Hypercoordinate P^{II}, P^{III}, and P^{IV} Phosphorus Derivatives with Intramolecular Coordination by Donor Groups

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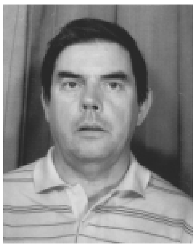
This review describes phosphanes and phosphane derivatives as well as phosphenium salts in which increase in coordination number was achieved by intramolecular coordination of donor groups. This effect was established by X-ray crystal structure analysis and was also inferred from ^1H-NMR studies in solution. Where possible, comparison with the corresponding silicon compounds was made.

Contents

1. Introduction

It is well established that the silicon atom can extend its coordination number beyond four and that, in many cases, such an increase in coordination number can be achieved by intramolecular coordination of donor groups[1]. The phosphorus atom can also increase its coordination number through intramolecular coordination by donor groups[2]. However, this aspect has been mainly studied with regard to phosphoranes and this matter has recently been reviewed[3]. For our part, we have studied intramolecular coordination of NMe_2 donor groups in P^{III} and P^{IV} phosphorus compounds. The purpose of this review is to survey these compounds, with emphasis on the physical techniques used to establish their structures in the solid state and in



Claude Chuit was born in Paris in 1935. He obtained his Doctorat d'Etat from the University of Orsay under the supervision of Dr. H. Felkin. After one year of postdoctoral studies at the University of Stirling (Scotland) with the late Professor W. Parker, he spent 10 years in Professor J. F. Normant's laboratory at the University P. and M. Curie in Paris. Since 1980 he has worked on hypercoordinate silicon and phosphorus compounds in Professor R. Corriu's laboratory at the University of Montpellier. He was appointed Directeur de Recherche at the CNRS in 1990. His current interests concern the elaboration of materials by the sol-gel process.

Catherine Reyé was born in France (Deux Sèvres). She received her Ph.D. from the University of Montpellier II under the supervision of Professor R. J. P. Corriu. Her principal research interests were then focussed on the chemistry of hypercoordinate silicon and phosphorus compounds. Initially, she worked in the area of reactions catalyzed by nucleophiles involving hypercoordinate silicon intermediates. Subsequently, she studied the structure and the reactivity of hypercoordinate silicon and phosphorus compounds. Her current interests concern the study of hybrid organic-inorganic materials obtained by hydrolytic polycondensation.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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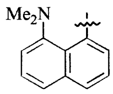
solution. Phosphanes with intramolecular N→P interactions are referred to as pseudo-hypercoordinate phosphanes, taking into account the phosphorus lone electron pair. Comparisons with the corresponding silicon compounds are made where analogies exist between hypercoordinate silicon and phosphorus chemistry[4][5]. Phosphenium salts stabilized by intramolecular coordination of two NMe_2 donor groups at the phosphorus atom are also surveyed. Analogies with the corresponding stabilized silylenium salts are noted.

Intramolecular chelation at the phosphorus atom can principally be achieved by using ligands **1**, **2**, and **3**, introduced by van Koten and co-workers[6] in tin chemistry, and used extensively in silicon chemistry[1]. Each of these has its own particularly interesting features. The rigid geometry of ligand **1**, in which the donor group is fixed in close proximity to the phosphorus centre, facilitate intramolecular coordination. In contrast, the geometry of ligand **2** does not enforce coordination to the phosphorus centre. However, a favourable conformation allowing interaction between the donor atom and the phosphorus atom exists, which is adopted when suitable substituents are also attached at the phosphorus. Finally, ligand **3** permits the study of mono- or bis-coordination at the phosphorus atom, also as a function of the other ligands. Furthermore, it allows the study of fluxional coordination-decoordination processes.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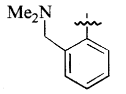
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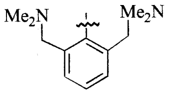
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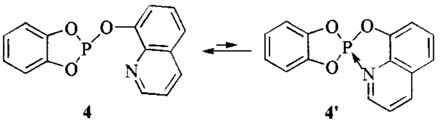
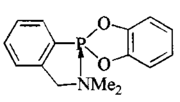
2. Hypercoordinate P^{III} and P^{IV} Phosphorus Derivatives

2.1 Pentacoordinate Phosphonite, Phosphonate, and Thiophosphonate Compounds

An intramolecular N→P interaction was suggested for compound **4**[7] in view of its temperature-dependent ^{31}P-NMR spectrum, the chemical shift decreasing from $\delta = +125$ at 25°C to $\delta = +121.4$ at -80°C. This observation was attributed to an equilibrium between **4** and **4′** (Eq. 1).


4 **4′** (1)

Following this result, we prepared compounds **5**, **6**, **7**, **8**, and **9**[8], which all include the potentially chelating ligand **2**. In Table 1, we report the ^{31}P-NMR resonances of **5−9**, alongside those of the corresponding phosphorus derivatives lacking the NMe_2 group.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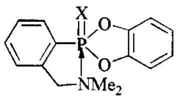

6 : X = O
7 : X = S

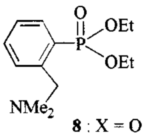
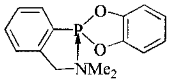
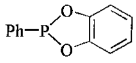
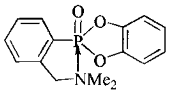
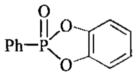
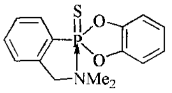
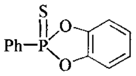
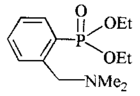
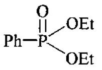
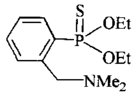
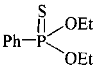
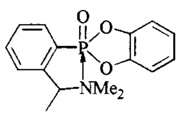

8 : X = O
9 : X = S

Table 1. ^{31}P-NMR chemical shifts (at 293 K) of **5−9** compared to those of the corresponding phosphorus derivatives lacking NMe_2 groups

Compound	δ (ppm)	Compound	δ (ppm)	Δδ
 **5**	+130.7		+177.0[9]	-46.0
 **6**	+13.3		+35.7[10]	-22.4
 **7**	+72.9		+107.1[11]	-34.2
 **8**	+19.6		+16.9[12]	-2.7
 **9**	+83.3		+86.7[8]	+0.4

