sodium/benzophenone. Deuterated solvents were dried over CaH_2. PCl_3 was distilled under vacuum.

IR spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510 FT-IR spectrometer, and are presented as wavenumber (cm^{-1}) maxima, with ranked intensities for each absorption given in parentheses. The most intense peak is given a ranking of 1. Melting point samples were placed in 1.0 mm (O.D.) Pyrex capillaries, sealed under nitrogen, and measured using an Electrothermal® melting point apparatus. Solution and variable-temperature (VT) NMR spectra were recorded on a Bruker AC-250 NMR spectrometer. Solution NMR samples were flame-sealed in 5 mm Pyrex tubes. NMR spectra were referenced to the solvent and chemical shifts are reported in ppm relative to an external standard (TMS for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P).

^{31}P NMR spectra of reactions between PCl_3 and RNH_2 (*R* = Dipp or Ph)

Table 1 summarizes ^{31}P NMR spectra obtained for reaction mixtures, prepared at 0°C by the addition of $DippNH_2$ in toluene to PCl_3 in toluene at approximately 1 M concentration. The mixtures were stirred overnight with warming to room temperature and were filtered. Spectra of similar reaction mixtures involving $PhNH_2$ revealed many products. At equimolar stoichiometry, the prominent peaks were assigned to **1** (*R* = Ph, 151 ppm) and **7** (*R* = Ph, 201 ppm), with substantial unreacted PCl_3 (220 ppm). The aminodiphosphine **4** (*R* = Ph, 155 ppm) (12) was observed as a minor component. It was not possible to make other unequivocal assignments for reaction mixtures containing excess $PhNH_2$.

Isolation procedures and characterization data

DippN(H)PCl$_2$ (1)

$DippNH_2$ (4.0 mL, 21 mmol) in benzene (15 mL) was added via cannula to a stirred solution of PCl_3 (1.9 mL, 21 mmol) in benzene (15 mL) at 0°C. The resultant slurry was stirred overnight and the white precipitate was filtered through a fine glass filter. Benzene was slowly removed from the pale yellow solution to give colourless rod-shaped crystals. Yield 2.23 g (43%); mp 58–61°C. IR (Nujol mull) (cm^{-1}): 3314 (17), 2959 (2), 2923 (1), 2852 (3), 1583 (19), 1519 (13), 1462 (4), 1383 (11), 1364 (12), 1329 (14), 1252 (8), 1182 (6), 1100 (7), 1043 (9), 931 (10), 885 (15), 797 (5), 749 (18), 512 (16). ^1H NMR: 1.08 (d, $^3J_{HH}$ = 12 Hz),

Table 1. Summary of ^{31}P NMR spectroscopic data for reaction mixtures of PCl_3 $DippNH_2$ at seven different stoichiometric combinations.

δ ^{31}P (ppm)		155	221	139	140	148 182	8	161 195	224	242	118	133	136	211	165
Assignments		**1**	PCl_3	(**2**)	(**3**)	(**8**)		(**5**)	(**6**)		**9**			**7**	**4**
Reaction stoichiometry PCl_3:$DippNH_2$	2:1	100	80												
	1:1	100	20												
	1:2	100		15											
	1:3	10		100	30	10	10	5	1	1		5	5		
	1:4	10		100	10	5	5	2				2	2		
	1:5			100	40	60		5	5	5	5		5	1	
	1:6			100	30	90	70	10	10	10	10		1	5	

Note: Chemical shifts are listed in order of peak intensity. Approximate peak intensities in each spectrum are given relative to the most intense peak (100%). Assignments are confirmed for **1**, **4**, **7**, and **9** (3) by characterization of isolated samples. Parentheses indicating assignments for **2**, **3**, **5**, **6**, and **8** are tentative and other minor signals are not assigned.

3.25 (sept, $^3J_{HH}$ = 12 Hz), 4.53 (s), 6.93–6.96 (m). ^{31}P NMR: 155. Anal. calcd. for DippN(H)PCl_2: C 51.81, H 6.52, N 5.03; found: C 51.36, H 6.79, N 5.08.

