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N,N′,N′-Trimethylethylenediamine as a substituent group at main group centers: intramolecular donor–acceptor interactions and unusual modes of coordination in compounds of silicon and phosphorus and their transition metal complexes

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ABSTRACT

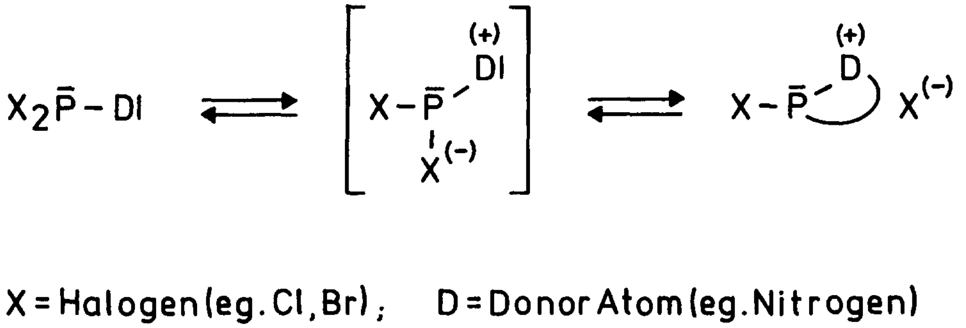
This review is concerned with the role of the *N,N′,N′*-trimethylethylenediamine group as a substituent at phosphorus atoms in different coordination and/or oxidation numbers. A few examples for silicon are also presented.

Intramolecular donor–acceptor interactions between the nitrogen atom of the dimethylamino group and Si or P as the central atom were first noted in some *N,N′,N′*-trimethylethylenediamine-substituted fluorosilanes ($LSiF_3$, $PhSiF_2L$) and P(III)Cl systems, e.g. $LPCl_2$ and PhP(Cl)L (L = *N,N′,N′*-trimethylethylenediamine group). These observations gave rise to a more detailed study of the coordinating behavior, especially of further phosphorus compounds of different substitution pattern. Spontaneous intramolecular coordination with formation of salt-like products was observed, especially, for compounds in which a phosphorus-bonded halogen atom is available to dissociate as an anion. A dependence both on the nature of the halogen atom and on the nature of other ligands at P(III) [or P(V)] was noted and will be discussed. Through the action of Lewis acids, e.g. $AlCl_3$ of PF_5, or in the reaction with tetraphenylborate as a non-coordinating anion, halide abstraction and consequent formation of the $Me_2N \rightarrow P$ coordinative bond from acyclic *N,N′,N′*-trimethylethylenediamine-substituted halophosphines or trimethylethylenediamine-substituted fluorophosphoranes could be induced. No such $Me_2N \rightarrow P$ coordination took place during oxidation of *N,N′,N′*-trimethylethylenediamine-substituted phosphorus(III) compounds with oxidizing agents, e.g. sulfur, selenium, *o*-quinones or hexafluoroacetone. Numerous oxidation reactions were conducted on intramolecularly stabilized phospholidin-1-ium salts. They furnished the expected oxidation/addition products. This was accompanied in some cases (depending on the nature of the substituents at P(III)) by a scission of the coordinative $Me_2N \rightarrow P$ bond. The reaction of phospholidin-1-ium salts with phenyl azide, dimethyl sulfoxide and sulfur furnished phosphonic acid diamides and substituted λ^4-phospholidin-1-ium salts, as well as substituted diazadiphosphetidines, as a result of the dimerization of P=N species. Intramolecular donor–acceptor interaction in *N,N′,N′*-trimethylethylenediamine-substituted fluorophosphoranes was only observed in the presence of the Lewis acid, phosphorus pentafluoride leading to the formation of hexafluorophosphate salts. The reaction of dialkylamino-substituted tetrafluorophosphoranes with *N*-trimethylsilyl-*N,N′,N′*-trimethylethylenediamine took an unusual course. Instead of the expected P–F cleavage and formation of an *N,N′,N′*-trimethylethylenediamine-substituted dialkylaminotrifluorophosphorane, cyclic tetrafluorophosphates with a λ^6P atom, and dialkylaminotrimethylsilane were formed. The reaction of phosphorus(III)–*N,N′,N′*-trimethylethylenediamine compounds with transition metal compounds [Fe(0), Cr(0), Mo(0), Pt(II)] furnished mono-, di- or trisubstituted coordination compounds, depending on the nature of the metal. The P(III) ligand was bonded in some cases via P(III) only (as a monodentate ligand) and in other cases as a chelating ligand coordinated via P(III) and N.

A variety of variable-temperature NMR experiments have examined the dynamic processes occurring at room temperature in solution, and X-ray single-crystal structure determinations have been conducted in many cases to characterize these new and unusual compounds.

1. INTRODUCTION

This review follows from the synthesis of *N*-trimethylsilyl-*N,N′,N′*-trimethylethylenediamine, $Me_3Si(Me)NCH_2CH_2NMe_2$, and subsequent investigations on silicon and phosphorus derivatives, and also transition metal complexes involving the $N(Me)CH_2CH_2NMe_2$ grouping. Systems involving the *N,N′,N′*-trimethylethylenediamine substituent group at phosphorus and, in a few cases, at silicon, and the intramolecular donor–acceptor interaction between the NMe_2 nitrogen atom and the phosphorus center are reviewed. *N*-Trimethylsilyl-*N,N′,N′*-trimethylethylenediamine (**1**), the precursor compound for such systems, appeared in the literature in 1986. Its reaction with substituted halosilanes and phosphorus halides (involving various oxidation and coordination numbers of phosphorus) has given rise, in many cases, to novel products. Many of them are distinguished by the above-mentioned intramolecular $N \rightarrow P$ interaction between the Me_2N nitrogen atom of the $-N(Me)CH_2CH_2NMe_2$ group and either a silicon or, especially, a phosphorus atom in the same molecule. In the case of phosphorus they are formed, in general, with elimination of a halide anion, according to Scheme 1. There are many reports of intermolecular donor–acceptor complexes involving silicon and, especially, phosphorus(V) as acceptor atoms. In contrast, comparatively few cases of intramolecular donor–acceptor interaction of compounds of silicon and phosphorus are known ([1–27] for silicon and [28–43] for phosphorus are representative).

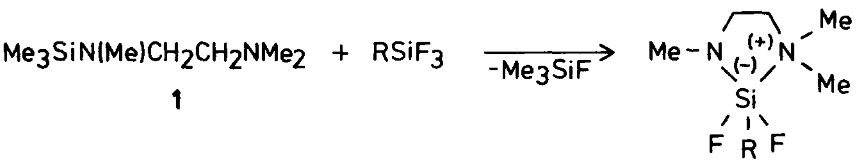


Scheme 1.

2. INTRAMOLECULARLY STABILIZED COMPOUNDS OF SILICON INVOLVING THE *N,N′,N′*-TRIMETHYLETHYLENEDIAMINE SUBSTITUENT GROUP

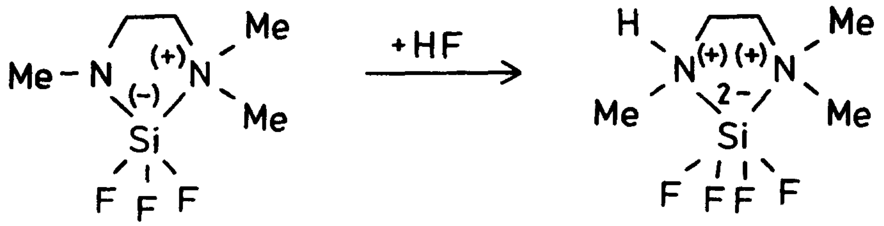
Intramolecularly stabilized complexes of silicon (and phosphorus) involving the *N,N′,N′*-trimethylethylenediamine group have been known since 1986. The precursor compound to the synthesis of such complexes, *N*-trimethylsilyl-*N,N′,N′*-trimethylethylenediamine (**1**), was first synthesized by Krebs et al. [23] from *N,N′,N′*-trimethylethylenediamine and trimethylchlorosilane [44]. Compound **1** is a colourless liquid of b.p. 86°C (45 mmHg) [23,41]. The formation of an intramolecular complex with the *N,N′,N′*-trimethylethylenediamine donor group and silicon functioning as acceptor atom was first observed in the reaction of **1** with both silicon tetrafluoride and phenyltrifluorosilane, in accord with eqn. (1).

As a result of intramolecular $Me_2N \rightarrow Si$ coordination, complexes with pentaco-



(1)

R = F, **2**
R = Ph, **3**



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(2)

ordinate (λ^5) silicon were isolated. A single-crystal X-ray diffraction study on an HF adduct of **2** confirmed the proposed structure (eqn. (2); Fig. 1) [45]. The ^{19}F NMR solution spectra of the products originating from the reaction of **1** with either silicon tetrafluoride or phenyltrifluorosilane were found to exhibit dynamic behavior. Thus, the half-width of the ^{19}F NMR signal observed for **2** [eqn. (1)] at room temperature was very broad (ca. 100 Hz) with a coalescence point of −30°C. At −70°C the rate of the dynamic process (e.g. pseudorotation or scission of the SiN bond, followed by rotation around this bond and restitution of the intramolecular Si ← N coordination), was significantly reduced, so that a triplet was observed for the ^{19}F resonance of an axial fluorine atom, and a doublet for the two equatorial fluorine atoms at trigonal bipyramidal silicon [45]. This characteristic pattern was in accord with trigonal bipyramidal geometry at the central silicon atom, with one axial NSi and one axial FSi bond, assuming that the intramolecular N → Si coordination gave rise to a five-membered ring system attached axially–equatorially. In the case of **3** (R = Ph), the

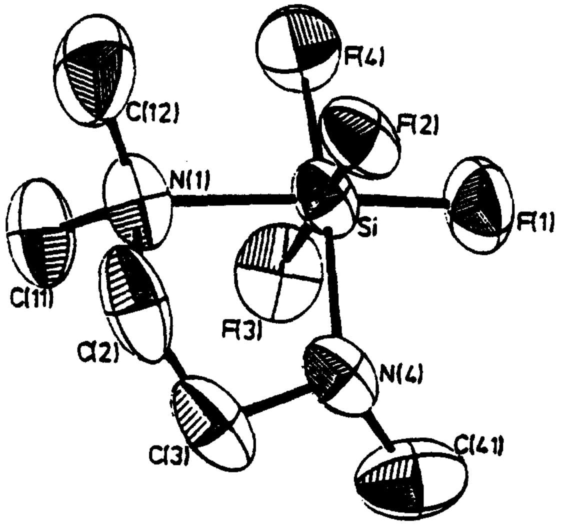


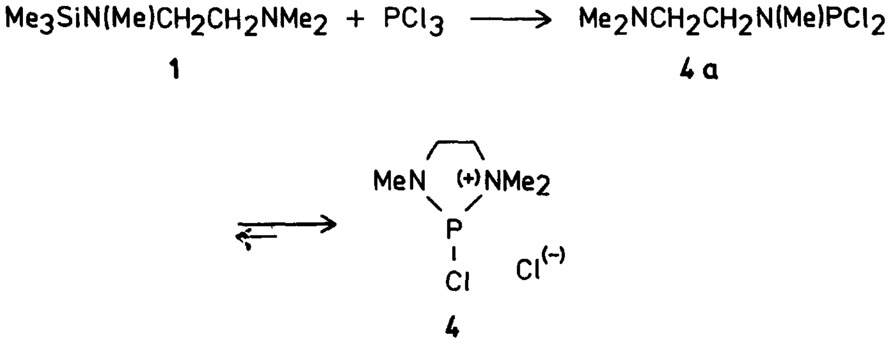
Fig. 1. Molecular structure of 2,2,2,2-tetrafluoro-1,1,3-trimethyl-1,1,3-diazonia-2λ^6-silacyclopentane in the crystal [45]; reprinted by permission of Professor D. Schomburg.

presence of two chemically non-equivalent fluorine atoms was established by ^{19}F NMR spectroscopy at low temperature (−115°C) and the trigonal bipyramidal (tbp) geometry at silicon was suggested [45]. The observation of two additional signals suggested the existence of a diastereoisomer, which may be rationalized as a result of the decrease in the rate of inversion of the uncoordinated nitrogen atom.

3. λ^3-PHOSPHORUS(III) COMPOUNDS BEARING THE *N,N',N'*-TRIMETHYLETHYLENEDIAMINE SUBSTITUENT AT PHOSPHORUS

3.1. *The system* $Me_2NCH_2CH_2N(Me)SiMe_3/PX_3$ *(X = F, Cl, Br, I)*

The formation of P–O and, especially, of P–N bonded systems in the reaction of the appropriate $OSiMe_3$ and $NSiMe_3$ compounds with phosphorus halides is well known [46,47]. The compounds resulting from PCl_3, involving the $-OPCl_2$ or $>NPCl_2$ grouping, are distillable liquids up to a molecular mass of ca. 200 [48]. The formation of a solid product in the reaction of the silylamine $Me_2NCH_2CH_2N(Me)SiMe_3$ (**1**) with phosphorus trichloride in a 1:1 molar ratio was, therefore, unexpected. In accord with eqn. (3), the SiN bond in **1** was broken in the usual manner, with the Me_3Si group leaving as Me_3SiCl. The composition of the product **4a**/**4** corresponded to the expected $Me_2NCH_2CH_2N(Me)PCl_2$; however the ^1H NMR spectrum was not in accord with this formulation. One doublet was observed for each of the NMe and NMe_2 groups. $^1H\{^{31}P\}$ decoupling gave single lines and showed that the doublets were due to ^1H–^{31}P coupling. The $\delta(P)$ value (160.3 ppm) was typical of R_2NPCl_2 compounds [49]. In the mass spectrum the molecular ion (M^+, *m/z* 202/204/206) was observed in the characteristic isotopic distribution. The identity of **4** in the solid state was established after crystals suitable for a single-crystal X-ray diffraction study were obtained [50] (Fig. 2). It is suggested that the covalent character is increasing, in accord with the transformation **4**→**4a**, both during the sublimation or on recording the mass spectrum.



$$\underset{\mathbf{1}}{Me_3SiN(Me)CH_2CH_2NMe_2} + PCl_3 \longrightarrow \underset{\mathbf{4a}}{Me_2NCH_2CH_2N(Me)PCl_2} \qquad (3)$$

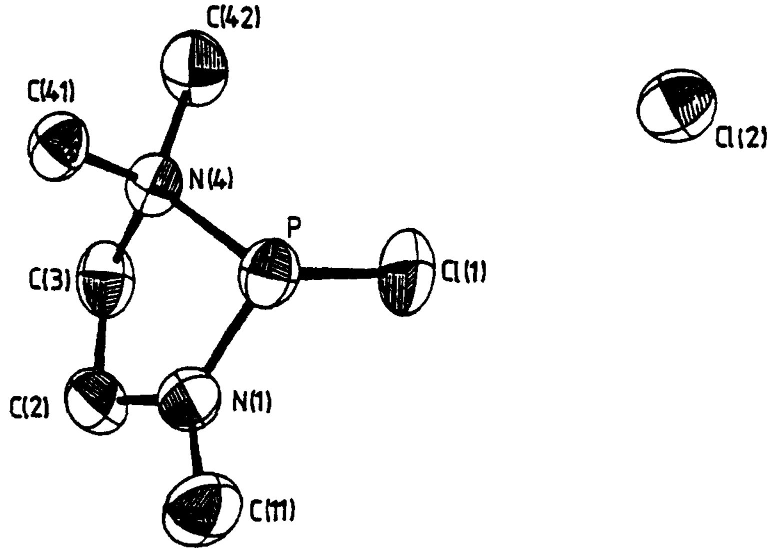
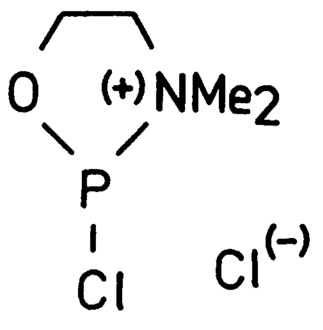
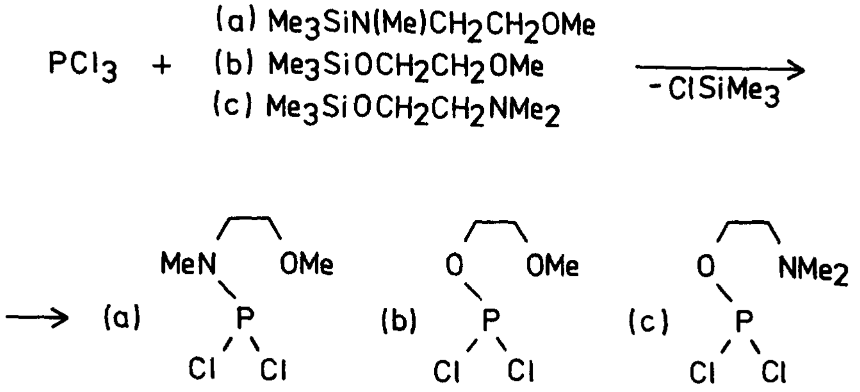


Fig. 2. Molecular structure of **4** in the solid state [50]; reprinted by permission of Gordon and Breach Science Publishers.

The PN coordinative bond in **4** (184 pm) is 14 pm longer than a normal covalent PN bond, e.g. in P(pip)$_3$ (pip = piperidyl) [51]. The bond between phosphorus and the planar three-coordinate nitrogen atom in **4** (162 ppm) is comparatively short, suggesting that the positive charge resides partially at phosphorus, and partially at nitrogen. While the PCl(1) bond distance (212.0 pm, i.e. 8.1 pm longer than in PCl$_3$ [52]) indicates a normal covalent PCl bond, the PCl(2) bond distance of 367.4 pm excludes any covalent formulation, and supports the ionic structure. A related five-membered heterocycle containing the fragment $Me_2NCH_2CH_2O$– and involving possible intramolecular $Me_2N \rightarrow P$ coordination was described as early as 1966 [53]. In the absence of supporting data (e.g. NMR) the identity of $Me_2NCH_2CH_2OPCl_2/[Me_2NCH_2CH_2OPCl]^+Cl^-$ as an intramolecularly stabilized complex was only assumed. The formation of the complex

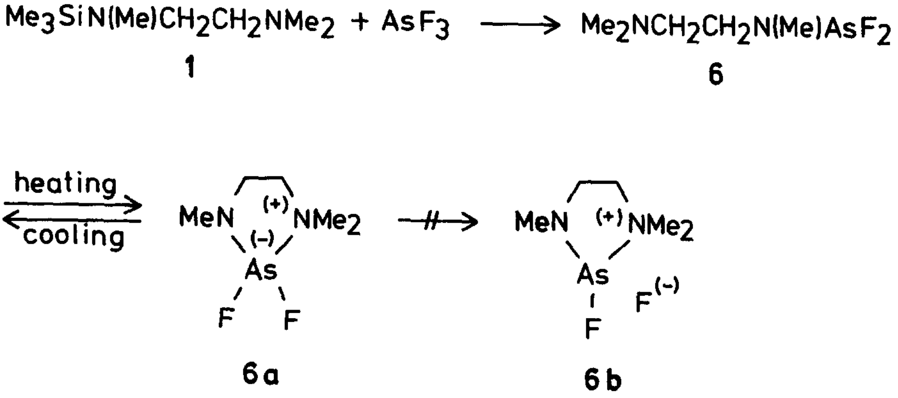


$[Me_2NCH_2CH_2OPCl]^+Cl^-$ in the reaction of PCl_3 with the appropriate silyl ether, $Me_2NCH_2CH_2OSiMe_3$, could not be established with certainty [50]. The reaction of some trimethylsilylated derivatives of amino alcohols or ethylene glycol with PCl_3 did not give intramolecular complexes comparable to **4**, but led to the acyclic, isomeric PCl_2 species [50], (a), (b) and (c) [eqn. (4)].