Significant upfield shifts are observed for **5**, **6**, and **7**, suggesting N→P interactions in these derivatives. Such shifts were not evident for **8** and **9** and the lack of N→P interactions in **8** and **9** was confirmed by their ^1H-NMR spectra, in which the signal of the NMe_2 group appears as a singlet over the temperature range studied (183−293 K) in both cases. In contrast, it was found that **7** is pentacoordinated at room temperature: Its ^1H-NMR spectrum displays two doublets attributable to the NMe_2 protons. These signals appear as doublets because of P,H coupling [$^3J(PH) = 4.8$ Hz]. The situation for **5** and **6** is intermediate. At 183 K, the ^1H-NMR spectra of **5** and **6** display two singlets for the NMe_2 protons. On raising the temperature, coalescence of these signals is observed ($\Delta G^{\neq}_{233K} = 48$ kJ mol^{-1} for **5** and $\Delta G^{\neq}_{218K} = 46$ kJ mol^{-1} for **6**). Two processes could explain the equivalence of the methyl groups, namely pseudorotation around the phosphorus atom or cleavage of the N→P bond with subsequent rotation about the CH_2-N bond and inversion at nitrogen prior to recoordination. In order to clarify this point, we prepared compound **10** bearing a ligand with an asymmetric benzylic carbon atom. From the ^1H-NMR spectrum at room temperature, it was inferred that **10** exists as two isomers in solution in an 80:20 ratio, the NMe_2 protons of each isomer appearing as sharp singlets. The major isomer was isolated and was found to slowly epimerize (CH_2Cl_2, 3 h, 20°C) to give the 80:20 equilibrium mixture. On lowering the temperature, the singlet attributable to the NMe_2 protons of the minor diastereoisomer splits into two signals ($\Delta G^{\neq}_{223K} = 47$ kJ mol^{-1}), while the singlet of the major diastereoisomer gives only a broad signal ($\Delta G^{\neq}_{158K} = 32$ kJ mol^{-1}). The equilibration of the diastereoisomers of **10** can be explained by slow rotation about the P−C_{ipso} bond during the coordination-decoordination process. It is noteworthy that similar results have been observed for the tin derivative **11**[13], and the same explanation has been proposed.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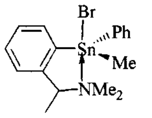
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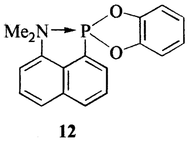
We have also prepared compounds **12−14**[8] incorporating ligand **1**, which imposes intramolecular coordination at the phosphorus atom. As a result, it is possible to study the permutational isomerization processes in these derivatives by dynamic ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of **12−14** exhibit only one singlet for the NMe_2 protons at room temperature. However, on lowering the temperature, the singlet splits into two signals in each case. From the coalescence temperature of the methyl group signals (273 K for **12** and **13**; 255 K for **14**), $\Delta G^{\neq}$ values of 57−58 kJ mol^{-1} can be estimated for the pseudorotation processes in these three compounds. For **15**, only one singlet is observed for the *N*-methyl protons, even at low temperature, indicating either a facile permutational isomerization process about the phosphorus atom or a symmetrical arrangement of the molecule. Therefore, the X-ray crystal structure of this compound was determined (Figure 1). It reveals a dissymmetric geometry, the lone pair of the nitrogen atom being directed towards the phosphorus atom *trans* to a P−OEt bond, with an N−P distance of 2.87 Å. Furthermore, the basic pyramidal configuration around the phosphorus atom is only slightly deformed, so that the molecule can be described as a mono-capped tetrahedron in which the phosphorus atom is [4+1] coordinated[8]. Thus, the non-diastereotopy of the NMe_2 protons is probably due to a fast permutational isomerization process occurring at the phosphorus centre.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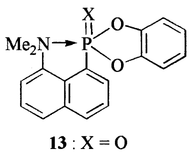
13 : X = O
14 : X = S

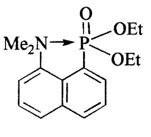
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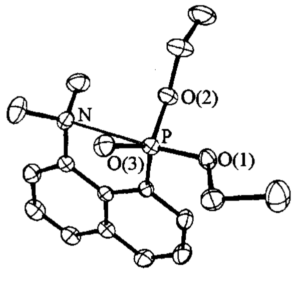
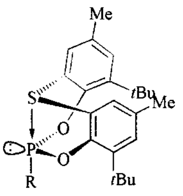
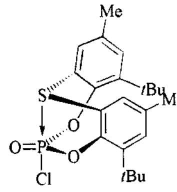
Figure 1. X-ray crystal structure of **15**



Similarly, Holmes et al.[14] have recently prepared the chloro and amino phosphites **16a** and **16b**, as well as the phosphate **17**. In these compounds, intramolecular S→P interactions are observed. Indeed, X-ray crystal structure determinations for these compounds have revealed S−P distances notably shorter than the sum of the van der Waals radii for phosphorus and sulfur (2.816, 2.952, and 3.114 Å for **16a**, **16b**, **17**, respectively), the geometry around the phosphorus atom being a pseudo-trigonal bipyramid for **16a** and **16b** and a trigonal bipyramid for **17**, with the eight-membered ring in the boat-boat conformation.