DippN(PCl_2)$_2$ (4)

PCl_3 (20 mL) and NEt_3 (40 mL) were distilled onto a frozen solution of $DippNH_2$ (5.0 g, 28 mmol) in hexane (30 mL). A yellow solution and a white precipitate formed on warming to room temperature. After stirring for 7 days, the solution was filtered and the solvent removed in vacuo. The resulting solid was sublimed onto a water cooled finger, under static vacuum with warming to 80°C, to give tan crystals of **4**. Yield 5.3 g (14 mmol, 50%); mp 69–71°C. IR (Nujol mull) (cm^{-1}): 1584 (20), 1433 (9), 1362 (8), 1322 (15), 1309 (18), 1158 (7), 1104 (12), 1095 (13), 1050 (17), 1040 (19), 903 (6), 883 (1), 799 (6), 718 (16), 515 (4), 490 (3), 481 (2), 451 (10), 437 (11), 417 (14). ^1H NMR: 1.19 (d, $^3J_{HH}$ = 7 Hz), 3.12 (sept, $^3J_{HH}$ = 7 Hz), 7.26 (m). ^{31}P NMR: 165 (reaction mixture), 165 and 211 (assigned to **7**). Anal. calcd.: C 38.03, H 4.52, N 3.70; found: C 38.08, H 4.52, N 3.75.

[DippNPCl]$_2$ (7)

$DippNH_2$ (10 mL, 53 mmol) in toluene (20 mL) was added via cannula to a three-chamber reaction vessel containing a stirring solution of PCl_3 (2.3 mL, 26 mmol) in toluene (15 mL) at 0°C. The solution was warmed to room temperature and a white precipitate formed. After stirring overnight, the mixture was degassed and filtered through a fine glass frit. Toluene was removed under vacuum and the resulting oil was dissolved in hexane (20 mL) to promote precipitation. The mixture was filtered and NEt_3 (3.7 mL, 26 mmol) was added, with the immediate production of a yellow solution and white precipitate. The mixture was filtered again and the solvent was slowly removed to give large white crystals, which were washed with fresh hexane. Yield 1.4 g (3.0 mmol, 23%); mp 208–215°C. IR (Nujol mull) (cm^{-1}): 1444 (4), 1363 (8), 1320 (11), 1276 (15), 1260 (14), 1249 (10), 1198 (5), 1180 (16), 1104 (9), 1056 (19), 1039 (17), 935 (13), 923 (7), 907 (2), 801 (1), 537 (12), 529 (18), 496 (5), 421 (3), 379 (20). ^1H NMR: 1.31 (d, $^3J_{HH}$ = 10 Hz), 3.04 (sept, $^3J_{HH}$ = 8 Hz), 7.2–7.4 (m). ^{31}P NMR: 211. Anal. calcd.: C 59.63, H 7.09, N 5.80; found: C 59.54, H 7.20, N 5.76.

X-ray crystallography

Crystals of **1**, **4**, and **7** were selected and mounted in Pyrex capillaries in the dry box. Data were corrected for Lorentz and polarization effects, and absorption. Structures were solved by direct methods and expanded using Fourier techniques. For compound **4**, only the chlorine atoms, the phosphorus atoms, and C(11) and C(12) were refined anisotropically. The standard reflections decreased by 25% during data collection, and a linear correction factor was applied. For compound **7**, only the chlorine atoms, phosphorus atoms, and C(9)-C(12) and C(19)-C(24) were refined anisotropically. Extinction corrections were not applied for compounds **4** and **7**. Hydrogen atoms were allowed to ride on the heavy atoms to which they are bonded, with C-H distances of 0.95 Å and fixed isotropic temperature factors. Calculations were performed using the teXsan crystallographic package (17). A summary of the crystallographic data is given in Table 2.[3]

Results and discussion

Reaction mixtures of PCl_3 and $DippNH_2$ with different stoichiometric combinations have been examined using ^{31}P NMR spectroscopy. Contrary to the reports describing isolation of phosphetidine (**7**) for many RNH_2 derivatives (R = alkyl and aryl) (4, 18), a number of products were observed for $DippNH_2$, with **7** as a minor component even at high excess of amine. Table 1 lists the ^{31}P chemical shifts observed for each stoichiometric combination, according to the relative peak intensity with respect to the most intense peak (100%). Chemical shift assignments for compounds **1**, **7**, and **9** (3) have been confirmed by characterization of isolated materials. In contrast to reactions involving amines

[3] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 191247–191249 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 2. Crystal data for compounds **1**, **4**, and **7**.