(4)

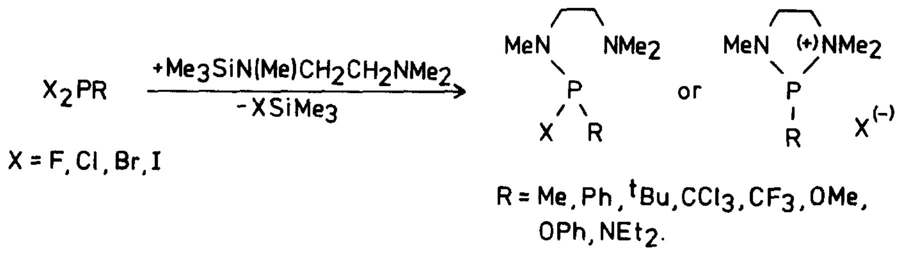
The reaction of PBr_3 with **1**, as described in eqn. (3) for PCl_3, led to compound **5**, the bromine analog of **4** [54], but the iodine analog could not be isolated from the reaction of PI_3 with **1** [55]. The reaction of PF_3 and $ClPF_2$ with **1** produced mixtures of products [56] contrary to expectation [e.g. eqn. (3)]. In the reaction of F_2PX (X = Cl, Br) with aminosilanes, the expected NPF_2 species and Me_3SiX (X = Cl, Br) were usually formed [57,58]. The arsenic–fluorine species **6**, related to **4a**, was obtained in the reaction of **1** with AsF_3 [53] [eqn. (5)], following the usual procedure [59]. In the ^{19}F NMR spectrum of **6**/**6a**, a marked decrease in the line width of the broad room-temperature signal of the AsF_2 unit was noted on cooling. This effect [c.f. eqn. (5)] was reversible. Fluoride ion was not detected by ^{19}F NMR spectroscopy, and the presence of **6b** is therefore unlikely [56].



(5)

3.2. Phosphorus(III) halide derivatives with the N,N′,N′-trimethylethylenediamine group from dihalophosphorus(III) compounds

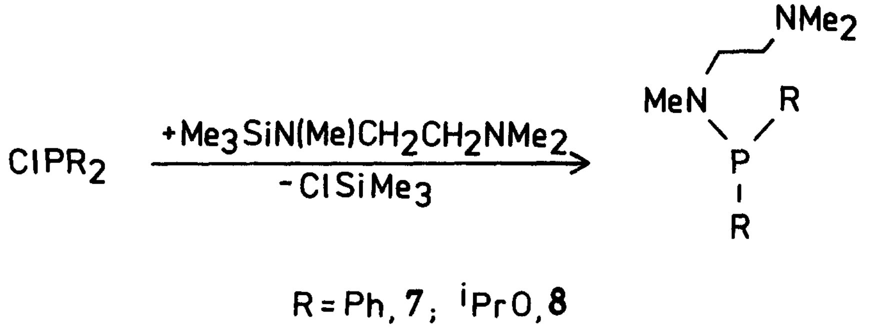
Based on the above findings, dihalophosphorus(III) compounds, RPX_2, were allowed to react with $Me_2NCH_2CH_2N(Me)SiMe_3$ (**1**). The products were studied with a view to detecting possible intramolecular donor–acceptor interactions within the resulting dimethylaminomonohalophosphines ($P \leftarrow NMe_2$ interactions). Further, it was established that intramolecular complexation was possible through halide abstraction (X = Cl, Br) from the covalent compounds formed in accord with eqn. (6).



(6)

3.3. Synthesis of covalent acyclic di- and monosubstituted phosphorus(III) halogen compounds with the N,N′,N′-trimethylethylenediamine substituent

The reaction of **1** with diphenylchlorophosphine and diisopropylchlorophosphite produced distillable liquids [59,60]. An intramolecular N → P interaction was not observed in these compounds at room temperature [eqn. (7)]. In a similar fashion, alkyl- (perhaloalkyl-) and aryl-substituted dichlorophosphines were allowed to react with **1**, furnishing the respective trimethylethylenediamine-substituted halophosphino derivatives [54,61] **9**–**13** [eqn. (8)]. The $\delta(P)$ values of **9**–**13** are in the region typical of phosphonamidous chlorides, $R_2NP(Y)Cl$. In Fig. 3 they are compared with those of the related phosphonous acid dichlorides, Cl_2PY [62]. There was no indication of intramolecular N → P interactions. The low reactivity of fluorophosphines [57,58], compared with that of chlorophosphines, required more



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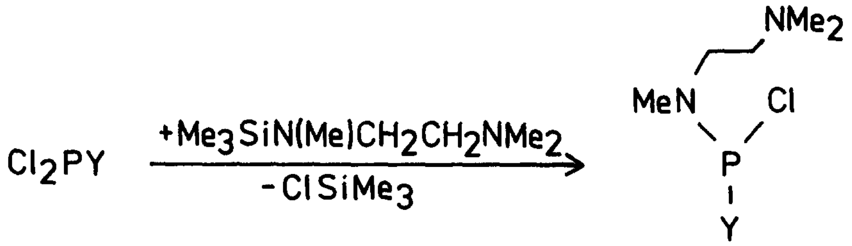


(8)

$Y = CH_3$, **9**; C_6H_5, **10**; CCl_3, **11**; CF_3, **12**; ^tBu, **13**

vigorous conditions, e.g. in the case of the reaction of phenyldifluorophosphine with **1** [eqn. (9)].

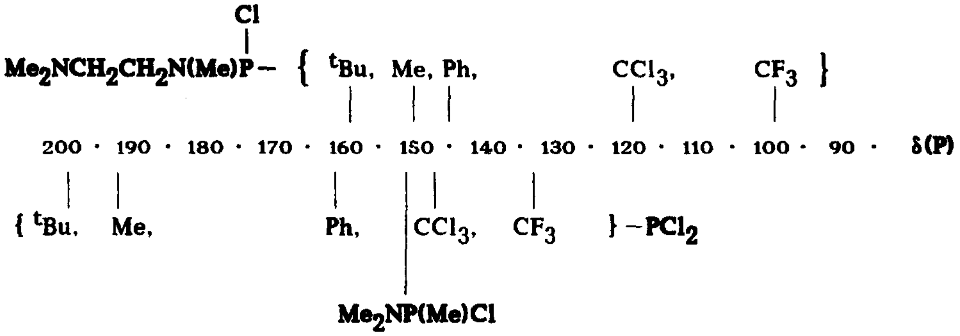
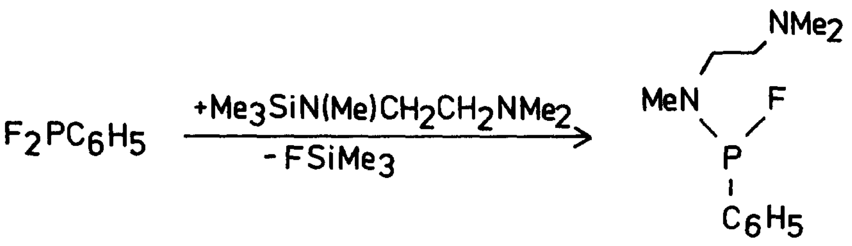


Fig. 3. Dependence of the δ(P) values on the substituent Y for different *N,N′,N′*-trimethylethylenediamine-substituted chloro-Y-phosphines, $Me_2NCH_2CH_2N(Me)P(Y)Cl$ (Y = Me **9**; Ph, **10**; CCl_3, **11**; CF_3, **12**; ^tBu, **13**) and comparison with the δ(P) values of dichloro-Y-phosphines, Cl_2PY (Y = Me, Ph, ^tBu, CCl_3, CF_3). The substituent groups Y are given in braces.



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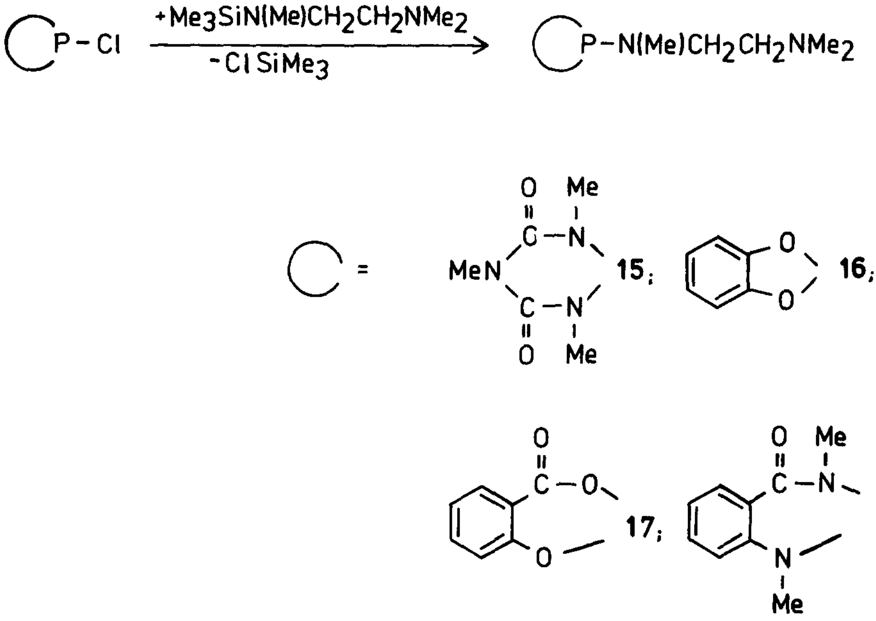
(9)

3.4. Synthesis of covalent N,N′,N′-trimethylethylenediamine-substituted heterocyclic $\lambda^3P(III)$ compounds

In the reaction of heterocyclic monochlorophosphorus(III) precursors with **1** the acyclic *N,N′,N′*-trimethylethylenediamine-substituted λ^3P derivatives **15–18** [eqn. (10)] were exclusively obtained [63–66]. The ^{1}H NMR spectra show no doublet fine structure due to intramolecular $(CH_3)_2N \rightarrow P$ coupling. Compounds **15–18** were found to have synthetic potential, and a series of addition and/or oxidation reactions were conducted (Section 5.3).

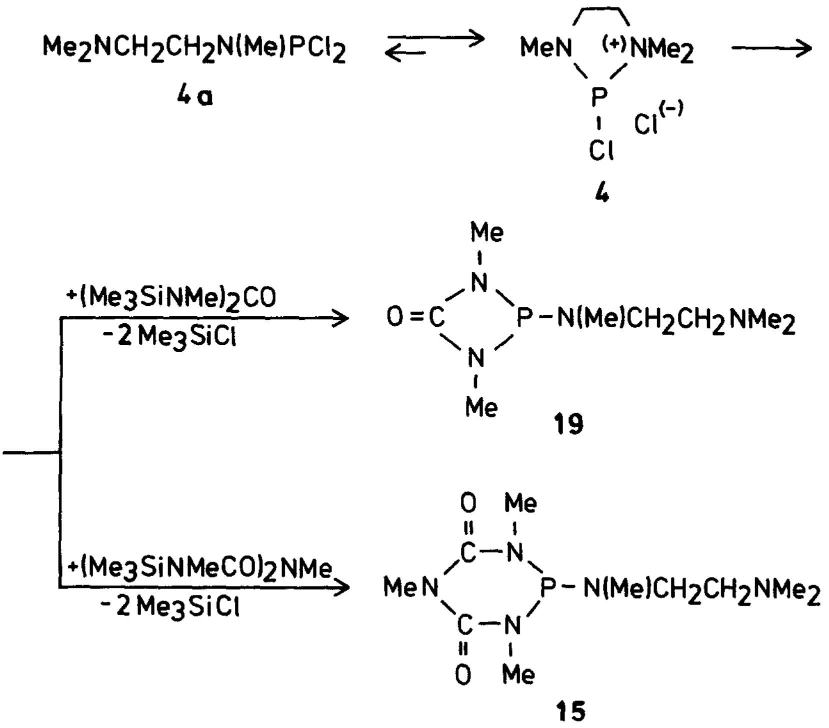


(10)

The related *N,N′,N′*-trimethylethylenediamine-substituted λ^3P-derivative **19** could not be synthesized in accord with eqn. (10), because the appropriate PCl precursor is unknown. It was prepared via the reaction of the isomeric mixture of **4** with *N,N′*-dimethyl-*N,N′*-bis(trimethylsilyl)urea, in accord with eqn. (11) [67]. An alternative synthesis of **15** involved the reaction of *N,N′*-bis(trimethylsilyl)biuret with **4** [eqn. (11)] [68]. In the case of **19** (as opposed to **15**) it was possible to induce an intramolecular $Me_2N \rightarrow P$ coordination through oxidation reactions at the λ^3P atom.

3.5. Synthesis of ionic, N,N′,N′-trimethylethylenediamine-substituted 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium halides

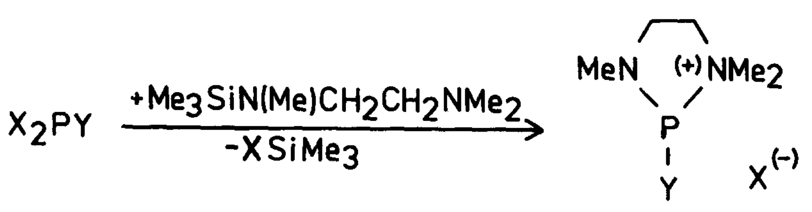
The reaction of dihalophosphorus(III) compounds X_2PY (X = Cl, Br; Y = OMe, OPh, NEt_2) with **1** did not furnish the acyclic *N,N′,N′*-trimethylethylenediamine-substituted halophosphorus(III) compounds; instead, the 1,1,3-



(11)

trimethyl-1,3,2λ^3-diazaphospholidin-1-ium halides **20**–**23** were formed [54,61]. The intramolecular $Me_2N \rightarrow P$ interaction was established by ^1H NMR spectroscopy, with the resonances of the Me_2N protons split into doublets, as a result of $^3J(PH)$ coupling, in contrast to compounds **9**–**14**. The $\delta(P)$ values of compounds **4**, **5** and **20**–**23** were comparable to those of compounds of the type $(Me_2N)_2PY$ (cf. Fig. 4).

The same dependence of $\delta(P)$ on the substituent Y was observed for the



(12)

X = Cl; Y = OCH_3, **20**; OC_6H_5, **21**; $N(C_2H_5)_2$, **22**;
X = Br; Y = $N(C_2H_5)_2$, **23**

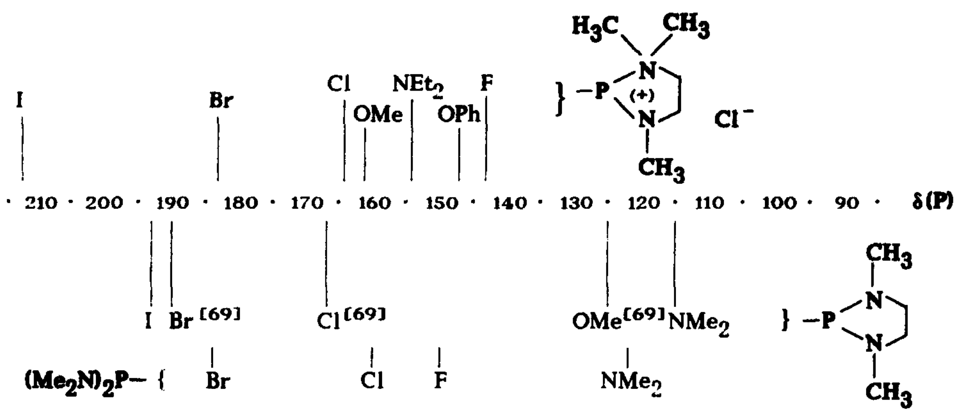


Fig. 4. Dependence of δ(P) on the substituent Y for different 2-Y-1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium chlorides, and comparison of the δ(P) values of 2-Y-1,3-dimethyl-1,3,2λ^3-diazaphospholidines and bis(dimethylamino)-Y-phosphines, $(Me_2N)_2PY$ (Y = F, Cl, Br, I, OMe, OPh, NR_2 (R = Me, Et)).

reference compounds [62] as for the 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium salts **4**, **5** and **20–23**. In all reactions of compounds of type X_2PY (X = halogen) with **1** ionic products, stabilized by intramolecular $Me_2N \rightarrow P$ coordination, were spontaneously formed when Y was either a halogen or an oxygen- and/or nitrogen-containing substituent.

In general, the following criteria must be met in order to permit the spontaneous formation of intramolecular complexes, in accord with eqn. (12):

(1) at least one R_2N grouping in the molecule;

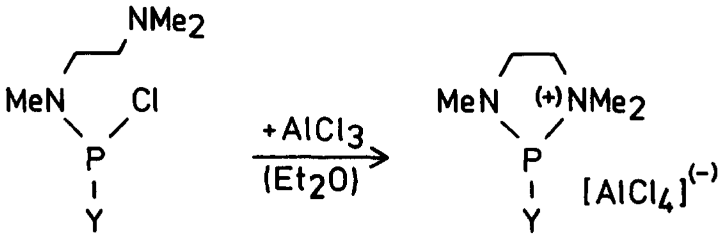
(2) the presence of a halogen substituent at phosphorus as a good leaving group in the course of nucleophilic substitution;

(3) at least one non-bonding pair of electrons at the substituent Y.

The stabilization of an intramolecular complex through an R_2N grouping may be rationalized in terms of the partial double bond character [70,71] of the N–P bond (p_π–d_π bonding), which leads to a delocalization of the positive charge. Substituents with non-bonding pairs of electrons also reduce partial charge density in the cation (+M effect). Good $-I$ substituents (e.g. CCl_3, CF_3) give rise to a low electron density at the acceptor center, thus facilitating attack of the donor. Unlike +M substituents, however, they do not contribute to the stabilization of the complex. In the case of these substituents the destabilizing influence apparently predominates.

3.6. Reaction of covalent N,N′,N′-trimethylethylenediamine λ^3P(III) halogen–phosphorus compounds with aluminum chloride as a Lewis acid: induced $Me_2N \rightarrow P$ coordination

The reaction of aluminum chloride with phosphorus(III) chlorides has been successfully employed in a number of cases as a means of generating species involving low-valent, cationic phosphorus centers [72]. As expected, the reaction of compounds **9–12** with $Cl_3Al \cdot OEt_2$ [eqn. (13)] furnished the ionic tetrachloroaluminates, **24–27** [54,55,61].



(13)

Y = CH_3, **9**; C_6H_5, **10**; CCl_3, **11**; CF_3, **12**

Y = CH_3, **24**; C_6H_5, **25**; CCl_3, **26**; CF_3, **27**

The formation of the $[AlCl_4]^-$ anion was established in a representative case through ^{27}Al NMR spectroscopy [54]. A comparison of the $\delta(P)$ values of the acyclic precursor compounds, **9–12**, with those of the tetrachloroaluminate salts, **24–27** (Table 1) revealed a significant low-field shift, between 12 and 30 ppm, for the resonances of the products formed, in accord with eqn. (13) [73]. The intramolecular substitution of the chloride ion in **9–12** by the NMe_2 group evidently effects a deshielding of the phosphorus center.