16 a : R = Cl
b : R = NMe_2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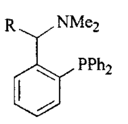
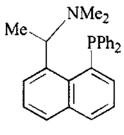
2.2 Pseudo-Pentacoordinate Phosphanes and Pentacoordinate Phosphane Derivatives

Phosphanes **18**[15−18], **19**[19,20], **20**[21], and **21**[22−24] have previously been prepared in order to study their abilities to act as mono- or bis-chelating ligands. However, to the best of our knowledge, the potential occurrence of N→P interactions has not been considered for these phosphanes, apart from in the case of **21**[22]. We have prepared phosphanes **21**[25], **22**[26], **23**[26], and **24**[27], as well as phosphane oxide **25**, phosphane sulphide **26**, and phosphonium salts **27−29**, all of which incorporate the rigid ligand **1**. X-ray crystal structure analyses of phosphanes **21**[25] and **23**[26] (Figure 2) and of the phosphonium salt **29**[26] reveal that the phosphorus atom resides in a nonsymmetric environment in each case, the lone pair of the nitrogen atom being directed towards the phosphorus atom *trans* to one P−C bond in **21** and **23**, and *trans* to the benzyl group in **29**[26]. The N−P distances in **21**, **23**, and **29** are 2.71, 2.62, and 2.83 Å, respectively, and these distances increase as a result of steric hindrance around the phosphorus atom. Furthermore, in these three compounds, the pyramidal configuration around the phosphorus atom is retained with only a slight deformation. Thus, the geometry of these compounds can be described as mono-capped tetrahedral, where the phosphorus atom is pseudo-[4+1]-coordinated in **21** and **23**, and [4+1]-coordinated in **29**. It is noteworthy that the silicon compound **30** also has a dissymmetrical structure, with the lone pair of the nitrogen atom directed towards the silicon atom, *trans* to an Si−C_{sp} bond[26], with an N−Si bond length of 2.72 Å.

Dynamic ^{1}H-NMR studies of compounds **21−28** have been carried out in solution. At 273 K, the spectrum of phosphane **21** ($CD_2Cl_2/CFCl_3$) exhibits a singlet due to the NMe_2 protons, which splits into two signals[25] on lowering the temperature. The same behaviour is observed for phosphane **23**[26] and the phosphane derivatives **25−28**[25,27].



18 a : R = H
b : R = Me



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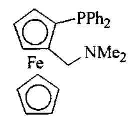

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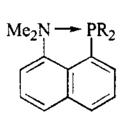
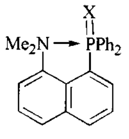
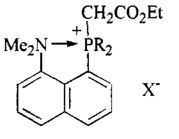


21 : R = Ph
22 : R = Me
23 : R = C≡CPh
24 : R = H

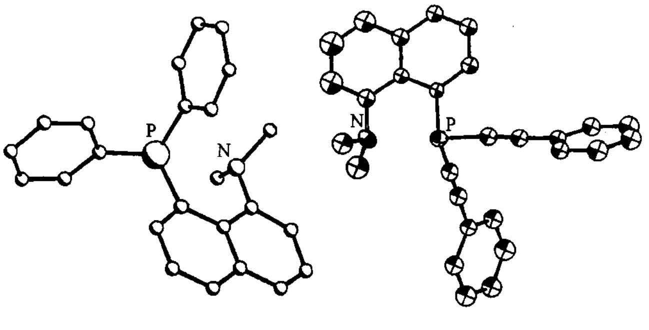


25 : X = O
26 : X = S



27 : R = Ph, X = Br
28 : R = Me, X = I

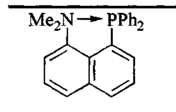
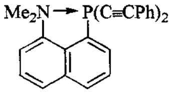
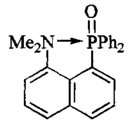
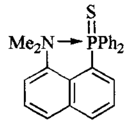
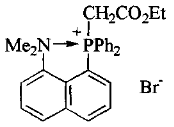
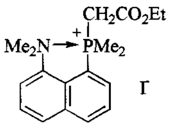
Figure 2. X-ray crystal structures of **21** (left) and **23** (right)

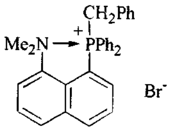


For phosphanes **22**[26] and **24**[27], only broadening of the singlet attributable to the NMe_2 protons is observed at 173 K. This shows that all these compounds (**21**−**29**) are pseudo-pentacoordinated or pentacoordinated in solution, with dissymmetrical geometries, in agreement with the solid-state structures of **21**, **23**, and **29**. In solution at room temperature they undergo a fast permutational isomerization process, the calculated $\Delta G^{\neq}$ values of which are reported in Table 2. These values indicate that isomerization is easier for phosphanes than for phosphane derivatives. This process should also be easier for compounds with Me substituents at the phosphorus atom than for compounds with Ph substituents, since the decoalescence of the NMe_2 signals could not be observed for phosphanes **22** or **24**. It is noteworthy that the behaviour in solution of the silicon compound **30**[26] has also been studied by ^{1}H-NMR spectroscopy. It is similar to that of **23**, with a $\Delta G^{\neq}$ value of 55.2 kJ mol^{-1} for the equivalence of the NMe_2 groups.

The diphosphane **31** has also been prepared[26]. It was found by ^{1}H-NMR studies that **31** and **21** show similar behaviour in solution. Thus, at room temperature, all the NMe_2 protons are equivalent and appear as a singlet, which splits into two signals at 178 K. This indicates that **31** is pentacoordinated in solution and undergoes a permutational isomerization process at room temperature. The calculated $\Delta G^{\neq}$ for this process is 36.8 kJ mol^{-1}, this value being very similar to that found for phosphane **21**.

Table 2. ^{1}H-NMR data (CD_2Cl_2) for NMe_2 groups and calculated $\Delta G^{\neq}$ values for the permutational isomerization process in compounds **21**, **23** and **25**−**28**

Compound	T (K)	δ (NMe_2)	T_c (K)	$\Delta G^{\neq}$
 **21**	273	2.32	183	37.5[25]
	163	1.87-2.50		
 **23**	273	2.63	183	37.2[26]
	183	2.60 (broad)		
 **25**	293	2.15	253	53.0[25]
	253	1.60-2.47		
 **26**	273	2.05	243	48.1[25]
	203	1.42-2.50		
 **27**	293	1.89	273	55.2[25]
	233	1.32-2.61		
 **28**	293	2.68	233	42.8[27]
	183	2.25-2.75		



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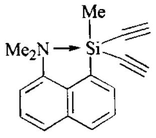
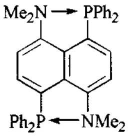