	$Dipp(H)NPCl_2$	$DippN(PCl_2)_2$	$[DippNPCl]_2$
Compound label	**1**	**4**	**7**
Empirical formula	$C_{12}H_{18}Cl_2NP$	$C_{12}H_{17}Cl_4NP_2$	$C_{24}H_{34}P_2N_2Cl_2$
Formula weight	278.16	379.03	483.40
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	23.80(1)	14.34(1)	9.814(9)
b (Å)	5.531(2)	9.455(4)	17.579(8)
c (Å)	23.82(6)	26.478(9)	16.002(5)
β (°)	109.21(3)	103.70(5)	103.37(4)
V (Å^3), Z	2962(2), 8	3487(3), 8	2686(3), 4
D_{calc} (mg m^{-3})	1.248	1.444	1.195
λ (Å)	0.71069	0.71069	0.71069
μ (cm^{-1}), F(000)	5.22, 1168	8.48, 1552	3.74, 1024
Crystal size (mm^3)	0.08 × 0.28 × 0.60	0.20 × 0.40 × 0.50	0.15 × 0.20 × 0.60
Diffractometer	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC5R
Scan type	ω–2θ	ω–2θ	ω–2θ
Temperature (K)	296(1)	296(1)	296(1)
Absorption correction	1.0–0.68	ψ-scan	ψ-scan
Transmission factors	0.6791–1.0000	0.6263–1.0000	0.9030–0.9977
Data collected	3777	5767	4616
Unique data	3233	5479	4316
Observed data [$I > 3\sigma(I)$]	1104	889	841
R_{int}, $2\theta_{max}$ (°)	0.063, 46.1	0.031, 50.1	0.053, 50.1
Refined parameters	200	223	192
Refinement on	F	F	F
$R(F)$, $wR(F)$, $S(F)$[a]	0.068, 0.073, 2.27	0.074, 0.084, 1.86	0.068, 0.083, 2.05
Final Δρ map (e Å^{-3})	0.33, –0.30	0.44, –0.51	0.34, –0.33

[a] $R(F) = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR(F) = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$; $S(F) = [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$; n = number of data; p = number of refined parameters.

with small substituents (R = Me, Et, Bu) (18), the aminodiphosphine **4** (R = Dipp, 165 ppm) was not observed, even at a two-fold excess of PCl_3. Instead, compound **4** has been isolated from reactions in the presence of NEt_3 (see below).

Referring to Table 1, PCl_3 is observed as an excess component in the equimolar reaction with $DippNH_2$, and the prominent peak (155 ppm) is assigned to monoaminophosphine (**1**). The prominent peak (139 ppm) at a three-fold excess of $DippNH_2$ is assigned to the diaminophosphine (**2**), and is the prominent component at all reactions involving higher excesses of $DippNH_2$. Evidence for P-N-P linkages is only observed above a two-fold excess of $DippNH_2$, with two sets of doublets (148, 182 ppm; 161, 195 ppm; $^2J_{PP}$ = 45 Hz) exhibiting typical two-bond coupling constants. Although high-order tetraphosphorus assemblies are possible, these doublets are speculatively assigned to the nonsymmetric systems **5** and **8**, which are the likely precursors to **9** (3). Previous reports confirm that derivatives of **5** can been isolated (9). They are, however, prone to rapid cyclisation to give the phosphetidine framework (13), and on this basis the more prominent doublet signals are assigned to **8**.