The reaction of boron trifluoride (as $F_3B \cdot OEt_2$) with $Me_2NCH_2CH_2N(Me)P(Ph)X$ (X = F, **14**) was also studied, with a view to removing F^- from phosphorus and creating an intramolecular complex with the same cation as described for **25**, and a tetrafluoroborate anion. As illustrated in eqn. (14) the reaction took an entirely different course and BF_3 was found to coordinate solely to the nitrogen atom of the NMe_2 group while the PF bond was not affected [eqn. (14)].

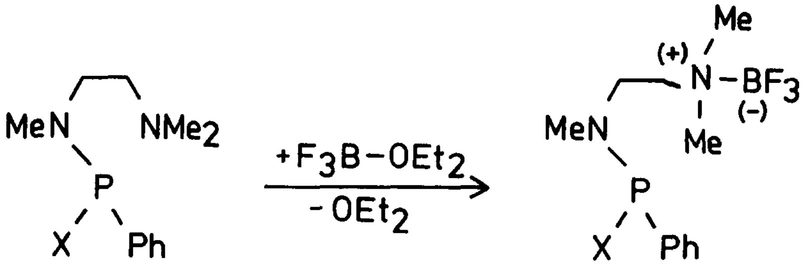
TABLE 1

$\delta(P)$ values (ppm) for the tetrachloroaluminates $[Me_2NCH_2CH_2N(Me)P(Y)]^+$ $[AlCl_4]^-$, **24–27** and comparison with the $\delta(P)$ values of the acyclic precursor compounds **9–12**

Y	$\delta(P)$ **9–12**	$\delta(P)$ **24–27**	$\Delta\delta(P)$
CH_3	+149.8	+179.7	−29.9
C_6H_5	+143.8	+165.0	−21.2
CCl_3	+118.5	+130.2	−11.7
CF_3	+98.6	+119.3	−20.7

9–12, $Me_2NCH_2CH_2N(Me)P(Y)Cl$: **9**, Y = CH_3; **10**, Y = C_6H_5; **11**, Y = CCl_3; **12**, Y = CF_3. **24–27**, $[Me_2NCH_2CH_2N(Me)P(Y)]^+$ $[AlCl_4]^-$: **24**, Y = CH_3; **25**, Y = C_6H_5; **26**, Y = CCl_3; **27**, Y = CF_3.

The same observation was made in the case of **10** (X = Cl). The conceivable formation of $[BF_4]^-$ [74] or of $\lambda^3P \rightarrow BF_3$ complexes [75, 77] was not observed.



(14)

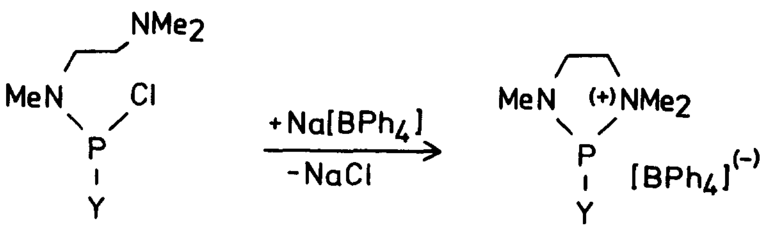
X = Cl, **10**
X = F, **14**

X = Cl, **28**
X = F, **29**

3.7. *Reaction of N,N',N'-trimethylethylenediamine-substituted P(III)Cl compounds and 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium chlorides with sodium tetraphenylborate*

3.7.1. *Reaction of covalent N,N',N'-trimethylethylenediamine-substituted P(III)Cl compounds with sodium tetraphenylborate*

In accord with eqn. (15), the reaction of the acyclic compounds **9–13** with sodium tetraphenylborate led to the crystalline tetraphenylborate salts **30–34**, involving the 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium ring system [61,76]. Although the ^{1}H NMR spectra of the acyclic precursor compounds **9–13** did not reveal any evidence for an intramolecular donor–acceptor interaction between the nitrogen atom of the Me_2N group and phosphorus, the reaction following eqn. (15) assumes the presence of ionic isomeric structures of the precursor compounds [according to eqn. (3)] in equilibrium, with the covalent forms predominating. The spontaneous formation of intramolecular complexes from *N,N',N'*-trimethyl-



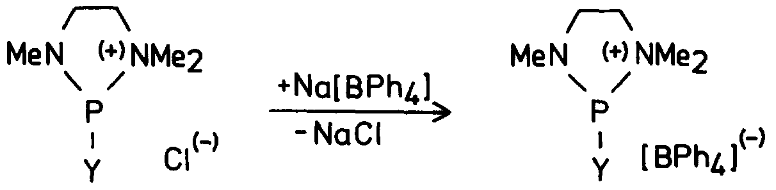
(15)

Y = CH_3, **9**; C_6H_5, **10**; CCl_3, **11**; CF_3, **12**; $^tC_4H_9$, **13**

Y = CH_3, **30**; C_6H_5, **31**; CCl_3, **32**; CF_3, **33**; $^tC_4H_9$, **34** ethylenediamine-substituted NP(III)Cl compounds [eqns. (3) and (12)] is restricted to substituents Y which bear non-bonding pairs of electrons at the atom bonded to phosphorus. As is evident from eqn. (15), this restriction is not valid when the chlorine atom is exchanged for a non-coordinating anion, e.g. $[BPh_4]^-$. In this case the substituent Y may be almost any group. Only the PN(Me) grouping, the chloride ion to be exchanged and the Me_2N donor nitrogen atom must be present in the P(III) chlorine species (cf. Section 3.5).

3.7.2. Reaction of 1,1,3-trimethyl-1,3,2λ³-diazaphospholidin-1-ium chlorides with sodium tetraphenylborate

In the reaction of the 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium chlorides **4** and **20–22** with sodium tetraphenylborate the corresponding tetraphenylborates **35–38** {eqn. (16); [61,76]} were formed. The use of the tetraphenylborate ion in such metathesis reactions has been reported previously [78]. Compounds **30–38** were present as intramolecular complexes. In the ^{31}P NMR spectra (Table 2) the δ (P) values of the tetraphenylborates **30–33** were significantly shifted to lower field in comparison with the acyclic precursor compounds **9–11** and **13** [expressed as



(16)

Y = Cl, **4**; OCH₃, **20**; OC₆H₅, **21**; N(C₂H₅)₂, **22**

Y = Cl, **35**; OCH₃, **36**; OC₆H₅, **37**; N(C₂H₅)₂, **38**

TABLE 2

δ(P) values (ppm) for the 2-Y-1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium tetraphenylborates **30–38** and comparison with the δ(P) values of the *N,N′,N′*-trimethylethylenediamine substituted P(III)Cl compounds **9–13** and the 2-Y-1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium chlorides **4** and **20–22**

Y	δ(P) **9–13**	δ(P) **30–33**	Δδ(P)	Y	δ(P) **35–38**	δ(P) **4, 20–22**
CH_3	+149.8	+184.8	−35.0	Cl	+168.4	+160.3
C_6H_5	+143.8	+162.4	−18.6	OCH_3	+160.6	+160.1
CCl_3	+118.5	+130.2	−11.7	OC_6H_5	+147.3	+147.3
t-C_4H_9	+161.0	+190.8	−29.9	$N(C_2H_5)_2$	+153.8	+153.9
CF_3	+98.6	—	—			

9–13: $Me_2NCH_2CH_2N(Me)P(Y)Cl$. **30–33** and **35–38**: $[Me_2NCH_2CH_2N(Me)P(Y)][BPh_4]^-$. **4**, **20–22**: $[Me_2NCH_2CH_2N(Me)P(Y)]\ Cl^-$.

$\Delta\delta(P)$] [79]. The $\delta(P)$ values of the 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium chlorides **4** and **20–22** were comparable to those of the corresponding tetraphenylborates **35–38**, with only the anions differing. No $\delta(P)$ value is available for **34**.

In the ^1H NMR spectra of the tetraphenylborates **32**, **33** and **38** two sets of doublets were observed at room temperature for the $(CH_3)_2N$ protons. This confirms their formulation as intramolecular complexes [eqn. (3)]. The tetraphenylborates cannot revert to an isomeric covalent structure. The room-temperature ^1H NMR spectra of **30**, **31** and **36** are complicated [61]. The diastereotopic methyl groups at the donor nitrogen atom could be distinguished only at low temperature. The more complex pattern of the room-temperature ^1H NMR spectra of the tetraphenylborates **30**, **31** and **36** is the result of an equilibrium of these structures with those of the related phosphenium cations [61] whose stabilization via nitrogen atoms bonded to phosphorus is known [80].

The X-ray crystal structure analysis of **31** confirmed its identity as an intramolecular complex in the solid state (Fig. 5) [61]. The N→P coordinative bond (188.2 pm) is ca. 4 pm longer than in the chloride analog [50]. For a coordinative P(III)N bond it is rather short.

4. INTRAMOLECULARLY STABILIZED λ^4-PHOSPHORUS(III) COMPOUNDS WITH THE *N,N',N'*-TRIMETHYLETHYLENEDIAMINE SUBSTITUENT

Reaction of the intramolecular complexes **4** and **5** with a second equivalent of **1** [eqn. (17)] furnished the spirocyclic salts **39** and **40** [54], respectively. In order to

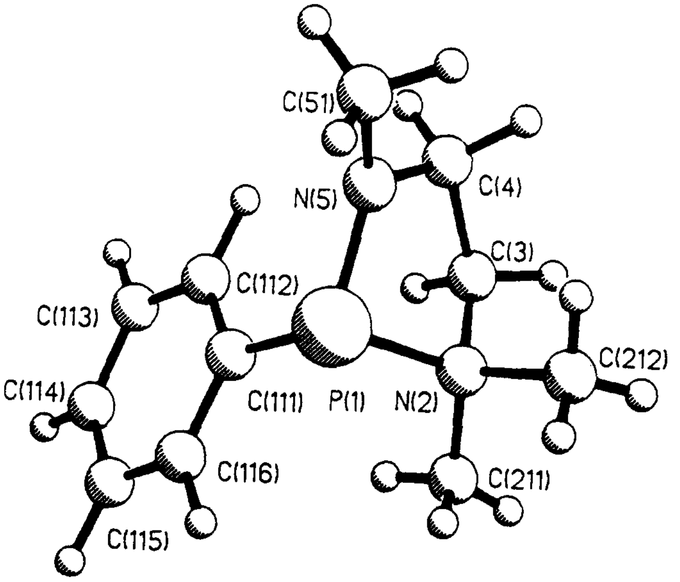
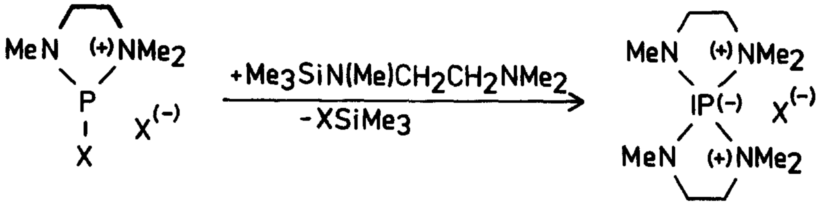


Fig. 5. Molecular structure of the cation of **31** in the solid state [61]; reprinted by permission of Gordon and Breach Science Publishers.

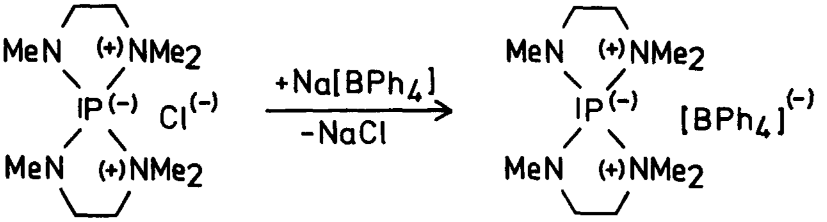


(17)

X = Cl, **4**; X = Br, **5**

X = Cl, **39**; X = Br, **40**

obtain a more stable product, the chloride ion was exchanged for tetraphenylborate



(18)

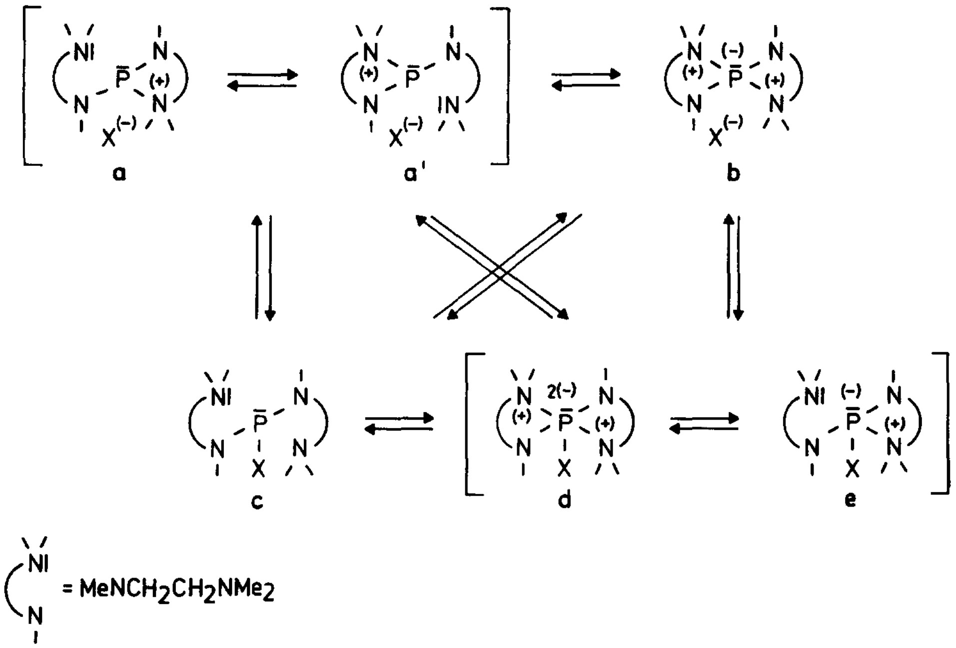
39 **41**

in **39** [eqn. (18)]. In contrast to the tetraphenylborate salts **30–38**, compound **41** proved to be unstable in air and in solution. Based on the ^1H, ^{13}C and ^{31}P NMR spectroscopic results, the presence of isomeric structures was proposed for **39** and **41**, in equilibrium with each other in solution. In accord with Scheme 2, equilibria between the isomers **a**, **a′**, **b**, **c**, **d** and **e** were suggested. In the case of $[BPh_4]^-$ as a non-coordinating anion, structures **c**, **d** and **e** are not possible.

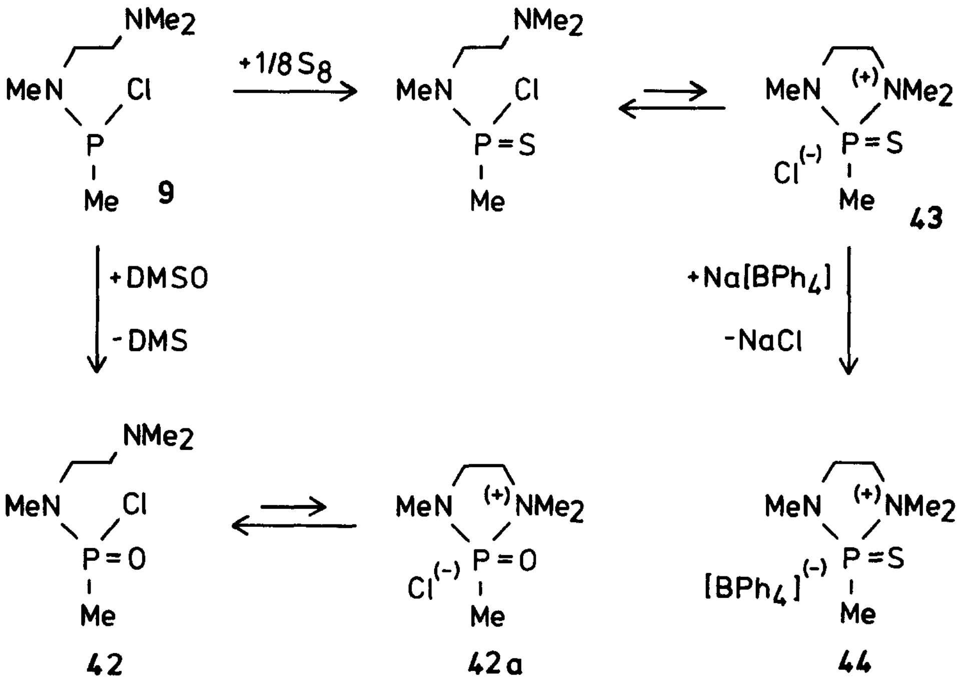
5. *N,N′,N′*-TRIMETHYLETHYLENEDIAMINE-SUBSTITUTED COMPOUNDS OF TETRA- AND PENTACOORDINATED PHOSPHORUS OF OXIDATION NUMBER 5

5.1. Formation of N,N′,N′-trimethylethylenediamine-substituted $\lambda^4P(V)$ compounds from reactions of methyl(N,N′,N′-trimethylethylenediamine)-phosphinous chloride and bis(2-chloroethyl)phosphoramidic dichloride

In accord with Scheme 3, the phosphoroamidic chloride **42** was obtained by oxidation of the *N,N′,N′*-trimethylethylenediamine-substituted compound **9** with dimethyl sulfoxide in a known fashion [82]. In the reaction of **9** with elemental sulfur, the expected phosphonamidothioic chloride was formed. Its reaction with sodium tetraphenylborate (Scheme 3) led to the formation of the crystalline 2-thio-1,1,3-trimethyl-1,3,2λ^4-diazaphospholidin-1-ium tetraphenylborate (**44**) [83]. A reaction product **45**, involving the same skeleton as **42** and **43**, was observed in

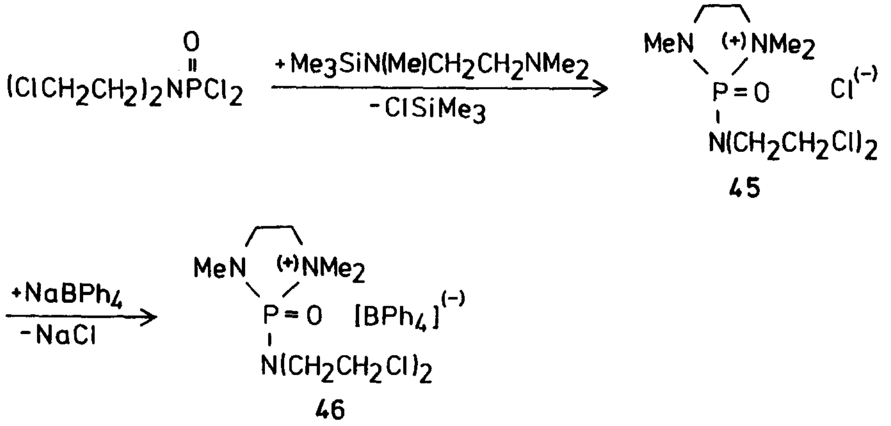


Scheme 2.



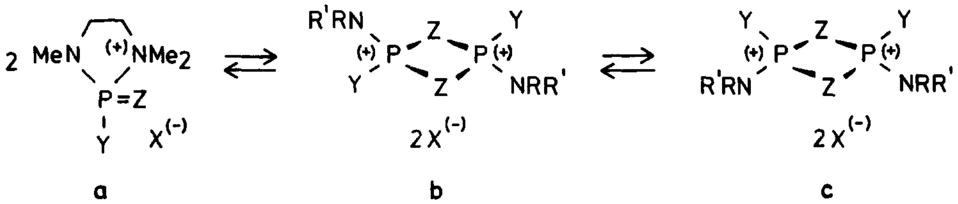
Scheme 3.

the reaction of bis(2-chloroethyl)phosphoramidic dichloride with **1** [eqn. (19)] [68], and was transformed into **46** by reaction with sodium tetraphenylborate.