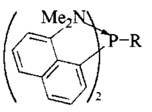
30

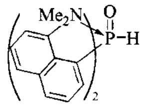


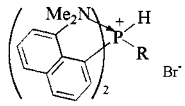
31

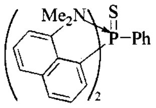
2.3 Pseudo-Hexacoordinate Phosphanes and Hexacoordinate Phosphane Derivatives

We have prepared phosphanes **32** and **33**, as well as their derivatives **34**−**37**. X-ray structure analyses of the phosphane **32**[28] and of phosphorus derivatives **35**[29] and **37**[28] have been performed (Figure 3). In each case, they reveal that the nitrogen lone pairs are directed towards the phosphorus atom, one NMe_2 group being *trans* to the P−Ph bond, while the other is opposite to a P−naphthyl bond with N−P−N angles of 102.4°, 94.9°, and 106.9°. The N−P distances are 2.70−2.73 Å in **35**, 2.78−2.79 Å in **32**, and 3.01 Å in **37**. The longer distance in **37** is probably due to the steric hindrance at the phosphorus atom, while the short distance in **35** is most probably attributable to the positive charge on the phosphorus atom. In each case, the pyramidal configuration around the phosphorus atom is retained and the geometries of these compounds correspond to a bi-capped distorted tetrahedron (taking into account the nitrogen lone pair in **32**) rather than to a distorted octahedron. It is noteworthy that X-ray structure analysis of the analogous silicon compound **38**[30] showed the same geometry.


32 : R = Ph
33 : R = Me


34


35 : R = Ph
36 R = H


37

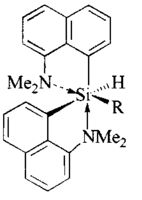
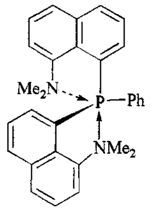
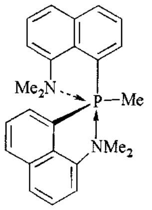
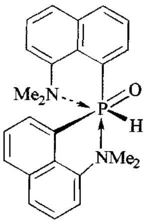
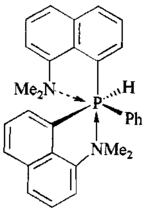

38 (R = H, F)

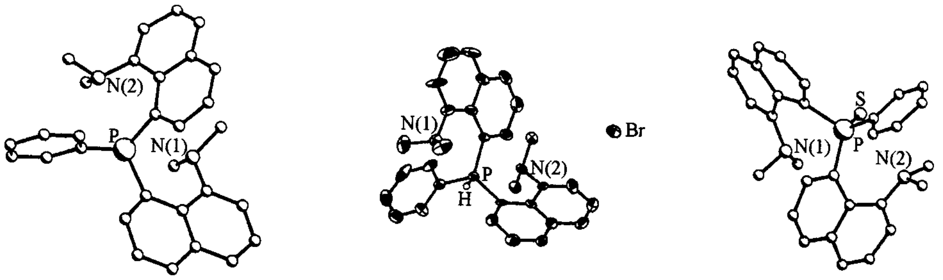
Table 3. ^{1}H-NMR data for NMe_2 groups and calculated $\Delta G^{\neq}$ values for the permutational isomerization process in compounds **32**−**35**

Compound	Solvent	T (K)	δ (NMe_2)	$\Delta G^{\neq}$ (300 K)
 **32**	($CDBr_3$)	258	3.18, 1.94, 2.06, 2.93	62.3
		398	2.56[a]	
 **33**	(toluene-d_8)	233	2.84, 1.63, 2.43, 2.69	57.5
		373	2.22, 2.54	
 **34**	(toluene-d_8)	233	3.06, 1.92, 0.82, 2.71	56.2
		373	2.52, 1.92	
 **35**	($CDBr_3$)	283	3.20, 1.67, 1.88, 3.02	59.9
		395	2.44, 2.49	

[a] Unresolved doublet.

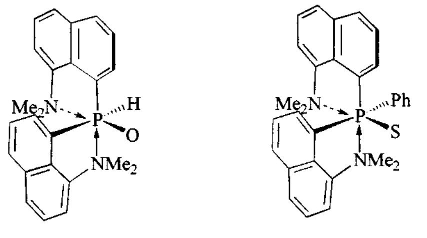
The solution ^{1}H-NMR spectra of phosphanes **32** and **33**, that of phosphane oxide **34**, and those of phosphonium salts **35** and **36**, at limiting temperatures for slow exchange, display four sharp signals attributable to the NMe_2 protons[31]. Selective irradiation of each methyl signal shows a transfer of saturation occurring between pairs of equivalent sites, one methyl of an NMe_2 group being equivalent to one methyl of the other NMe_2 group. At the same temperature, the ^{1}H-NMR spectra of these derivatives also show two discrete sets of naphthyl group signals. These data indicate that compounds **32**−**36** are hexacoordinated in solution, with dissymmetrical geometries, in agreement with the X-ray structures of **32**, **35**, and **37**. Furthermore, the ^{1}H-NMR spectra of these compounds are temperature-dependent. On raising the temperature there is coalescence of the four methyl signals into two essentially well-resolved signals (Table 3). Dynamic ^{1}H-NMR study of phosphonium salt **36**, which is the first known phosphonium salt with two P−H bonds, was not possible since it decomposes in solution at room temperature[27]. The ^{1}H-NMR spectrum of phosphane oxide **34** at 233 K shows a strongly deshielded signal at δ = 9.78. This downfield signal was assigned to the proton of the naphthyl group located in the deshielding zone of the P=O bond. This suggests that **34** adopts a conformation in which the N→P bond interaction is *trans* to the P=O bond (Figure 4). The coalescence of the four methyl group signals to give two signals can be explained

Figure 3. X-ray crystal structures of **32** (left), **35** (centre), and **37** (right)



by a permutational isomerization process around the phosphorus atom, which occurs without cleavage of the N→P bond. The $\Delta G^{\neq}$ value for this process lies in the range 58−62 kJ mol^{-1} (Table 3). We note that similar solution behaviour was observed for the silicon compound **38** (R = F) by ^{1}H-NMR spectroscopy, the permutational isomerization process[32] taking place with a $\Delta G^{\neq}$ value of 62.4 kJ mol^{-1}.