^{31}P NMR spectra of reaction mixtures containing equimolar amounts of PCl_3 and $PhNH_2$ show **1** and **7** (R = Ph) as well as unreacted PCl_3, consistent with the established facile isolation of the phosphetidine **7** (8), but the spectra are more complicated in the presence of excess $PhNH_2$. In this context, the relative impedance of dehydrochloride PCl_3–$DippNH_2$ coupling is interpreted in terms of the steric imposition of the Dipp substituent restricting intermolecular interactions and influencing the nucleophilicity of the amine.

The absence of aminodiphosphine (**4**) in all reaction mixtures of PCl_3 with $DippNH_2$, and the prominence of the mono- (**1**) and diaminophosphine (**2**) (R = Dipp), indicates that the nucleophilicity of the nitrogen centre in **1** is insufficient to interact with a second PCl_3, so that attack at the phosphorus centre in **1** by $DippNH_2$ is relatively favoured. In this context, it is reasonable to assign the peak at 140 ppm to the trisaminophosphine (**3**) (R = Dipp), and to conclude that the formation of **5** is preferred over **4**, which facilitates the formation of **7** and renders **4** redundant in the reaction pathway.

High yield formation of compound **4** from PCl_3 and $DippNH_2$ in the presence of NEt_3 indicates that the nucleophilicity of the nitrogen center in **1** is enhanced by the presence of triethylamine, presumably due to partial or full deprotonation. ^{31}P NMR spectra of reaction mixtures containing NEt_3 show **4** and **7** as the only products, emphasizing the special stability of the phosphetidine (**7**).

Assignments of peaks in the ^{31}P NMR spectra to compounds **1**, **4**, **7**, and **9** (3) (R = Dipp) have been confirmed by isolation and structural characterization, as illustrated in Fig. 2. Some of the structural features of these compounds

Fig. 2 Views of the solid state structures of **1**, **4**, **7**, and **9** (3) for *R* = Dipp.