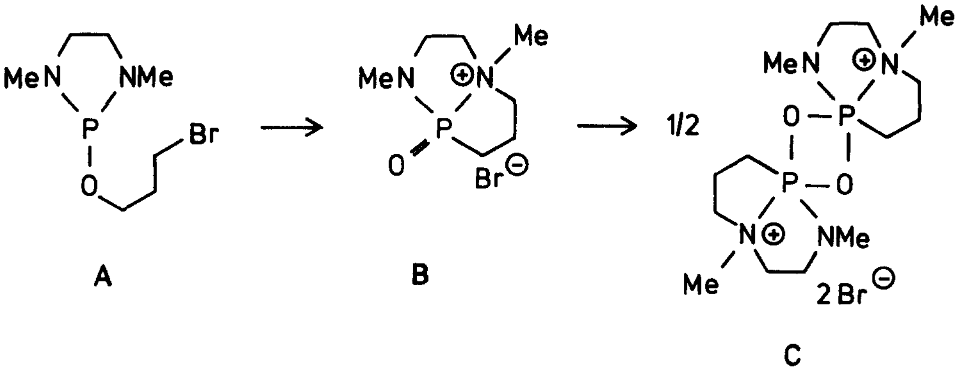
(19)

The ^{1}H NMR data for **42–45** reflected the ^{31}P NMR parameters. Three sets of signals were found for the tetraphenylborates **44** and **46**, which were attributed to three isomers, **a**, **b** and **c**. In accord with the ^{1}H NMR data, a mechanism of isomerization is proposed in Scheme 4. Isomer **a** dimerizes with formation of the dioxa- and dithiadiphosphetidine structures **b** and **c**, respectively [68,83]. This is similar to the dimerization of phosphine imides to diazadiphosphetidines (e.g. [84,85]). Dimerization of species containing a P=O– grouping is uncommon because of the high stability of these bonds in P(V) compounds. The unusual formation of a dioxadiphosphetidine from a species containing a P=O double bond has been reported [86]. In a slow reaction, the formation of **C** from **A** (Scheme 5) was



NRR' = $Me_2NCH_2CH_2(Me)N$;
X = Cl, Y = Me, Z = O : **42**;
X = Cl, Y = Me, Z = S : **43**;
X = [BPh_4], Y = Me, Z = S : **44**;
X = Cl, Y = $(ClCH_2CH_2)_2N$, Z = O : **45**;
X = [BPh_4], Y = $(ClCH_2CH_2)_2N$, Z = O : **46**

Scheme 4.



Scheme 5.

observed. The postulated intermediate **B** is comparable to form **a** described in Scheme 4. For compound **C**, cisoid and transoid geometries, relative to the plane of the four-membered ring, were established side by side, in analogy to forms **b** and **c** (Scheme 4). The structure of **44** was established by a single-crystal X-ray structure determination (Fig. 6). It was in agreement with the structural evidence deduced from the ^{1}H and ^{31}P NMR parameters of isomer **44a**.

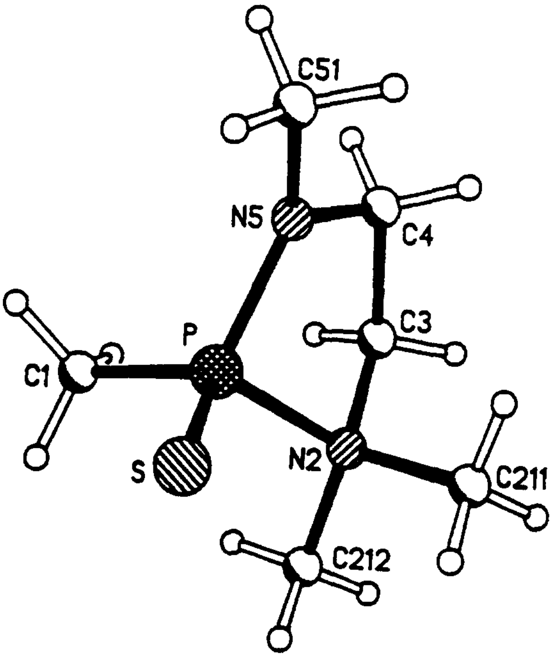


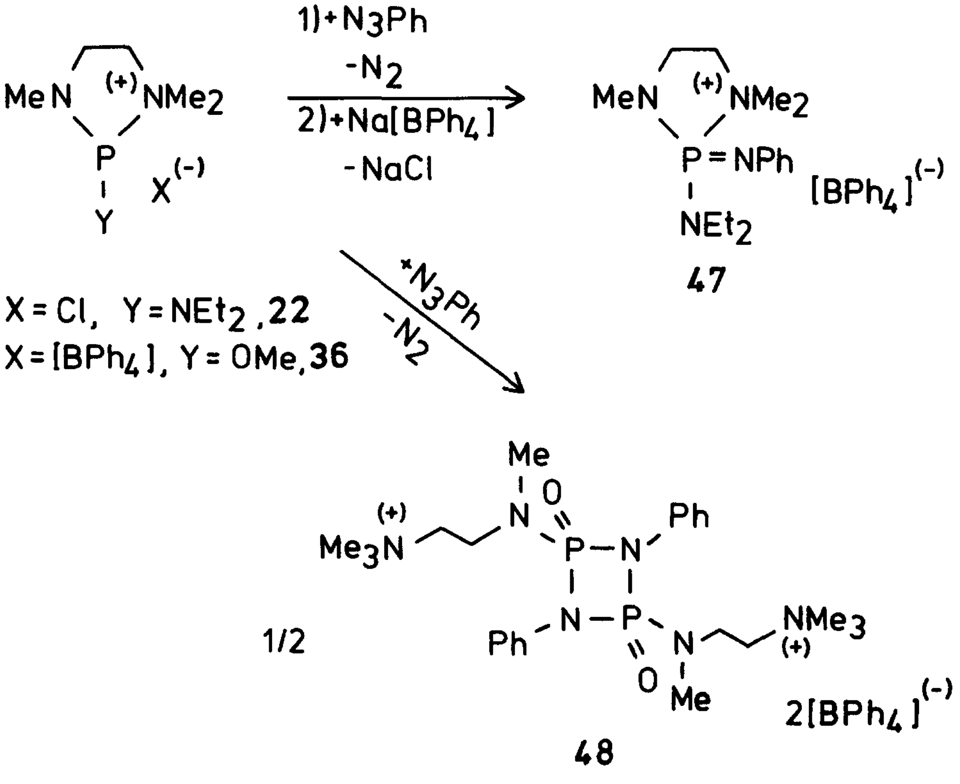
Fig. 6. Structure of the cation of **44** in the solid state [83]; reprinted by permission of VCH Verlagsgesellschaft.

5.1.1. Reaction of the 2-diethylamino-1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium salt ***22*** *with phenyl azide*

The reaction of **22** with phenyl azide led to the formation of the unstable phosphorodiamidimidic chloride $Me_2NCH_2CH_2(Me)NP(=NPh)(NEt_2)Cl$, which, after metathesis with $[BPh_4]^-$, was isolated as the tetraphenylborate salt **47** (Scheme 6) [83]. The reaction of the 2-methoxy-1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium salt **36** with phenyl azide gave the dimeric diazadiphosphetidine bis(tetraphenylborate) **48** by methylation of the Me_2N nitrogen atom (Scheme 6). The X-ray crystal structure determination (Fig. 7) confirmed the structure of **48**, proposed on the basis of solution NMR spectroscopic results. Bond lengths and angles of the four-membered ring were in good agreement with the corresponding data for 1,3-di-*tert*-butyl-2,4-dichloro-2,4-dioxo-1,3,2λ^4-diazadiphosphetidine [87]. The exocyclic P—O bond lengths were also comparable.

5.2. Phosphonium halides with the N,N′,N′-trimethylethylenediamine substituent

The reaction of bromotriphenylphosphonium bromide and chlorotrimethylphosphonium chloride with **1** furnished the corresponding *N,N′,N′*-trimethylethylene-



Scheme 6.

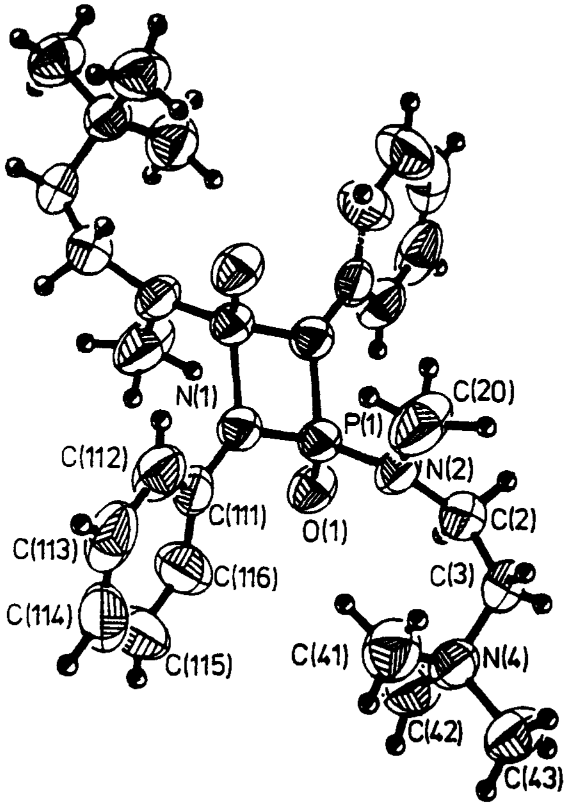
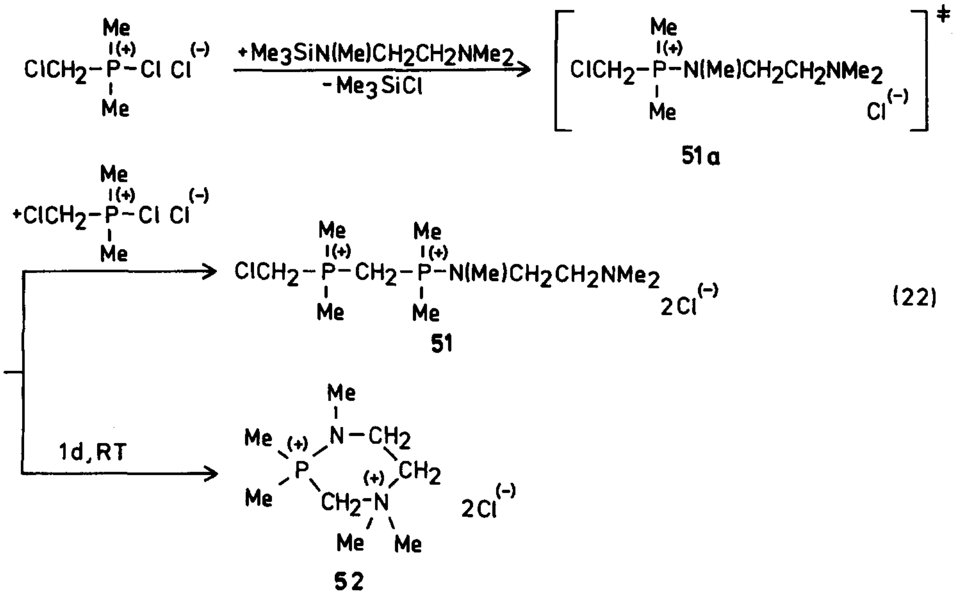


Fig. 7. Structure of the dication of the diazadiphosphetidine bis(tetraphenylborate) **48** in the crystal [83]; reprinted by permission of VCH Verlagsgesellschaft.

diamine-substituted phosphonium halides **49** and **50** [88] according to eqns. (20) and (21). Compounds **49** and **50** were found to exist as acyclic species. Intramolecular donor–acceptor interaction between the nitrogen atom of the dimethylamino grouping and the phosphorus center was not observed by ^{1}H NMR spectroscopy. Attempts to exchange the chloride ion for tetraphenylborate were unsuccessful, as were reactions of **1** with other alkyl- or dialkylamino-substituted halophosphonium halides [88].

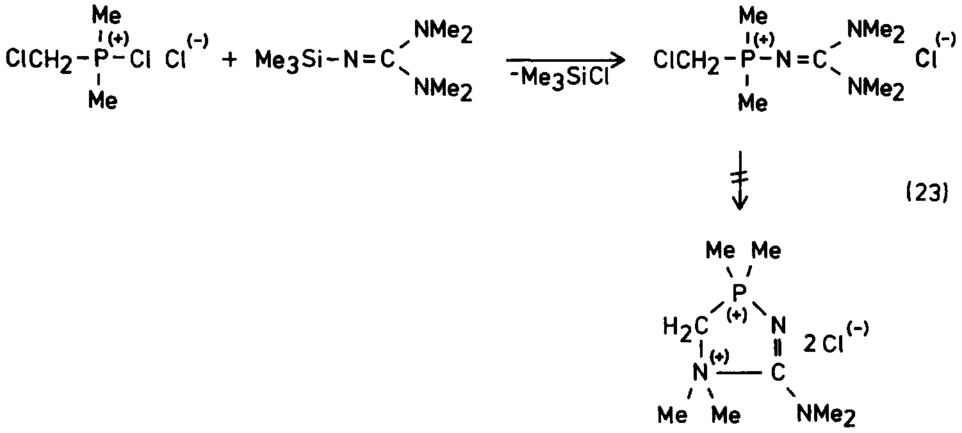
$$[Ph_3PBr]^{(+)}Br^{(-)} \xrightarrow[-Me_3SiBr]{+Me_3SiN(Me)CH_2CH_2NMe_2} \underset{\textbf{49}}{[Ph_3P{-}N(Me)CH_2CH_2NMe_2]^{(+)}Br^{(-)}} \qquad (20)$$

$$[Me_3PCl]^{(+)}Cl^{(-)} \xrightarrow[-Me_3SiCl]{+Me_3SiN(Me)CH_2CH_2NMe_2} \underset{\textbf{50}}{[Me_3P{-}N(Me)CH_2CH_2NMe_2]^{(+)}Cl^{(-)}} \qquad (21)$$



(22)

The unusual reaction of an α-chloromethyl-substituted chlorophosphonium chloride with **1** produced compounds **51** and **52** [89] [eqn. (22)]. In concentrated (ca. 2 molar) solution the formation of **51** (and some side products) predominated, while in strongly diluted solutions (ca. 0.1 molar) the heterocyclic compound **52** was favoured. The formation of both products probably proceeded via an intermediate, **51a**, which was suggested on the basis of ^{31}P NMR evidence, but could not be isolated. A compound, related to **52**, showing intramolecular N → P donor–acceptor interaction with formation of a cyclic dication, was not observed in the reaction of *N*-trimethylsilyl-*N′*,*N′*,*N″*,*N″*-tetramethylguanidine and chloromethyldimethylchlorophosphonium chloride [eqn. (23)]. It was assumed that the formation of a



(23)

five-membered heterocycle involving a P=N double bond [eqn. (23)] was not possible because of higher ring strain, in contrast to the formation of the six-membered heterocyclic species **52** [eqn. (22)].

5.3. Reactions of the compounds described under Section 3.4 which involve cyclic substituent groups; synthesis of oxidation, addition and coordination compounds

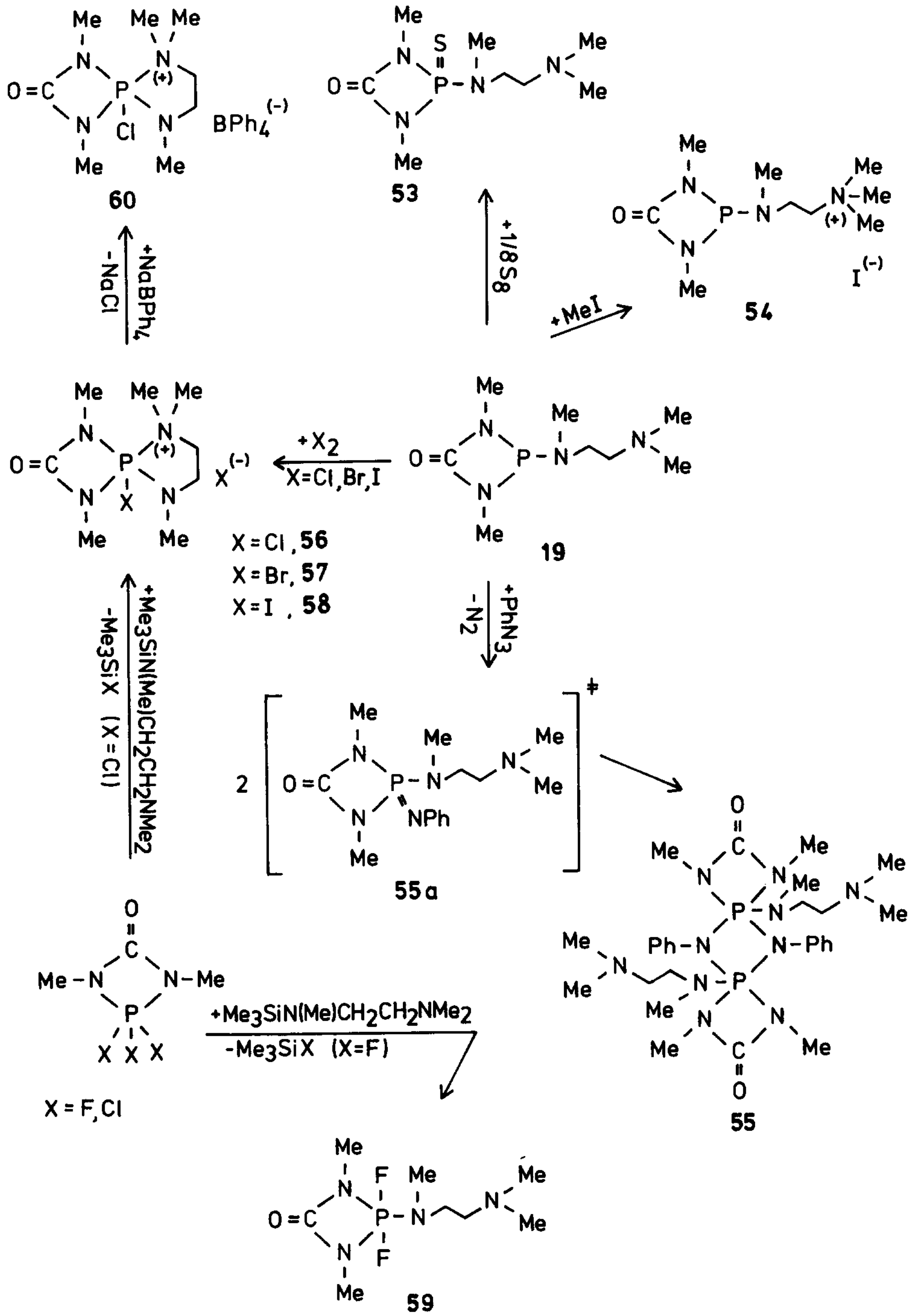
5.3.1. Compounds with the 1,3-dimethyl-1,3-diazaphosphetidinone ring system

Compound **19** was allowed to react with a variety of reagents according to Scheme 7, and the effect of these reactions on the intramolecular donor–acceptor behavior was investigated [67]. The reaction of **19** with elemental sulfur yielded the thiophosphoryl compound **53** [90], for which no indication of intramolecular $Me_2N \rightarrow P$ coordination was found. In the reaction of **19** with methyl iodide, the nitrogen atom of the dimethylamino group was methylated, and not the phosphorus atom, to give **54** [67]. In this case, intramolecular $Me_2N \rightarrow P$ coordination was no longer possible.