Figure 4. Schematic representation of **34** and of the minor isomer of **37**

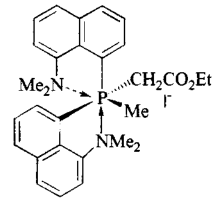


34 **37** (minor isomer)

Further raising of the temperature leads to the decomposition of **34** and **35** above 400 K. Coalescence of the two slightly separated signals into one was observed only for phosphane **32** (at 418 K in [D$_4$]-*o*-dichlorobenzene), thus indicating the cleavage of the N→P bond with an estimated $\Delta G^{\neq}$ value of 90 kJ mol^{-1}.

The solid-state ^{31}P-NMR spectrum of **37** shows one signal at δ = 50.9. In contrast, the ^{31}P-NMR spectrum of **37** in C_6D_6 displays two resonances at room temperature (at δ = 63.9 and δ = 53.5), which indicates that **37** exists as two isomers in solution. This was confirmed by a dynamic ^{1}H-NMR study. At the limiting temperature for slow exchange, the ^{1}H-NMR spectrum of **37** exhibits eight signals for the *N*-methyl protons, indicating the existence of two isomers in solution, the ratio of which depends on the solvent (50:50 in bromoform and 80:20 in toluene). Furthermore, comparison of the ^{31}P-NMR chemical shifts of **37** in solution and in the solid state shows that one of the isomers observed in solution (δ = 53.5) is presumably that present in the solid state (δ = 50.9). The structure of the other isomer (δ = 63.9 in C_6D_6) was inferred from a low-temperature ^{1}H-NMR study of the naphthyl protons. At 233 K (in [D$_8$]toluene), the ^{1}H-NMR spectrum of this isomer displays one signal at δ = 9.8, suggesting a structure similar to that of **34**, with the N→P bond lying *trans* to the P=S bond (Figure 4). COSY experiments on the mixture of isomers of **37** show that each methyl group of the NMe$_2$ groups exchanges with the other three, indicating an interconversion of the two isomers in solution. On raising the temperature, each methyl signal broadens, and they finally coalesce into a very broad signal at 373 K. Further raising of the temperature leads to the decomposition of the isomers at 405 K. Thus, two phenomena take place: (a) a permutational isomerization process occurring independently on each isomer, and (b) the interconversion of these isomers. This latter phenomenon was detected by means of COSY and NOESY experiments.

The ^{1}H-NMR spectra of **39** and **40** at room temperature show that these compounds are also hexacoordinated in solution, with dissymmetrical geometries[29]. Indeed, the ^{1}H-NMR spectrum of **39** exhibits four sharp singlets for the methyl groups and two sets of naphthyl proton signals. The PCH$_2$ protons are diastereotopic and appear as doublets of doublets. The ^{1}H-NMR spectrum of **40** displays eight singlets for the methyl groups and a multiplet for the diastereotopic PCH$_2$ protons, thus indicating that this compound exists as two isomers in solution, as in the case of **37**. Further evidence for the existence of two isomers is provided by the ^{31}P-NMR spectrum of **40**, which also exhibits two resonances.



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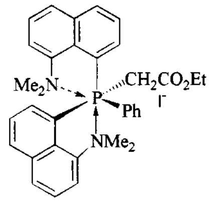

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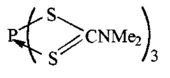
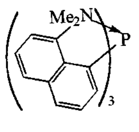
2.4 Pseudo-Heptacoordinate Phosphanes

The first pseudo-heptacoordinate P^{III} phosphorus derivative **41** was described by Paine and co-workers[33]. This complex was obtained by insertion of CS$_2$ into the P−N bond of the aminophosphane P(NMe$_2$)$_3$. Single-crystal X-ray structure analysis of **41** showed that the phosphorus centre is formally seven-coordinated, with six sulfur atoms (three short P−S bonds of mean length 2.178 Å and three long P−S bonds of mean length 2.966 Å) and the phosphorus lone pair forming a distorted capped trigonal antiprism.



41



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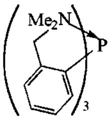
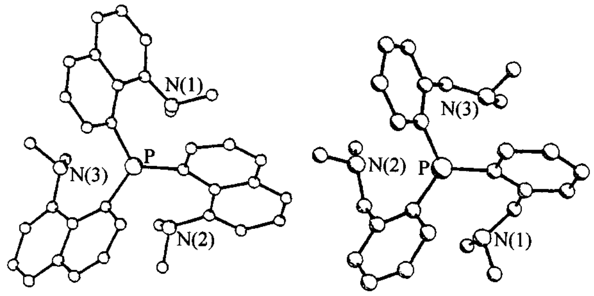
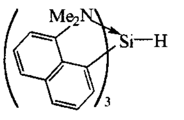


43

We have prepared the phosphanes **42** and **43**[34], the X-ray crystal structures (Figure 5) of which reveal in both cases three weak N→P interactions with N−P distances of 2.80, 2.84, and 2.85 Å in **42** and 3.00, 3.01, and 3.07 Å in **43**. The pyramidal configuration around the phosphorus atom is retained and nitrogen coordination is observed *trans* to a P−C bond. Thus, the geometry of these phosphanes corresponds to a tri-capped tetrahedron[34] (taking into account the nitrogen lone pair). It is important to emphasize that phosphanes **42** and **43** adopt the same geometry, even though there is no steric constraint in phosphane **43** to force the NMe$_2$ groups to interact with the phosphorus centre. However, their ^{1}H-NMR spectra are notably different. Thus, while the ^{1}H-NMR spectrum of **43** exhibits only one sharp singlet for the methyl protons, even at low temperature, that of **42** displays two singlets for the methyl protons, even up to 90°C (250 MHz). This notable difference indicates that N→P interactions are maintained in solution in the case of **42**, while an equilibrium between the opened and closed forms should be operative in solution for **43**. The same tri-capped tetrahedral geometry was also found in the silanes **44**[35] and **45**[36].