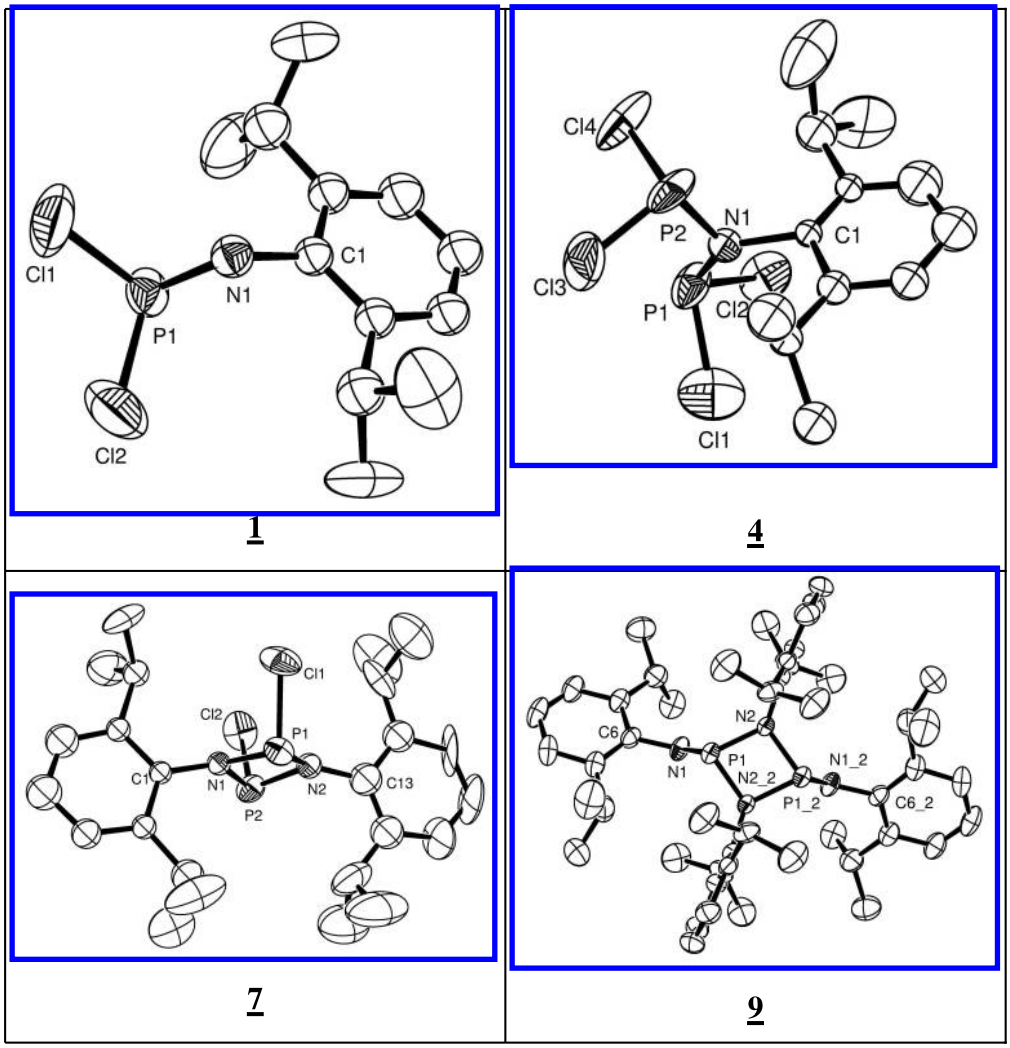


Table 3. Comparison of selected bond lengths (Å) and angles (°) for **1**, **4**, **7**, and **9** (3) for *R* = Dipp.

	$R(H)NPCl_2$[a]	$RN(PCl_2)_2$ [ii]	$[RNPCl]_2$	$[RNPN(H)R]_2$[4]
Compound label (*R* = Dipp)	**1**	4	7	9
P(1/2)—N(1/2)	1.64(1), 1.63(1)	1.59(3), 1.69(2), 1.76(2), 1.68(2)	1.71(1), 1.69(1), 1.73(1), 1.69(2)	1.727(3), 1.739(3)
P(1)—Cl(1/2); P(2)—Cl(3/4)	2.033(7), 2.062(7); 2.010(8), 2.024(8)	2.11(2), 2.03(2); 2.05(2), 2.02(2) 2.06(2), 2.01(2); 2.06(2), 2.07(1)	P(1)—Cl(1): 2.071(8); P(2)—Cl(2): 2.085(8)	—
N(1/2)-P(1/2)-N(1/2)	—	—	81.3(7), 80.5(7)	80.01(15)
P(1)-N(1/2)-P(2)	—	122(2), 122(1)	98.6(7), 97.9(8)	97.54(14)
N(1)-P(1)-Cl(1/2); N(1)-P(2)-Cl(3/4)	99.5(5), 105.0(5); 95.9(4), 102.2(6)	102(1), 104(1), 106(1), 103(1), 102(1), 99(1), 102(1), 101(1)	N(1/2)-P(1)-Cl(1): 103.2(6), 105.8(6) N(1/2)-P(2)-Cl(2): 103.2(6), 106.1(6)	—
Σ@N(1/2)	—	359, 360	355.6, 354.9	348

[a]Two molecules in the asymmetric unit.

(Table 3) are worthy of comment. The aminodiphosphine (**4**) (*R* = Dipp) adopts a C_s conformation (*endo*,*exo*), contrasting the C_{2v} conformation (*exo*,*exo*) reported for the phenyl derivative of **4** (*R* = Ph) (12) and pentaphenylaminodiphosphine (5). Nevertheless, the structural trends indicate that larger substituents, such as Dipp, impose the (*endo*,*exo*) conformation (12). The typical planar environment at nitrogen bound to phosphorus is observed for all Dipp-N-P compounds described in this report, as demonstrated by the sum (approximately 360°) of the bond angles at nitrogen. The resulting $P(N)_2P$ plane in the phosphetidine (**7**) clearly demonstrates a *cis* conformation for the chlorine substituents,

consistent with the phenyl derivative (7), and the aryl substituents are perpendicular to the NP_2 plane.

Conclusions

Reactions of $DippNH_2$ with PCl_3 have been comprehensively evaluated by ^{31}P NMR spectroscopy. The observations confirm the intermediacy of aminophosphines in phosphetidine formation and offer insight to the mechanisms of P-N-P linkage assembly.

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