As in the case of **48**, the reaction of **19** with phenyl azide did not furnish the expected phosphine imide but the bisspiro compound **55** [67], as a result of dimerization [84] of the intermediate **55a**. Compounds **56–58** were formed in the reaction of **19** with elemental halogens (Cl_2, Br_2, I_2) [67]. In all three cases, spontaneous intramolecular $Me_2N \rightarrow P$ coordination with formation of the corresponding spirocyclic halides was observed by NMR spectroscopy. Dynamic behavior in solution was observed for **56** and **57** by ^1H NMR spectroscopy [91]. In polar solvents, spontaneous decomposition of **58** was evident, but its existence was unambiguously established by solid-state NMR spectroscopy (^{13}C, ^{15}N and ^{31}P) [92] and elemental analysis. The formation of an iodophosphorane involving a covalent λ^5P–I bond is unusual. Until now, only one example has been established [93].

The formation of **56** also proceeded via the reaction of 1,3-dimethyl-2,2,2-trichloro-1,3,2λ^5-diazaphosphetidine-4-one with **1** (Scheme 7). The reaction of the related trifluoro-substituted compound $(O{:})C(NMe)_2PF_3$ with **1** led to the monocyclic product **59**. The formation of an ionic species, e.g. analogous to **56**, was not observed [67]. Variable-temperature ^1H NMR spectra of **56** were recorded [91], and separate resonances for the protons of the five methyl groups were observed (cf. Fig. 8) at low temperature. The dynamic behavior of **56** in solution was rationalized in terms of an exchange mechanism (either **A** or **B**) involving the *N*-methyl groups (Fig. 9).

While it was not possible to distinguish between the mechanistic alternatives (**A** and **B**) by NMR spectroscopy, pathway **B** is considered to be energetically more favorable since it does not involve a species with positive charges on two neighboring atoms. After exchange of the chloride anion of **56** for the tetraphenylborate anion, compound **60** was formed and an X-ray crystal structure determination was carried out (Fig. 10) [91]. The results confirmed the proposed structure of the cations of **56** and **60**, respectively. A comparison of the distance between the donor nitrogen atom


60
53
54
+1/8 S8
+NaBPh4
-NaCl
+MeI
+X2
X=Cl,Br,I
19
X=Cl, 56
X=Br, 57
X=I, 58
+PhN3
-N2
+Me3SiN(Me)CH2CH2NMe2
-Me3SiX (X=Cl)
2
55a
55
X = F,Cl
+Me3SiN(Me)CH2CH2NMe2
-Me3SiX (X=F)
59

Scheme 7.

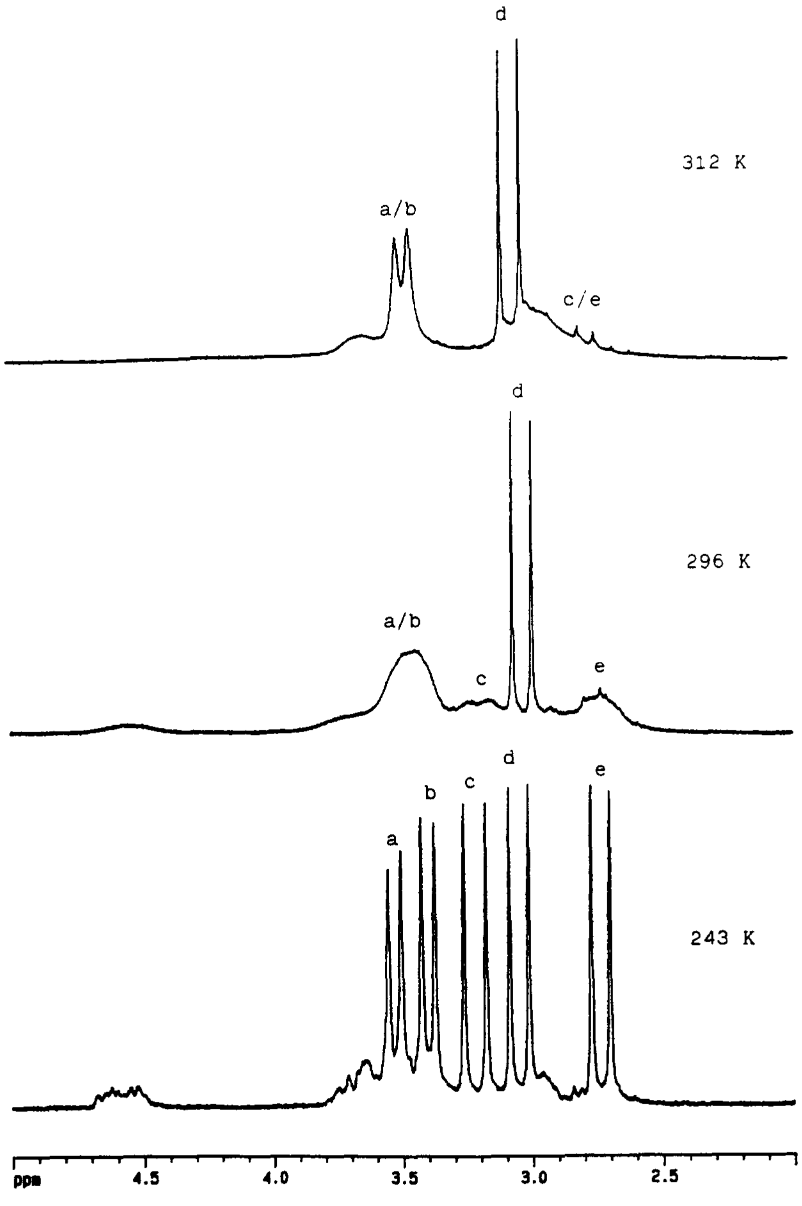


Fig. 8. Variable-temperature ^1H NMR spectra of **56** (in $CDCl_3$) [91]; reprinted by permission of Pergamon Press.

of the $(CH_3)_2N$ group and the phosphorus center (197.5 pm) with the sum of the van der Waals radii (335 pm [94]) suggested a strong bonding interaction. The distance was found to be significantly longer than that in the comparable compound **4** (184.2 pm [50]).

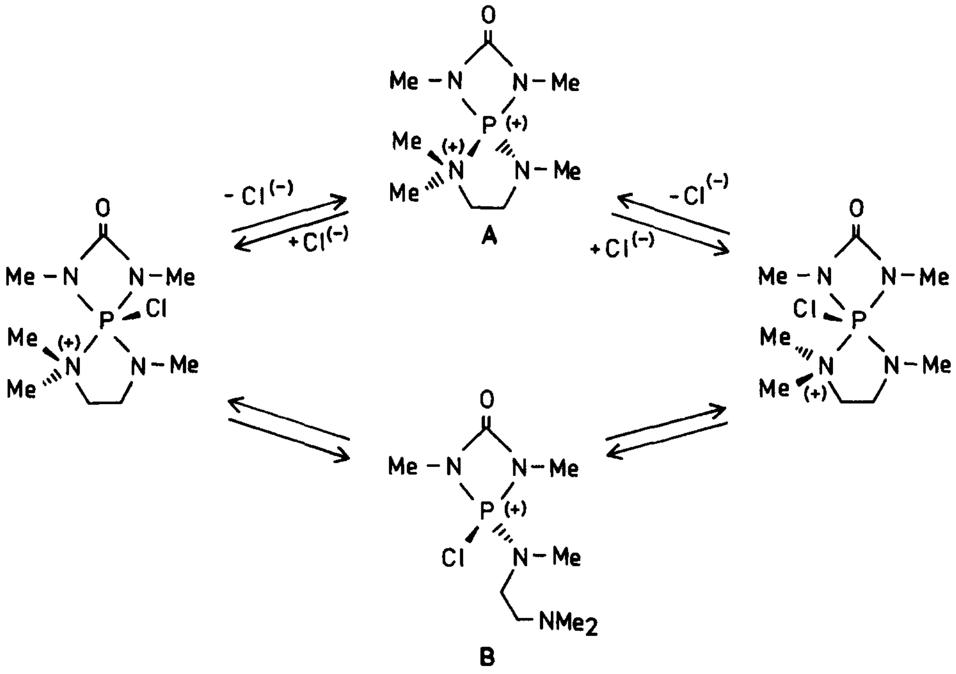


Fig. 9. Possible exchange mechanism of the *N*-methyl groups in **56** [91]; reprinted by permission of Pergamon Press.

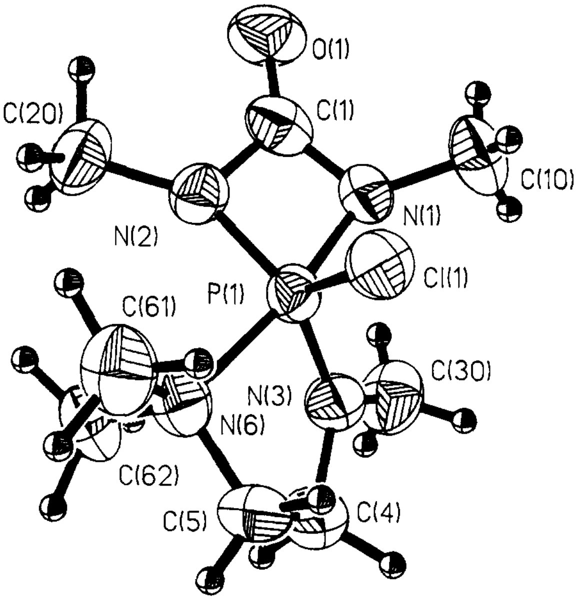


Fig. 10. Structure of the cation of **56** in the crystal [91]; reprinted by permission of Pergamon Press.

5.3.2. Compounds involving the 1,3,5-trimethyl-1,3,5,2-triazaphosphorinane-4,6-dione ring system

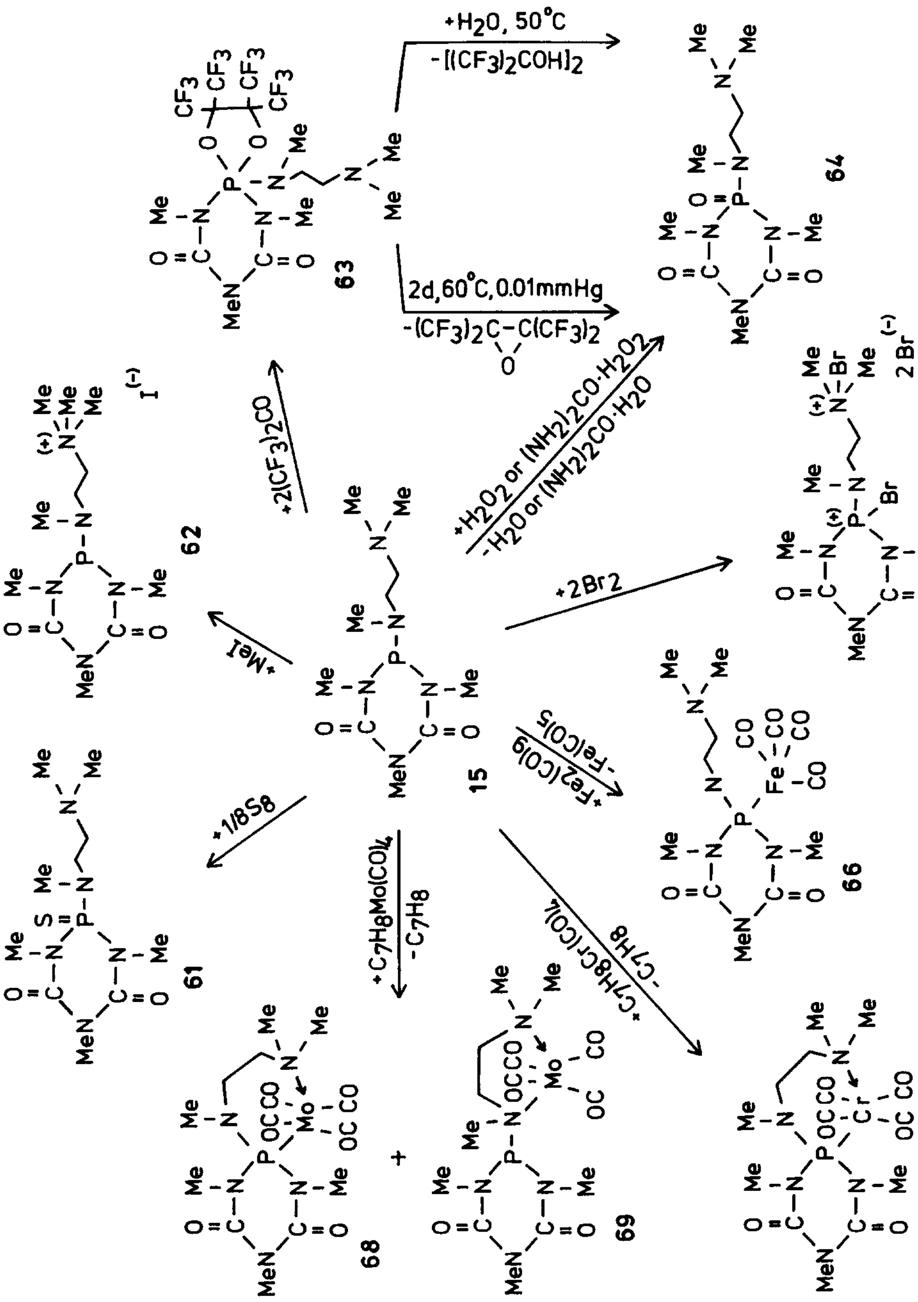
Compound **15** (cf. Section 3.4) was allowed to react with several oxidizing reagents, and its ligand potential was evaluated in reactions with some transition metal substrates [63,95]. The results of these reactions are presented in Scheme 8. The products of the reaction of **15** with sulfur or with methyl iodide (**61** and **62**) are analogous to the comparable products, **53** and **54**, described before. An X-ray crystal structure analysis was conducted for **62** (Fig. 11) [63].

In the reaction of **15** with two equivalents of hexafluoroacetone, compound **63** was formed. This type of oxidative addition of hexafluoroacetone to elements in a low-valent state is well known [96]. Even the existence of strongly electron-withdrawing substituents bonded to phosphorus could not induce intramolecular $Me_2N \rightarrow P$ interaction in **63** [95]. On heating **63** in vacuo, compound **64** was formed in an unusual fashion. The same product was isolated in low yield after reaction of **63** with water and loss of perfluoropinacol [97,98]. Compound **64** was formed in good yield, using hydrogen peroxide or the hydrogen peroxide–urea 1:1 adduct as oxidizing agents. A single-crystal X-ray structure determination of **64** revealed the presence of one molecule of H_2O_2, coordinated via a hydrogen bond to the nitrogen atom of the NMe_2 group (Fig. 12). This phenomenon was observed only when aqueous hydrogen peroxide was used as the oxidizing agent and not when **15** was allowed to react with the hydrogen peroxide–urea 1:1 adduct [95].

In contrast to the results of the reaction of **19** with elemental bromine (formation of **57**), the corresponding compound could not be isolated by reaction of **15** with Br_2. The formation of a bromodimethylammonium bromophosphonium dibromide **65** was established by IR and NMR spectroscopy and elemental analysis. An intramolecular $Me_2N \rightarrow P$ coordination, as observed for **57**, is no longer possible in the case of **65** [63]. The iron tetracarbonyl complex **66** was formed in the reaction of **15** with diiron enneacarbonyl. The phosphorus atom of **15** coordinated to iron and coordination of the nitrogen center was not observed [63]. The reaction of **15** with norbornadiene chromium tetracarbonyl gave the coordination compound **67**, where **15** functions as a bidentate ligand, coordinating to the metal through phosphorus and the nitrogen atom of the dimethylamino group [63]. According to Scheme 8, a mixture of two compounds was obtained in the reaction of **15** with norbornadiene molybdenum tetracarbonyl [63]. This mixture consisted of compounds **68** (comparable to **67** with molybdenum as transition metal) and **69**. For **69** ^1H, ^{13}C and ^{31}P NMR spectroscopy suggest coordination via both nitrogen atoms of the trimethylethylenediamine substituent of **15** to the metal.

5.3.3. Compounds with the 4,5-benzo-1,3,2-dioxaphosphole ring system

As seen in Scheme 9, the expected products **70–73** were formed in the reaction of **16** with elemental sulfur, selenium, tetrachloro-*o*-benzoquinone and hexafluoro-


+H2O, 50°C
-[(CF3)2COH]2
2d, 60°C, 0.01mmHg
-(CF3)2C-C(CF3)2 O
+H2O2 or (NH2)2CO·H2O2
-H2O or (NH2)2CO·H2O
+2(CF3)2CO
+2Br2
+MeI
+Fe2(CO)9
-Fe(CO)5
+1/8S8
+C7H8Mo(CO)4
-C7H8
+C7H8Cr(CO)4
-C7H8
15
61
62
63
64
65
66
67
68
69

Scheme 8.

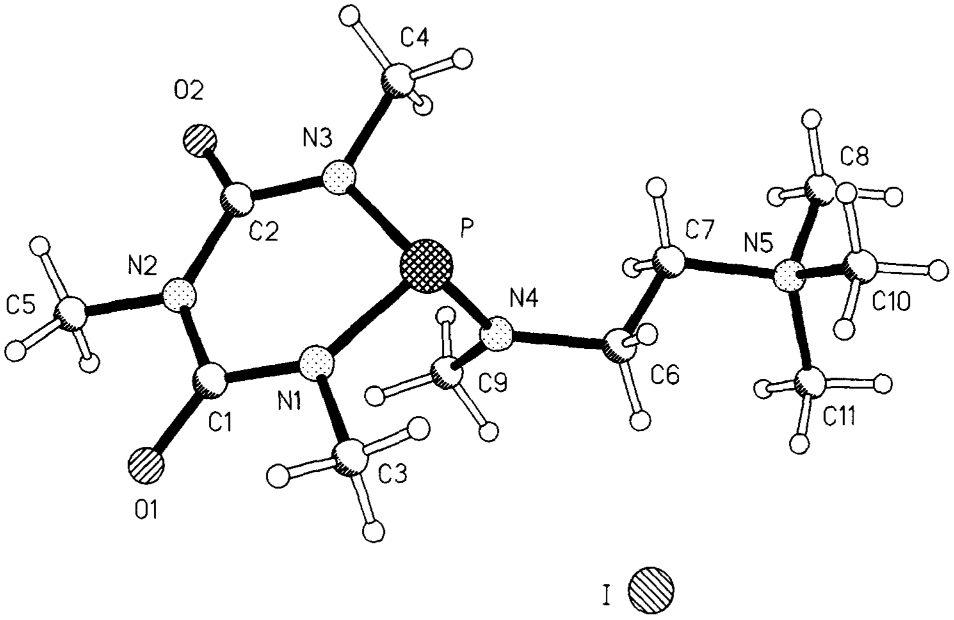


Fig. 11. Molecular structure of **62** in the solid state [63]; reprinted by permission of VCH Verlagsgesellschaft.