Figure 5. X-ray crystal structures of **42** (left) and **43** (right)





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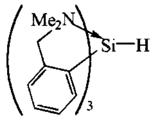


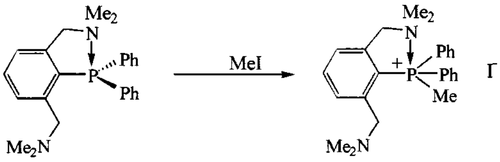
45

2.5 Reactivity of Pseudo-Hypercoordinate Phosphanes

The reactivity of phosphanes **21**, **32**, and **42**, incorporating one, two, or three 8-(dimethylamino)naphthyl ligands **1** decreases with the increasing number of ligands **1**, undoubtedly because of the increasing steric hindrance at the phosphorus atom and of the increasing number of N lone pairs in the P coordination sphere.

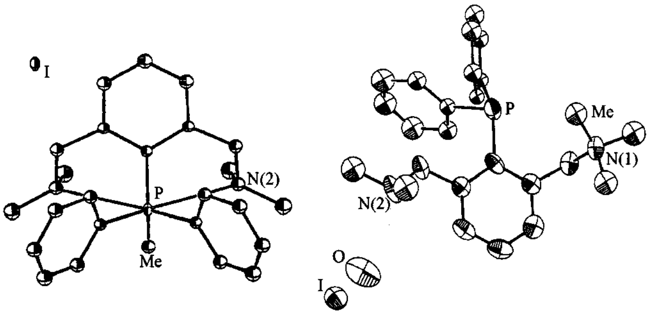
The reactivity of the pseudo-pentacoordinate phosphane **21** is very similar to that of triphenylphosphane. Thus, treatment of **21** with H_2O_2, S_8, CH_3I, or $BrCH_2CO_2Et$ affords the expected products in satisfactory yields[37] (58−65%). The pseudo-hexacoordinate phosphane **32** is less reactive than **21**. While its oxide and sulfide can be prepared under the classical reaction conditions in 60 and 67% yield, respectively, the formation of the phosphonium salt **40** required reaction with ICH_2CO_2Et for 24 h in refluxing toluene[27]. Finally, the reactivity of the pseudo-heptacoordinate phosphane **42**[34] is very different from that of **21** and **32**, as well as that of triphenylphosphane. It was not possible to obtain the corresponding oxide, nor the phosphane sulfide. However, reaction of **42** with CH_3I furnished the corresponding phosphonium salt in low yield (32%) after 10 days heating in a sealed tube at 100°C. In contrast, the pseudo-heptacoordinate phosphane **43**, incorporating three flexible ligands **2**, shows a reactivity similar to that of triphenylphosphane towards H_2O_2 or sulfur, but reacts with MeI to afford only the product of methylation at one amino group in 62% yield after 3 h at 100°C. This difference of reactivity between **42** and **43** towards MeI is consistent with their ^{1}H-NMR data in solution, which indicate a stronger N→P interaction in **42** than in **43**.

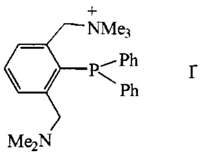
Phosphane **46**, incorporating the potentially bis-chelating ligand **3**, reacts with MeI to give the phosphonium salt **47** (Eq. 2), which undergoes a coordination-decoordination process in solution[38]. An X-ray structure determination of **47** (Figure 6) shows that the lone pairs of the two nitrogen atoms are directed symmetrically towards the phosphorus atom, with N−P distances of 3.14 and 3.16 Å. Furthermore, the tetrahedral geometry of the phosphorus atom is maintained so that the geometry around the phosphorus centre is that of a slightly distorted bi-capped tetrahedron. This conformation of the NCN ligand is similar to those found in transition-metal compounds incorporating this ligand[39]. During crystallization of **47**, a very small number of atypical crystals were found, the structure of which (Figure 6) revealed that they were composed of the ammonium salt **48**. The striking feature of this structure is that one methyl of the NMe_3^+ group is positioned close to the phosphorus atom, at a distance of 3.44 Å. This suggests that MeI could react with **46** to afford first the ammonium salt **48**, which should then undergo a fast rearrangement to **47** due to the favorable geometry of the NMe_3^+ group in relation to the P atom.



46 **47** (2)

Figure 6. X-ray crystal structures of **47** (left) and **48** (right)





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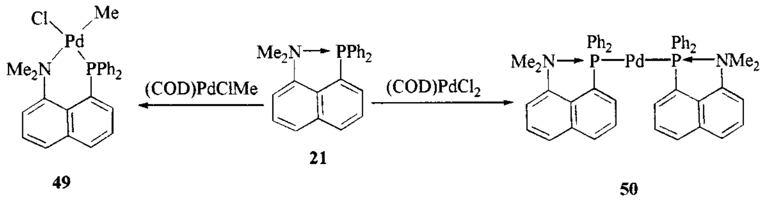
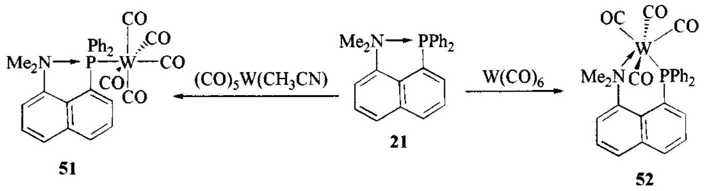
The reactivity of phosphanes **21**, **32**, and **42** towards transition-metal compounds was also investigated. The pseudo-pentacoordinate phosphane **21** may act as a monodentate ligand via the phosphorus atom or as a bidentate ligand via both the phosphorus and nitrogen atoms, depending on the experimental conditions. Thus, when $[(COD)PdCl_2]$ was allowed to react with 2 equiv. of **21**, complex **50** was formed, in which **21** coordinates to the Pd centre only via the phosphorus atom. On the other hand, **21** reacts with

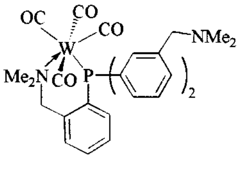
Scheme 1



Scheme 2



[(COD)PdClMe] as a bidentate ligand[24] to afford **49** (Scheme 1). Similarly, **21** reacts with [$(CO)_5W(CH_3CN)$] as a monodentate ligand to afford complex **51** (Scheme 2), but with $W(CO)_6$ as a bidentate ligand to form complex **52**, the X-ray structure analysis[24] of which was performed. Phosphane **32** does not react appreciably with $W(CO)_6$ and no complex was isolated under these conditions. As regards phosphane **42**, it is completely unreactive towards $W(CO)_6$, as well as towards [$THF \cdot W(CO)_5$]. Phosphane **43**, incorporating three flexible ligands **2**, reacts with $W(CO)_6$ to give complex **53**, an X-ray structure determination[37] of which showed that the tungsten atom is complexed by one nitrogen atom and by the phosphorus centre, leaving two free NMe_2 groups. A similar bidentate carbonyltungsten complex **54** had previously been proposed[21] on the basis of IR and ^{1}H-NMR spectra. The pattern of CO stretching bands in the IR spectrum of complex **52** (2012, 1885, 1856 cm^{-1}) is similar to that seen for **54** (2018, 1889, 1832 cm^{-1}), but different from that in the case of complex **51** (2070, 1978, 1834 cm^{-1}). This latter spectrum closely resembles that of $Ph_3PW(CO)_5$ (2075, 1980, 1938 cm^{-1})[40].



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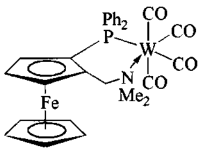

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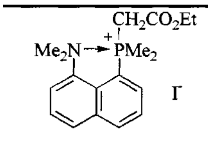
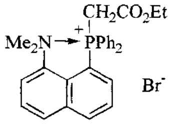
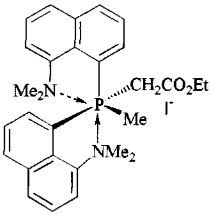
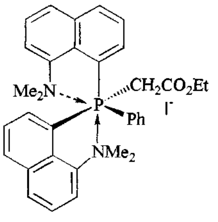
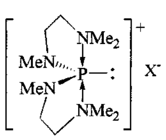
2.6 Reactivity of Hypercoordinate Phosphonium Salts

We have investigated the reactivity of some hypercoordinate phosphonium salts under Wittig conditions in order to study the effect of the N→P interaction on the rate and stereoselectivity of this reaction[29]. Some selected results are reported in Table 4. The pentacoordinate phosphonium salts **27** and **28** were found to react readily with benzaldehyde under Wittig conditions to give ethyl cinnamate, with **28** being more reactive than **27**. Furthermore, both substrates proved to be much more reactive than $Ph_3P^+CH_2CO_2Et$ under the same conditions, furnishing ethyl (*E*)-cinnamate with very good stereoselectivity. However, they were unreactive towards ketones under Wittig

Table 4. Results of Wittig reactions of phosphonium salts **27**, **28**, **39** and **40** with benzaldehyde under different experimental conditions; yields (*E*/*Z* ratio) of ethyl cinnamate

Phosphonium Salt	Reaction conditions NaNH$_2$ / Et$_2$O [reaction times]	 NaOH / C$_6$H$_6$ / H$_2$O [reaction times]
 **28**	75% (95/5) [1 h]	40% (86/14) [5 min]
 **27**	51% (99/1) [22 h]	77% (86/14) [2 h]
$Ph_3P^+CH_2CO_2Et\ Br^-$	8% (97/3)	-
 **39**	0% [44 h]	60% (92/8) [44 h]
 **40**	0% [96 h]	20% (97/3) [96 h]



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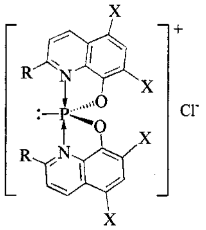
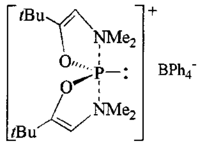


56 X = H, Br
R = H, Me



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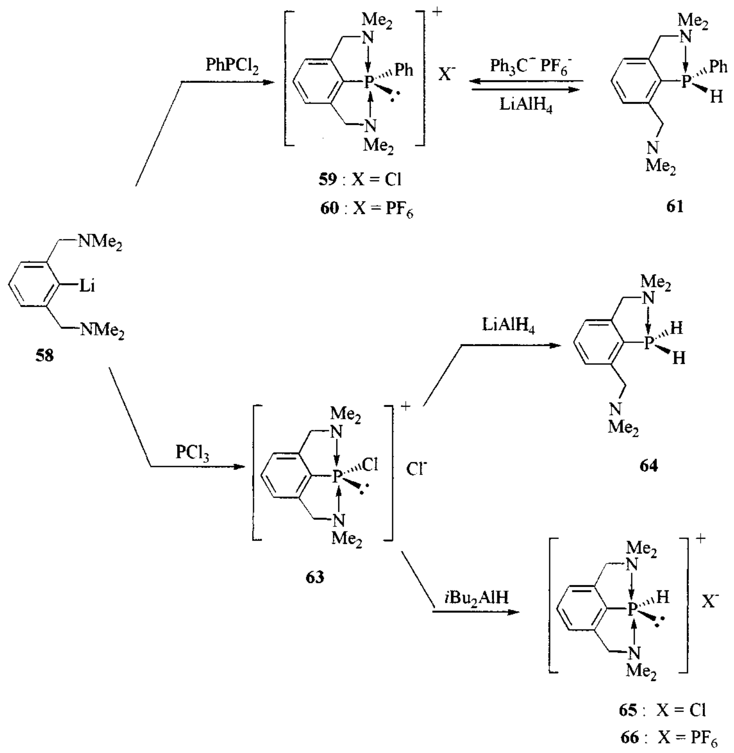
conditions. Due to the steric hindrance at the phosphorus atom, hexacoordinate phosphonium salts **39** and **40** are much less reactive than **27** and **28**. They react with PhCHO only under particular experimental conditions (Table 4), nevertheless showing good stereoselectivity. Thus, it can be concluded that electronic factors dominate over steric ones for compounds **27** and **28**, whereas for hexacoordinate phosphonium salts **39** and **40** incorporating two rigid ligands **1**, steric factors dominate the outcome of the Wittig reaction, resulting in poor reactivity.