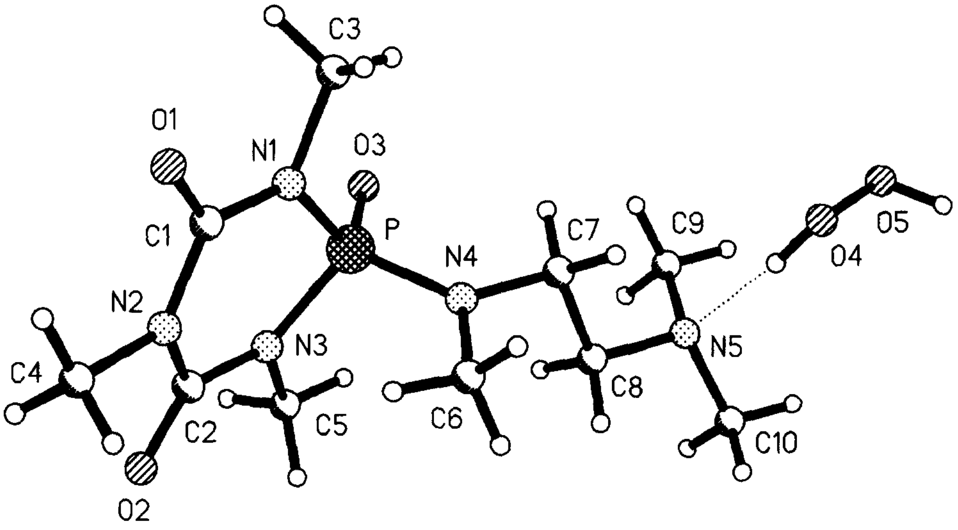
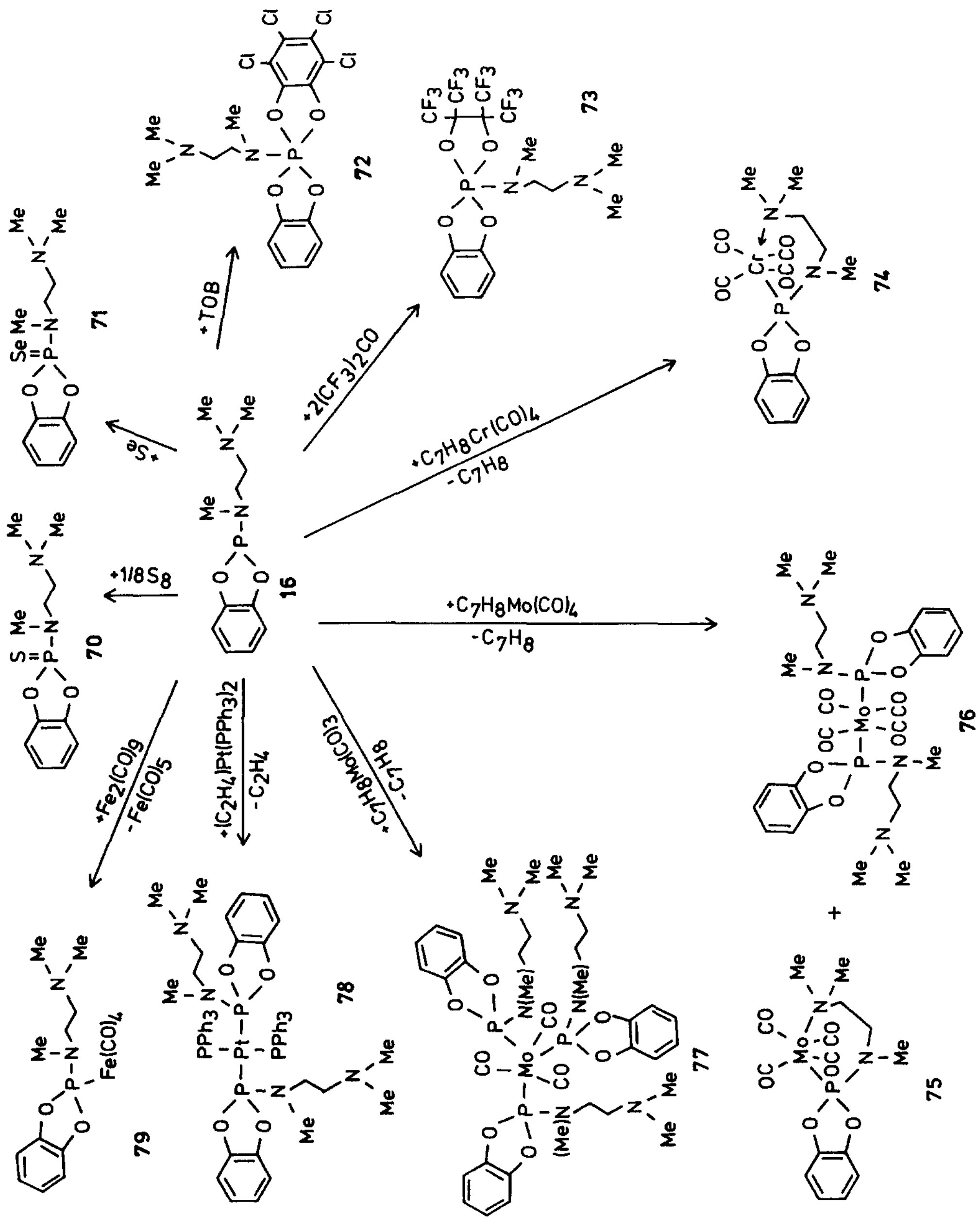


Fig. 12. Formula unit of **64** in the crystal.


16
+1/8S8
70
+Se
71
+TOB
72
+2(CF3)2CO
73
+C7H8Cr(CO)4
-C7H8
74
+C7H8Mo(CO)4
-C7H8
76
+
75
+C7H8Mo(CO)3
-C7H8
77
+(C2H4)Pt(PPh3)2
-C2H4
78
+Fe2(CO)9
-Fe(CO)5
79

Scheme 9.

acetone [60]. Although ligands of high electronegativity are attached to the phosphorus atom of **16**, in all cases, an intramolecular donor–acceptor interaction between the nitrogen atom of the dimethylamino group and the phosphorus atom was not observed in any of the products.

The reaction of **16** with norbornadiene chromium tetracarbonyl produced compound **74**, in the same manner as **67**, with **16** functioning as a bidentate ligand. The first X-ray crystal structure determination of a transition metal complex with *N*,*N′*,*N′*-trimethylethylenediamine as part of the ligand [64] confirmed the cis configuration of the ligand, coordinating via the phosphorus atom and the nitrogen atom N(2) of the NMe_2 group. The bond distances Cr–P and Cr–N(2) are 227 and 223 pm, respectively (cf. Fig. 13).

In the reaction of **16** with norbornadiene molybdenum tetracarbonyl, a mixture of the mono- and disubstituted molybdenum tetracarbonyl complexes **75** and **76** was obtained. The monosubstituted complex **75** involves coordination of only one ligand to the $Mo(CO)_4$ fragment in a similar fashion to that observed for the complexes **67**, **68** and **74**. In the case of **76**, the bidentate ligand norbornadiene in the starting transition metal complex is substituted by two molecules of **16**, coordinating to molybdenum via the phosphorus atom only [84]. These results are in contrast to those for the reaction of **15** with norbornadiene tetracarbonyl, which produced

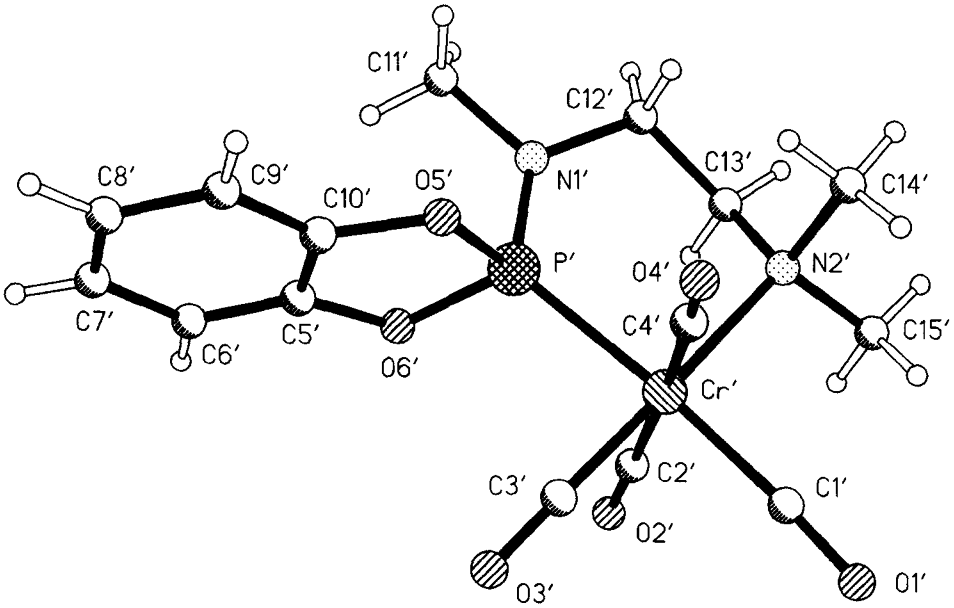
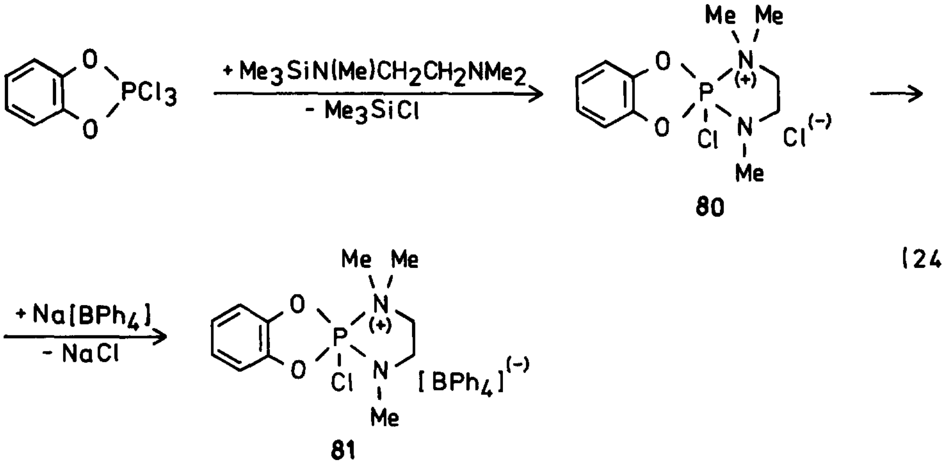


Fig. 13. One of the two independent molecules of **74** in the crystal [64]; reprinted by permission of VCH Verlagsgesellschaft.

monosubstituted molybdenum tetracarbonyl complexes. The reactions of **16** with cycloheptatriene molybdenum tricarbonyl, (η^2-ethylene)bis(triphenylphosphine)-platinum(0) and diiron enneacarbonyl gave the metal complexes **77–79** (Scheme 9). In all these cases **16** was found to coordinate solely via the phosphorus atom [164].

By analogy with **56** (Scheme 7), the intramolecularly stabilized spirocyclic salt **80** was synthesized from the reaction of 4,5-benzo-2,2,2-trichloro-1,3-dioxa-2-λ^5-



(24)

phospholane with **1** [eqn. (24)] [99]. Compound **80** exhibited dynamic behavior in solution and was studied by variable-temperature ^{1}H NMR spectroscopy [99]. The results were similar to those of the variable-temperature NMR spectroscopic investigation of **56**. The influence of the anion on the dynamic behavior of the cation of **80** in solution was investigated. For this reason the coordinating chloride was exchanged for the non-coordinating $[BPh_4]^-$ anion [eqn. (24)], forming compound **81**. ^{1}H NMR spectra of **81** in solution at room temperature were unambiguous, and in contrast to **80**, the cation of **81** did not display dynamic behavior in solution [99]. The structure of the cation of **81** in the solid state was confirmed by an X-ray crystal structure determination (cf. Fig. 14), and revealed a slightly distorted trigonal bipyramidal geometry at phosphorus. The coordinative P–N(2) bond [194.4(2) pm] was longer than the covalent P–N(1) bond [161.6(2) pm], in accord with expectation.

5.3.4. Compounds with the 5,6-benzo-1,3,2-diazaphosphorinane-4-one ring system

The phosphoryl compound **82** was formed by reaction of **18** with aqueous hydrogen peroxide, but a hydrogen peroxide adduct, analogous to **64** (cf. X-ray crystal structure of **64**, Fig. 12) was not observed by IR or NMR spectroscopy [89]. According to Scheme 10, reactions of **18** with sulfur, methyl iodide and bromine

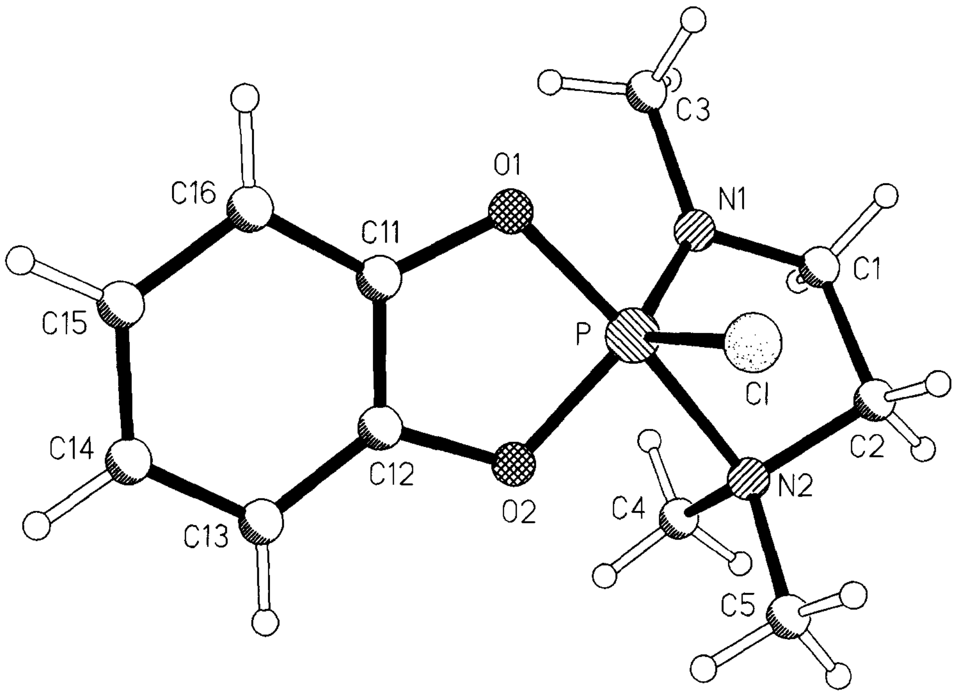


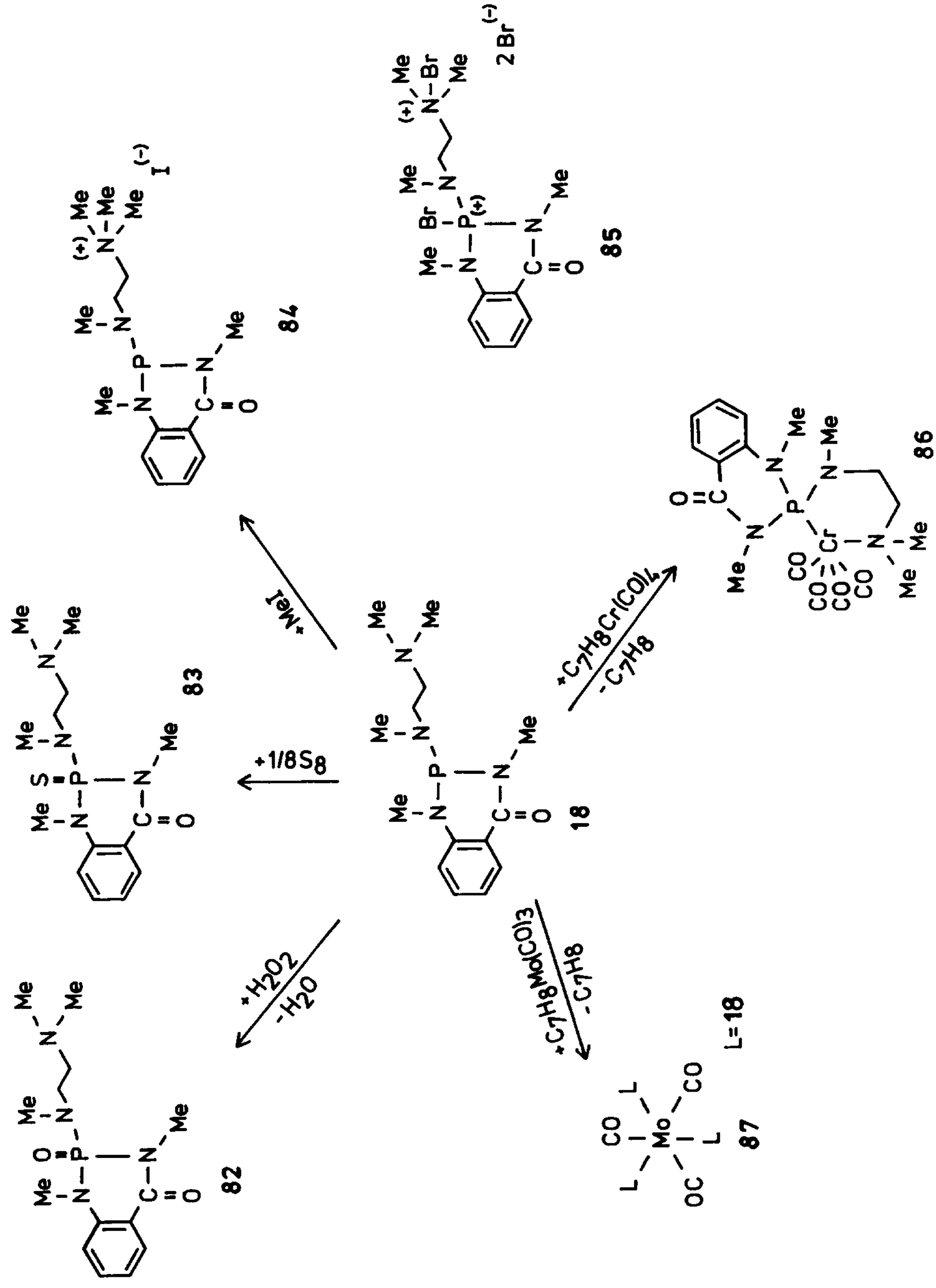
Fig. 14. Structure of the cation of **81** in the crystal [99]; reprinted by permission of Zeitschrift für Naturforschung.

formed the same type of products (compounds **83–85**) [66] as those described for the reactions of **15** with the same reagents (cf. Scheme 8). The complexes **86** and **87** did not exhibit special features [66]; their properties were in good agreement with those of the comparable compounds **74** and **77** (Scheme 9).