3. Pseudo-Pentacoordinate Stabilized Phosphenium Salts

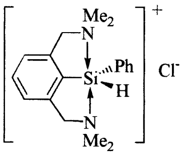
Phosphenium ions are reactive species[41] which can be stabilized by inter-[42−44] or intramolecular[45,46] coordination of donor groups on the phosphorus atom. The stabilization of phosphenium ions by twofold intramolecular coordination by nitrogen atoms was proposed by Schmutzler and Becker[47], who prepared the salt **55**. Subsequently, Lamandé and Munoz obtained salts **56**[48], the structures of which were inferred from ^{13}C- and ^{31}P-NMR studies. Finally, an X-ray crystal structure analysis of the salt **57**[49] revealed the pseudo-pentacoordination of the phosphorus atom in the cation, in a geometry close to a trigonal bipyramid, with N→P bond distances of 2.05 and 2.06 Å.

Ligand **3**, which has been found to stabilize silylenium ions[50−52], also permits the stabilization of phosphenium ions. Thus, reaction of the lithium derivative **58** with $PhPCl_2$ did not afford the phosphane $(Ar)_2PPh$, but rather an extremely air- and moisture-sensitive white powder **59** (Scheme 3), the ^1H-NMR spectrum of which featured two singlets for the NMe_2 protons and one AB pattern for the benzylic protons. The same ^1H-NMR pattern was found for the silylenium ion **62**[50−52]. Treatment of **59** with $NaPF_6$ furnished the corresponding hexafluorophosphate salt **60**, the ^{31}P-NMR spectrum of which exhibits two signals of equal intensity, one at $\delta = +95.5$, very close to that observed for **59**, and the other at $\delta = -143.6$ (PF_6^-). All these data are clearly consistent with an ionic structure for **59**. Reaction of this salt with $LiAlH_4$ afforded the phosphane **61** (Scheme 3), the ^{31}P-NMR chemical shift of which is upfield [$\delta = -77.5$, $^1J(PH) = 225$ Hz] with respect to that of Ph_2PH[53] ($\delta = -41.0$), thus suggesting an intramolecular N→P interaction. From the ^1H-NMR spectrum, it was inferred that phosphane **61** is pseudo-pentacoordinated at the phosphorus atom due to a rapid coordination-decoordination process of the NMe_2 groups. The increase in coordination number of the phosphorus atom in **61** gives rise to an unusual reactivity of the P−H bond. Indeed, **61** undergoes hydride abstraction upon reaction with Ph_3C^+-

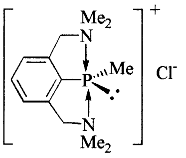
Scheme 3



PF_6^- (Scheme 3), reforming the stabilized phosphenium salt **60**. It is noteworthy that hydride abstraction does not occur in the case of "classical" secondary phosphanes, but rather quaternization of the phosphane takes place[54]. The modification of the reactivity of a bond because of extra coordination is a well-known phenomenon in silicon chemistry[1], but has not previously been observed in phosphorus chemistry. Reaction of the lithium derivative **58** with PCl_3 gives rise to the phosphorus salt **63**, which was found to be extremely air- and moisture-sensitive. $LiAlH_4$ reduction of **63** gave phosphane **64**, while $i\mathrm{Bu}_2AlH$ reduction unexpectedly afforded **65**, which represents the first stabilized phosphenium ion with a P−H σ bond (Scheme 3). The ^{1}H-NMR spectrum of this compound exhibits the same pattern for the NMe_2 and benzylic protons as **59**, indicating the coordination of both NMe_2 groups to the phosphorus atom[55]. The ^{1}H-NMR signals of the CH_2NMe_2 "arms" in the analogous P−Me salt **67**[27] are different from those in the case of salts **59** and **65**. At room temperature, the NMe_2 groups in **67** give rise to a single broad signal, while the benzylic protons appear as an AB pattern. On lowering the temperature, the NMe_2 signal splits into two signals and at 253 K the pattern due to the CH_2NMe_2 arms is the same as that seen for **59** and **65**. These observations can be explained in terms of a fast fluxional coordination-decoordination process of the NMe_2 groups at the phosphorus centre, which renders these groups equivalent at room temperature. However, the chirality at the phosphorus atom[27] is maintained, probably because of a slow rotation about the $P-C_{ipso}$ bond, thus explaining the diastereotopy of the benzylic protons. An X-ray crystal structure determination of the hexafluorophosphate **66**[55] has confirmed the pseudo-pentacoordination at the phosphorus atom, the geometry of the cation being that of a distorted trigonal bipyramid with N−P distances of 2.08 and 2.07 Å, distances very close to those observed in the salt **57**.



62



67

4. Conclusion

In this review, we have described hypercoordinate phosphorus compounds in which extra coordination at the phosphorus centre is provided by intramolecular interaction of strategically positioned NMe_2 groups. Pseudo-hypercoordinate phosphanes have structures very similar to those of the corresponding silicon derivatives with an Si−H bond, and both series of compounds show similar fluxional behaviour in solution. The N−P distances are generally rather long (2.7−3.0 Å), but amount to less than the sum of the van der Waals radii of phosphorus and nitrogen atoms (3.4 Å[56]). The geometry at the phosphorus atom invariably corresponds to a capped tetrahedron, which is generally somewhat distorted. It is noteworthy that the structural characteristics of the pseudo-hexacoordinate phosphanes and the hexacoordinate phosphane derivatives are quite different from those of the hexacoordinate phosphoranes in that the P−N distances are less than 2 Å[3] in the latter, which have octahedral geometries. This can be explained in terms of the generally high electronegativities of the ligands surrounding the phosphorus atoms in phosphoranes. Intramolecular N→P donor-acceptor interactions induce an increase in the reactivity of the phosphorus derivatives. Thus, the pentacoordinate phosphonium salts are much more reactive than the corresponding phosphorus derivatives lacking the NMe_2 groups. Indeed, an unusual reactivity of a P−H bond due to extra coordination at the phosphorus atom has been observed for the first time in the case of a hypercoordinate phosphane.

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