5.4. 1,1,3-Trimethyl-1,3,2-diazaphospholidin-1-ium salts: o-benzoquinone adducts and rearrangement reactions

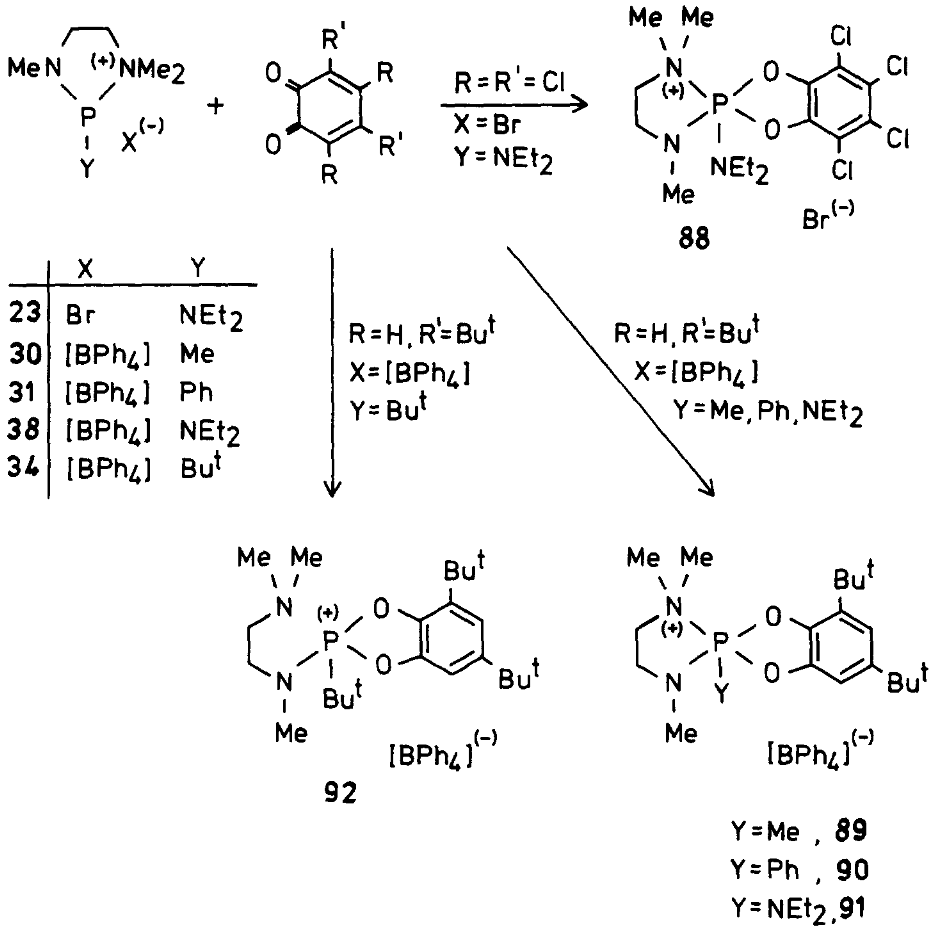
Phosphorane/phosphonium salt equilibria were discussed [100] as a possible form of isomerization of phosphoranes with benzo substituents. The "inner phosphonium salt" results from the phosphorane by heterolysis of a P–O bond of the benzo substituent. In this case, the negative charge remains on the oxygen center and the positive charge on the phosphorus center. The reaction of intramolecularly stabilized phosphenium cations with *o*-quinones proceeded according to Scheme 11. Analogous reactions of 1,3-dienes with non-stabilized phosphenium cations have been described [101].

The spirophosphoranes **88–91** and the phosphonium salt **92** were obtained according to Scheme 11 [102]. The ^1H and ^{31}P NMR data of **88–92** confirmed



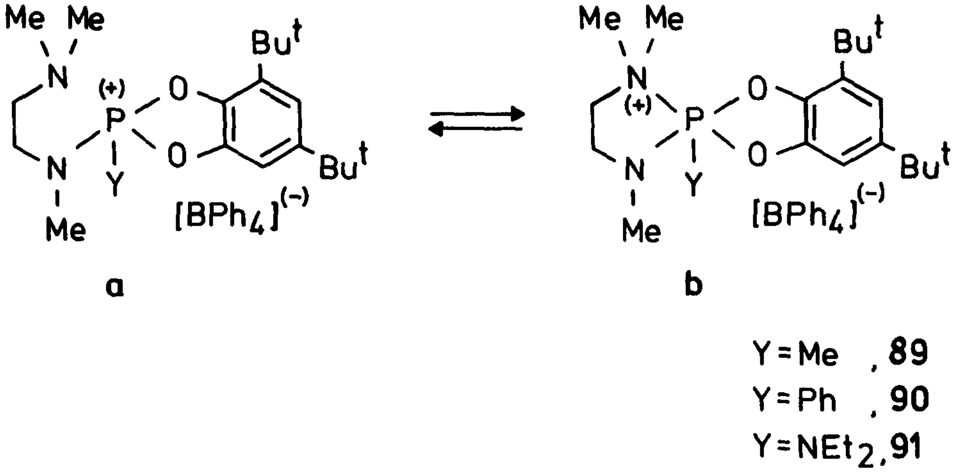
$+H_2O_2$
$-H_2O$
$+1/8\,S_8$
$+MeI$
$+C_7H_8Cr(CO)_4$
$-C_7H_8$
$+C_7H_8Mo(CO)_3$
$-C_7H_8$
$2\,Br^{(-)}$
$I^{(-)}$
L=18
18
82
83
84
85
86
87

Scheme 10.



Scheme 11.

the structures presented in Scheme 11. The expected phosphorus–proton coupling $^3J[P\mathrm{N}(CH_3)_2]$ is seen in the room-temperature ^{1}H NMR spectra of the spirophosphoranes **88**, **89** and **91**, but not in the case of the phosphonium salt **92**. The ^{31}P NMR spectra of **89**–**91** show some signals of low intensity besides the product resonances. These are due to small amounts of isomers that are in equilibrium with the spirophosphoranes (Scheme 12). The spirophosphorane structures **b** of **89**–**91** are probably in equilibrium with the corresponding phosphonium salt structures **a** (Scheme 12; Y = Me, Ph, NEt_2). No indication of the corresponding spirophosphorane structure could be found for the *tert*-butyl derivative **92**. Obviously, the bulk *tert*-butyl substituent in **92** efficiently prevents the coordination of a fifth substituent, whereas the λ^3-phosphorus atom in the 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium salt **34** is not sterically overloaded.



Scheme 12.

5.4.1. *Dynamic structure of the 3,5-di-tert-butyl-o-benzoquinone adduct **90** in solution*

The diastereotopic character of both methyl groups bonded to the donor nitrogen atom in **90** is evident in its ^{1}H NMR spectrum (cf. Fig. 15). Broad resonances for the protons involved in the exchange process are observed in the ^{1}H NMR spectrum recorded at room temperature. At low temperature, sharp signals can be observed and the diastereotopic character of the methyl groups of the Me_2N donor atom is evident. The results of the variable-temperature ^{1}H NMR spectroscopic investigation of compound **90** are shown in Fig. 15, which indicate the presence of two diastereomers, **D1** and **D2**. At high temperature, the scission and restitution of the Me_2N–P bond, in accord with Scheme 13, are conceivable as a mechanism of isomerization. The transformation of **D1** into **D2** (Scheme 13) could also occur without bond breaking, for example by pseudorotation according to the Berry mechanism, [103] illustrated in Scheme 14.

5.4.2. *Reaction of the 1,1,3-trimethyl-1,3,2λ^3-diazaphospholidin-1-ium salt **33** with tetrachloro-o-benzoquinone*

As expected, the reaction of **33** with tetrachloro-*o*-benzoquinone did not yield either a spirophosphorane (by analogy with **89–91**) or a phosphonium salt (as in the case of **92**). According to eqn. (25), a poorly soluble rearrangement product was isolated in low yield [102]. It was suggested that oxidative addition of tetrachloro-*o*-benzoquinone to **33** occurred in the first reaction step, followed immediately by spontaneous rearrangement and formation of the more stable phosphonium salt **93** [102].

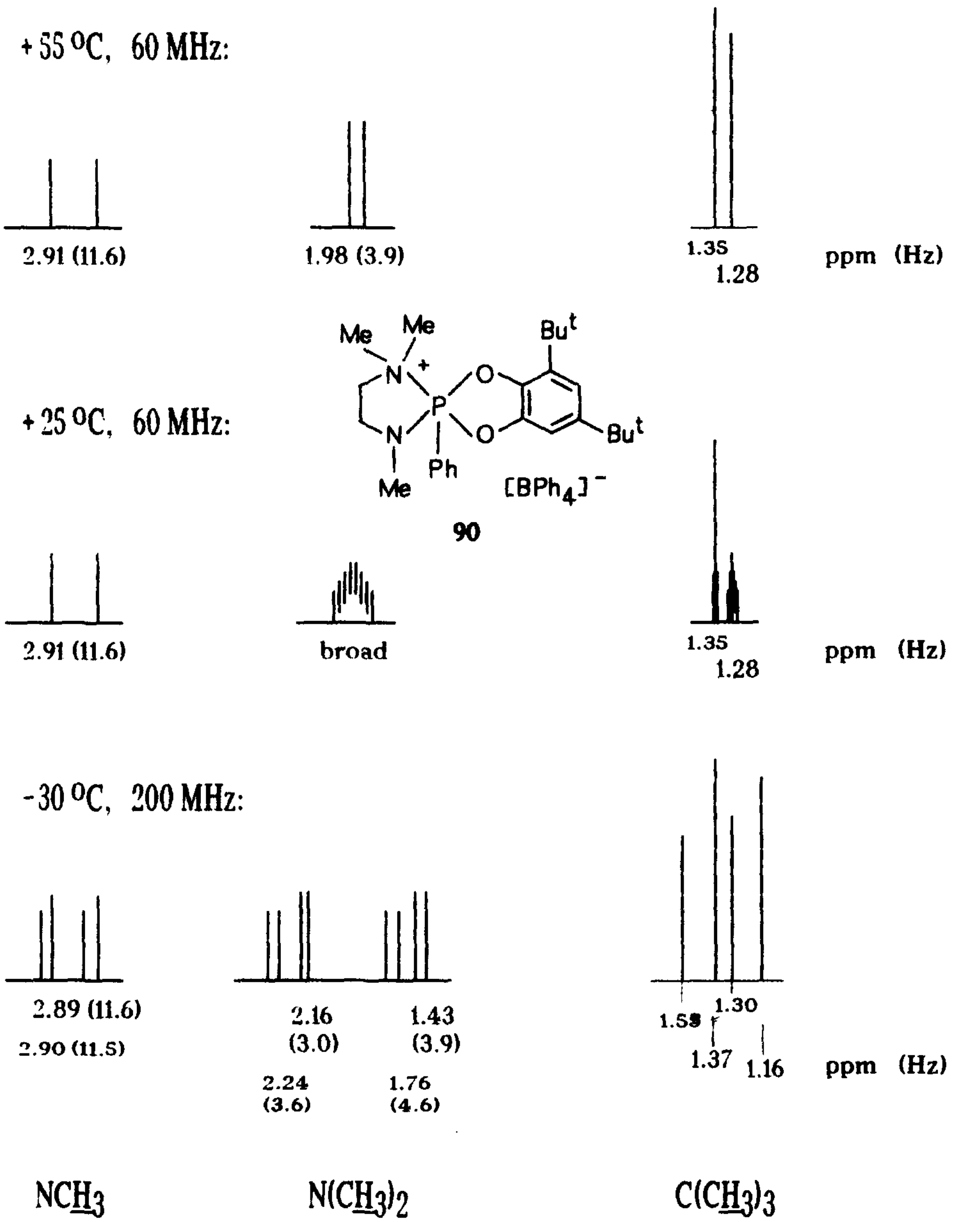
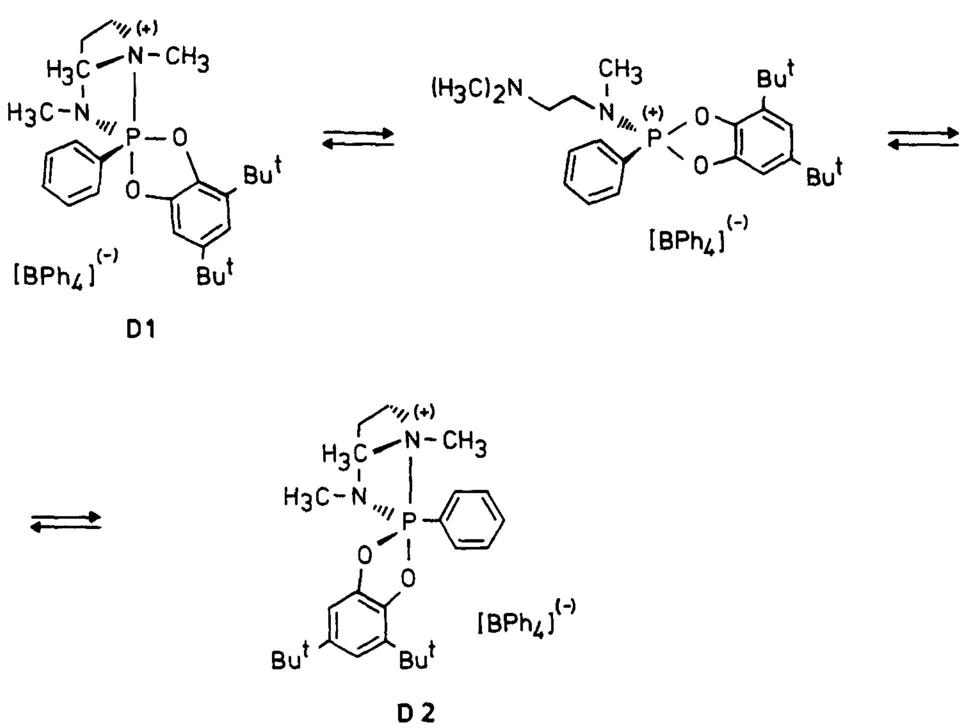


Fig. 15. Variable-temperature ^{1}H NMR spectra of the phenyldiazaphospholidinium 3,5-di-*tert*-butyl-*o*-benzoquinone adduct **90**. ^3J(PH) coupling constants (in Hz) are given in parentheses. Isomers are distinguished from each other by use of different type [102]; reprinted by permission of VCH Verlagsgesellschaft.

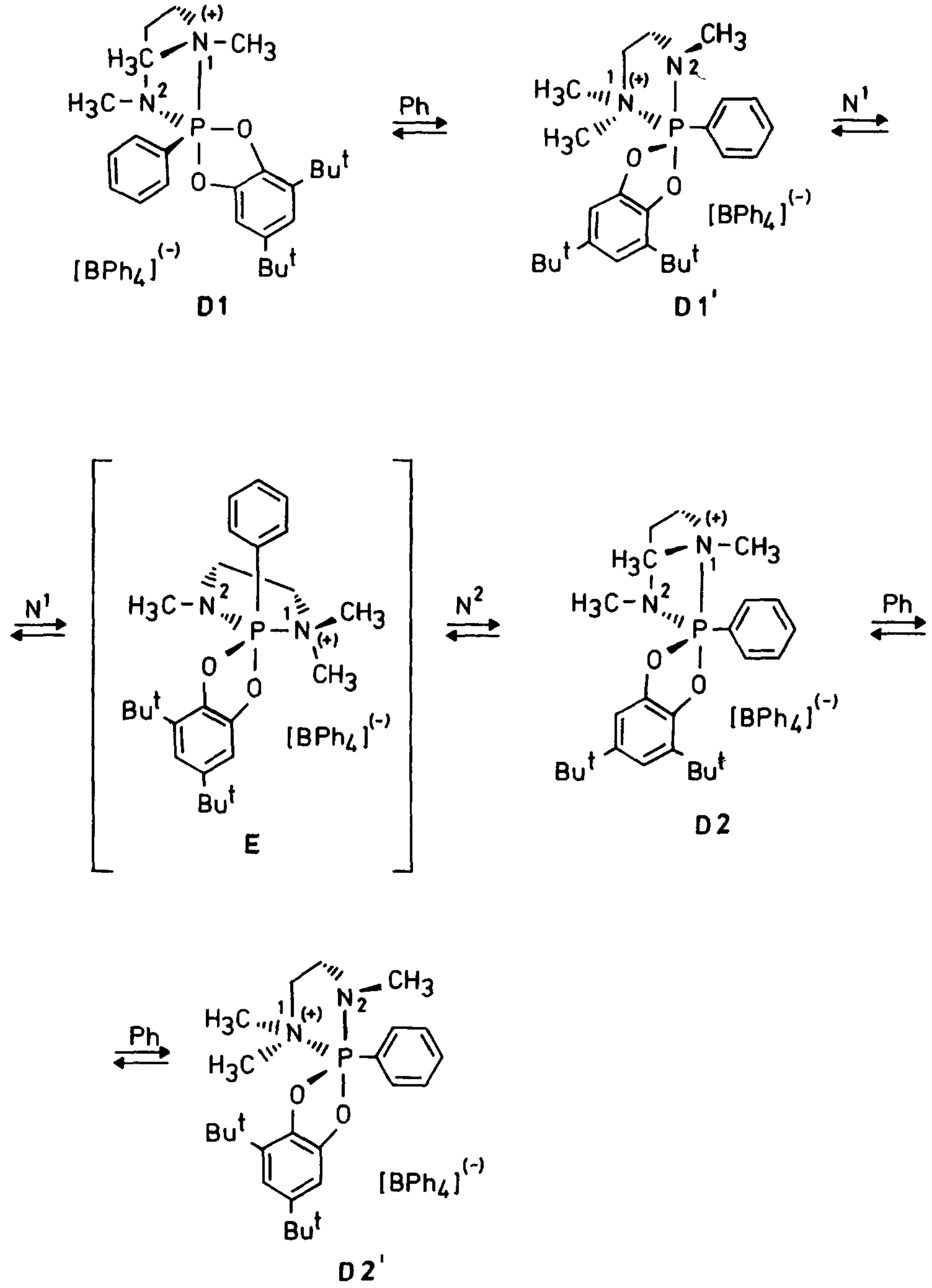


Scheme 13.

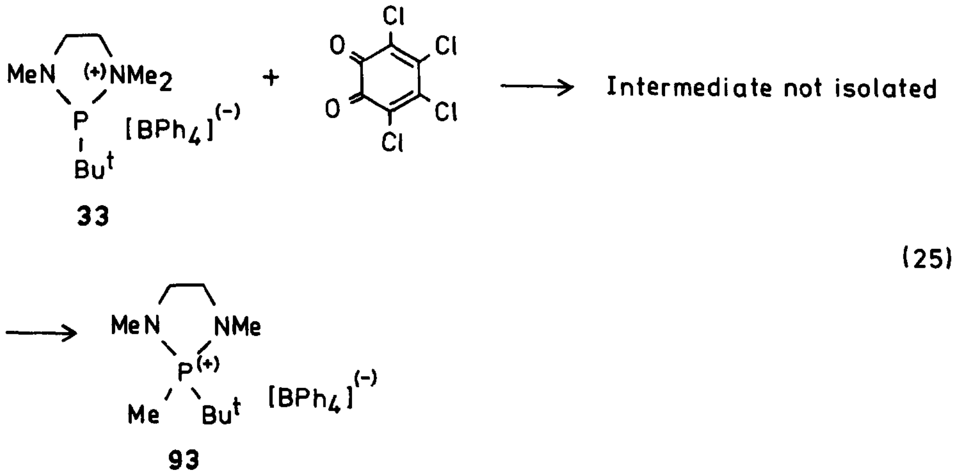
5.5. *Reactions of tri- and tetrafluorophosphoranes with N-trimethylsilyl-N,N′,N′-trimethylethylenediamine* **1**: *N,N′,N′-trimethylethylenediamine-substituted organofluorophosphoranes*

The formation of the di- and trifluorophosphoranes **94–100** [104], bearing the *N,N′,N′*-trimethylethylenediamine grouping was effected according to well known procedures [105–112], by reaction of the corresponding tri- or tetrafluorophosphoranes with **1** in accord with Scheme 15. NMR spectroscopic investigations (^1H, ^{13}C, ^{19}F, ^{31}P) confirmed the proposed structure of compounds **94–100**. All of the ^{19}F and ^{31}P NMR data served to prove the presence of two axial and one equatorial fluorine atom bonded to trigonal bipyramidal phosphorus in the trifluorophosphoranes **94–98**. The ^{19}F and ^{31}P NMR spectra of the difluorophosphoranes **99** and **100** revealed two equivalent axial fluorine atoms (cf. Table 3).

All NMR parameters were observed in the expected region (cf. Table 3). The $\delta(F)$ values of the axially bonded fluorine atoms were found to be shifted to lower field [113] than those of the equatorially bonded fluorine atoms (cf. Table 3). The ^1H NMR spectra of **94–100** did not indicate intramolecular donor–acceptor interaction between the nitrogen atom of the $(CH_3)_2N$ group and the phosphorus atom



Scheme 14.

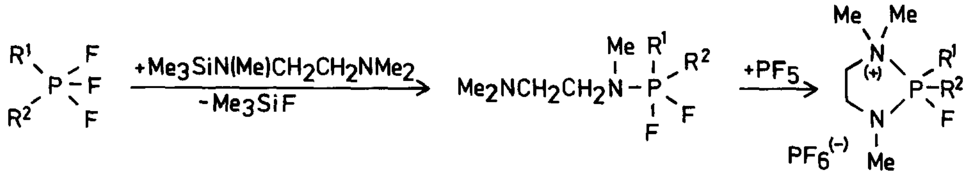


33

93

(25)

in any case; there was no splitting of the $(CH_3)_2N$ resonance by coupling to either ^{31}P or ^{19}F [104].



Nr.	R^1	R^2
94	F	Me
95	F	Me_3SiCH_2
96	F	Ph
97	F	C_6H_5
98	F	$2,5Me_2C_6H_3$
99	Ph	Ph
100	Ph	C_4H_4N

Nr.	R^1	R^2
101	F	Me
102	F	Me_3SiCH_2
103	F	Ph
104	Ph	C_4H_4N

Scheme 15.

5.6. Intramolecularly stabilized 1,1,3-trimethyl-1,3,2λ^5-diazaphospholidin-1-ium hexafluorophosphates by fluoride abstraction from N,N',N'-trimethylethylenediamine-substituted fluorophosphoranes with phosphorus pentafluoride

Reactions of phosphorus pentafluoride with certain substituted fluorophosphines and -phosphoranes, forming the corresponding alkylphosphenium or alkylphosphonium cations and hexafluorophosphate anion, have been described

TABLE 3

^{31}P and ^{19}F NMR data for the tri and difluorophosphoranes **94–100**

No.	^{31}P			^{19}F				
	δ(P)	$^1J(PF_{ax})$	$^1J(PF_{eq})$	$\delta(F_{ax})$	$\delta(F_{eq})$	$^1J(PF_{ax})$	$^1J(PF_{eq})$	^2J(FF)
94	−35.61	809	970	−29.7	−68.1	809	970	54
95	−33.00	805	958	−28.5	−67.0	805	958	51
96	−52.00	819	966	−42.3	−52.0	819	966	56
97	−58.00	817	962	−28.7	−59.5	817	962	66
98	−44.50	823	981	−33.4[a] −36.2[a]	−66.0	817[a] 816[a]	981[a]	59
99	−51.9	706		−37.5		706		
100	−66.4	773		−40.2		773		

δ Values in ppm; J in Hz.

[a] Recorded at −30°C.

[114–117]. Phosphorus pentafluoride exhibits the highest affinity for fluoride ion of all phosphorus halides [118]. The reaction of the trifluorophosphoranes **94–96** and of the difluorophosphorane **100** with phosphorus pentafluoride produced the corresponding fluorophosphonium cations according to Scheme 15 (Section 5.5), which are stabilized by immediate ring closure as a result of intramolecular donor–acceptor interaction between the nitrogen atom of the dimethylamino group and the phosphorus atom [104]. The observed δ(P) and δ(F) values and the splitting patterns are indicative of the fluorophosphoranes **101–104** (cf. Table 4).

The ^{31} NMR spectrum of the (trimethylsilyl)methyl-substituted compound **102** shows dynamic behavior at room temperature in solution and the expected splitting pattern at low temperature (−30°C). An intramolecular interaction of the trimethylsilyl group with one of the fluorine atoms was also observed by ^{1}H NMR spectroscopy, which corroborated the observations in the ^{31}P NMR spectra [104]. Because of an anisotropy effect [119–122], the ^{1}H NMR resonance of the dimethylamino group

TABLE 4

^{31}P and ^{19}F NMR data for the hexafluorophosphate salts **101–104**

No.	^{31}P			^{19}F				
	δ(P)	$^1J(PF_{ax})$	$^1J(PF_{eq})$	$\delta(F_{ax})$	$\delta(F_{eq})$	$^1J(PF_{ax})$	$^1J(PF_{eq})$	^2J(FF)
101	−17.00	836	1044	−36.9	−82.9	836	1044	47
102	−13.33	850	1042	−34.0	−82.0	850	1042	45
103	−26.85	833	1059	−37.4	−86.5	834	1059	56
104	−9.79	1037		−71.65		1043		

δ Values in ppm; J in Hz.

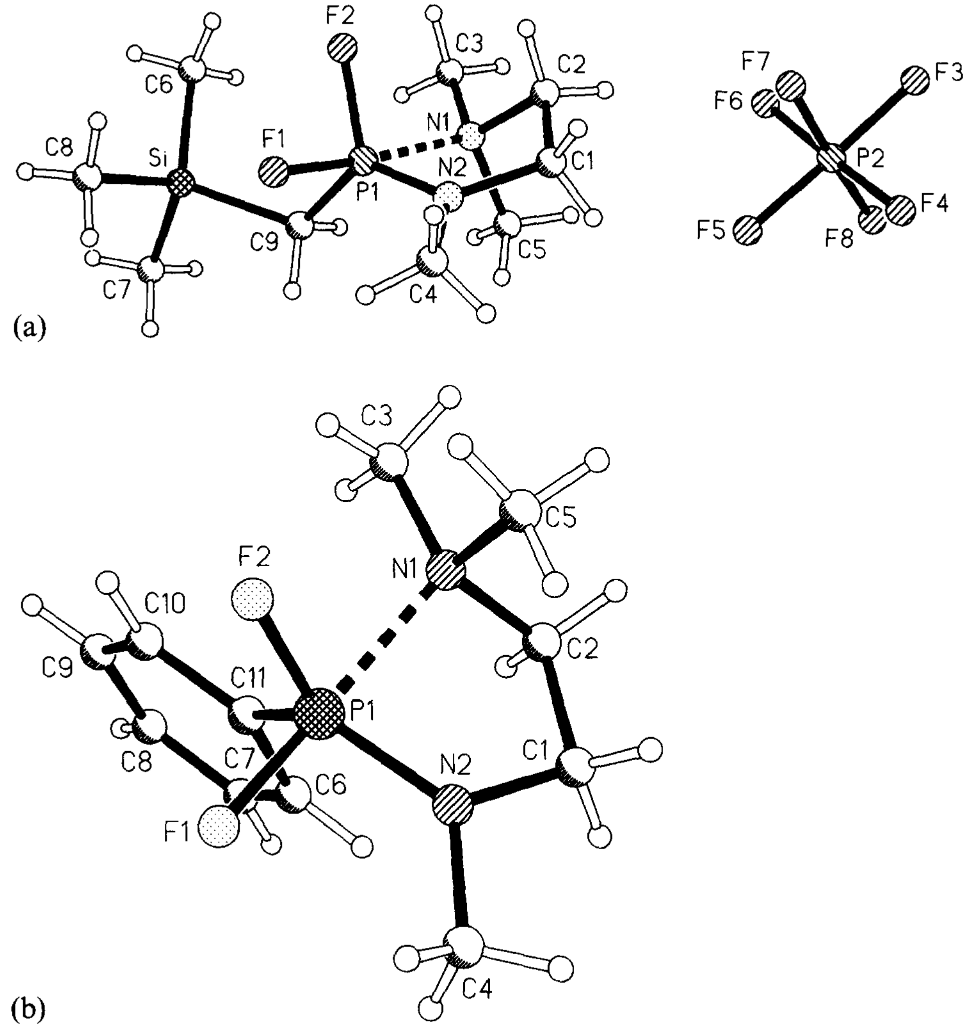


Fig. 16.

of the phenyl-substituted compound **103** exhibited two groups of signals at high field [123]. ^{19}F NMR spectroscopic data for compound **104** [chemical shift, splitting pattern, coupling constant $^{1}J(PF)$] suggested that the single fluorine substituent occupies an equatorial position at tbp phosphorus [104]. This seems to contradict the electronegativity rule [105,124,125], according to which the axial positions at the trigonal bipyramidal phosphorus are always occupied by the (most electronegative) fluorine atoms. The deviation from this rule is caused by the higher group electronegativity [126,127] of the pyrrolyl ligand in **104** [104].

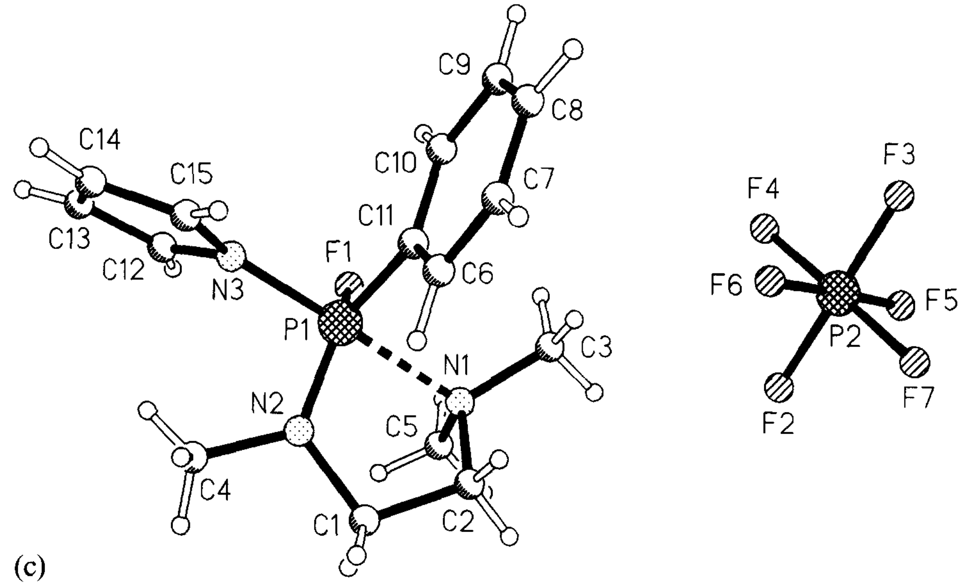


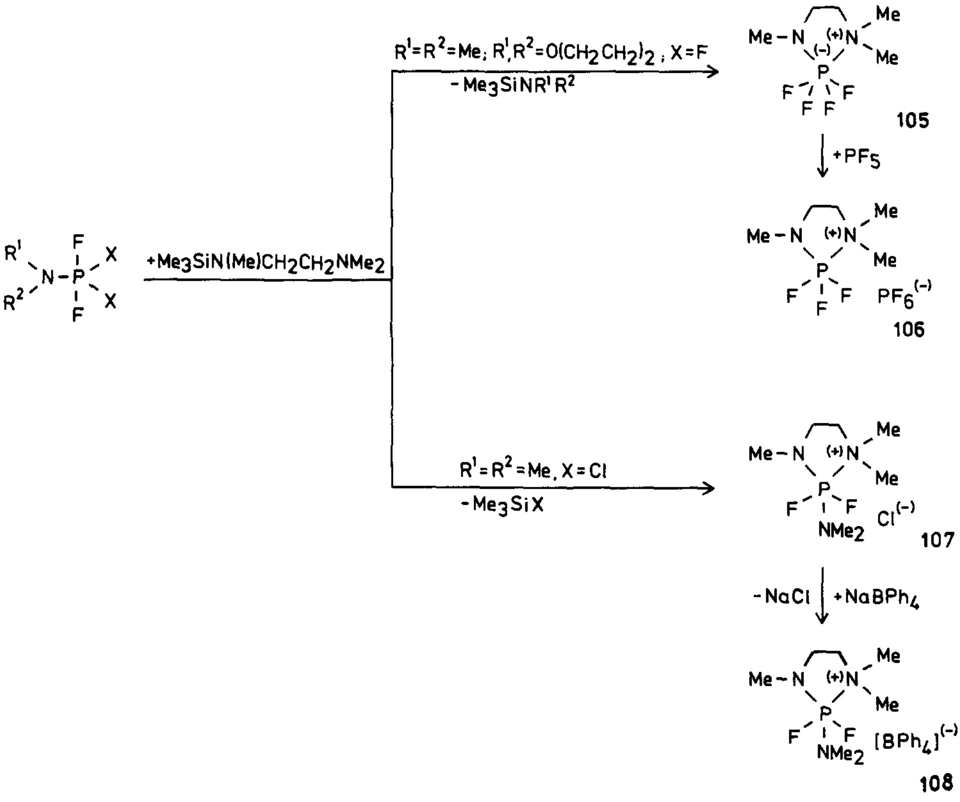
Fig. 16. (continued). Formula units of compounds **102–104** in the crystal. The long P—N bond is indicated by a broken line [104]; reprinted by permission of VCH Verlagsgesellschaft.

*5.6.1. X-ray crystal structure analysis of 1,1,3-trimethyl-1,3,2λ^5-diazaphospholidin-1-ium salts **102–104***

The structure and spatial arrangement of the substituents in **102–104** were confirmed by X-ray crystal structure analysis [104] [Fig. 16(a)–(c)].All compounds were found to exhibit the expected trigonal bipyramidal geometry at phosphorus. The phosphorus bonds to the $N(CH_3)_2$ group are all very long [**102**, 199.1(3); **103**, 199.6(3); **104**, 207.0(3) pm]. The exceptionally long P—N bond in **104** is consistent with the decreased Lewis acid character of a phosphorus center bearing only one fluorine substituent [104].

5.7. Unusual formation of a λ^6P-tetrafluorophosphate involving the N,N′,N′-trimethylethylenediamine group

The reactions of dimethylamino- and morpholinotetrafluorophosphorane with **1** did not proceed with cleavage of a PF bond and formation of a trifluorophosphorane, by analogy with **94–98**. According to Scheme 16, compound **105** was formed, involving intramolecular donor–acceptor interaction [128], with the appropriate trimethylsilylamine as the other product. The ^{19}F and ^{31}P NMR spectra of solutions of **105** at room temperature suggested that the solution structure is dynamic, and variable-temperature spectra were therefore recorded [128] (Figs. 17 and 18). The ^{31}P NMR spectrum of **105**, recorded at room temperature, displayed a sharp triplet



Scheme 16.

and two broad signals (Fig. 18). The line broadening served to illustrate the dynamic behavior of **105** in solution at room temperature. A ^{31}P NMR spectrum recorded at −45°C revealed a sharp doublet of doublets of triplets, due to coupling between ^{31}P and ^{19}F. The $\delta(P)$ value was significantly shifted to higher field and was typical of a hexacoordinate (λ^6) phosphorus center. The ^{19}F and ^{31}P NMR spectra recorded at low temperature were rationalized in terms of an A_2BCX spin system, indicating the presence of three chemically non-equivalent fluorine atoms in **105**. The ^{19}F and ^{31}P NMR spectra observed experimentally were accurately reproduced by a computer simulation (Figs. 17 and 18) [128].

5.7.1. *X-ray crystal structure analysis of the tetrafluorophosphate 105*

The crystal structure determination of **105** (Fig. 19) confirmed octahedral coordination at the phosphorus atom with a very long coordinative P–N(2) bond of 196.5 pm. The five-membered chelate ring adopts an envelope conformation, with C(2) 61 pm out of the plane of the other atoms [128].

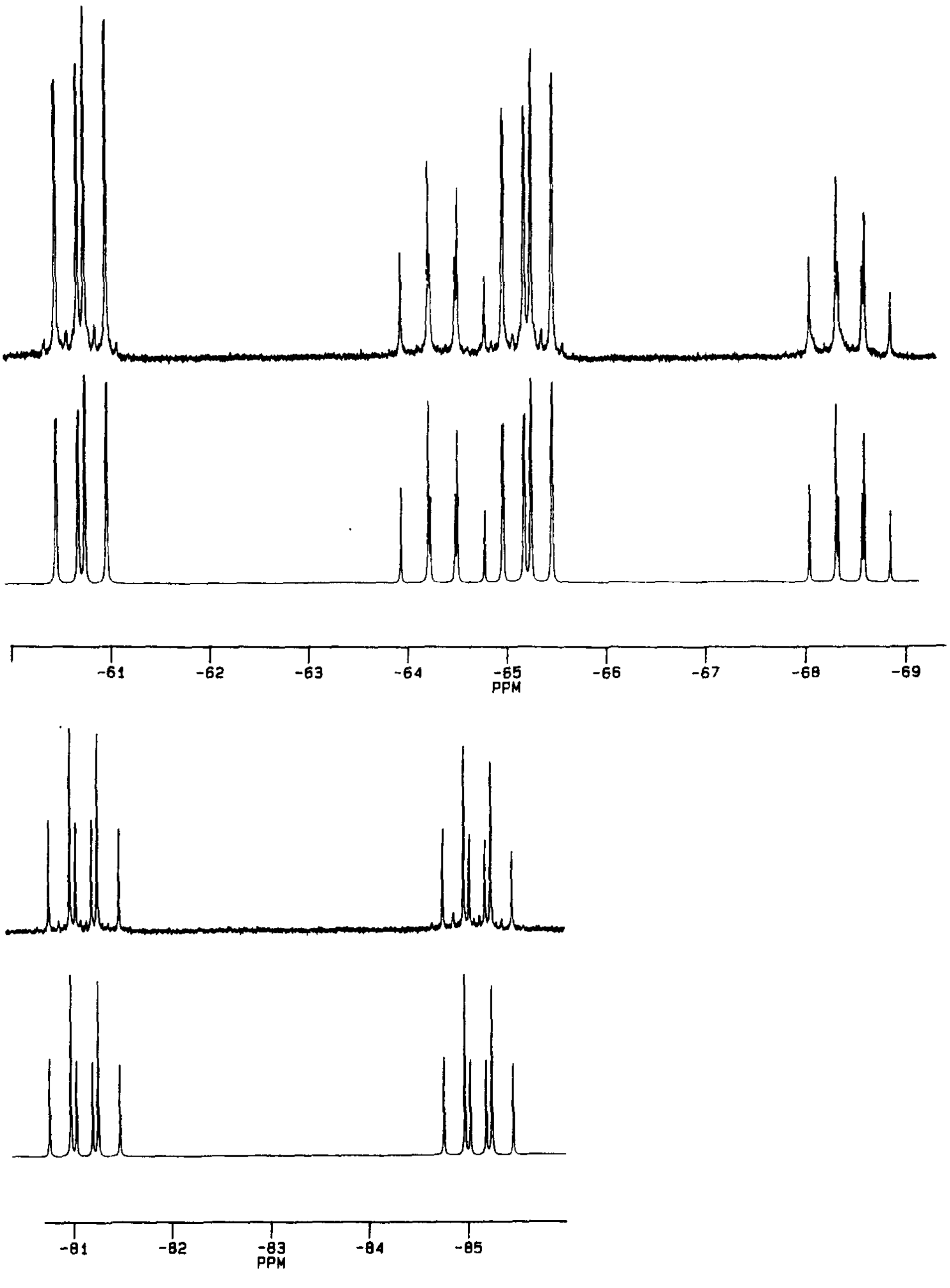


Fig. 17. Temperature-dependent ^{19}F NMR spectra of **105**. Top, ^{19}F NMR spectrum of **105** observed at −30°C; bottom, calculated ^{19}F NMR spectrum of **105** [128]; reprinted by permission of VCH Verlagsgesellschaft.

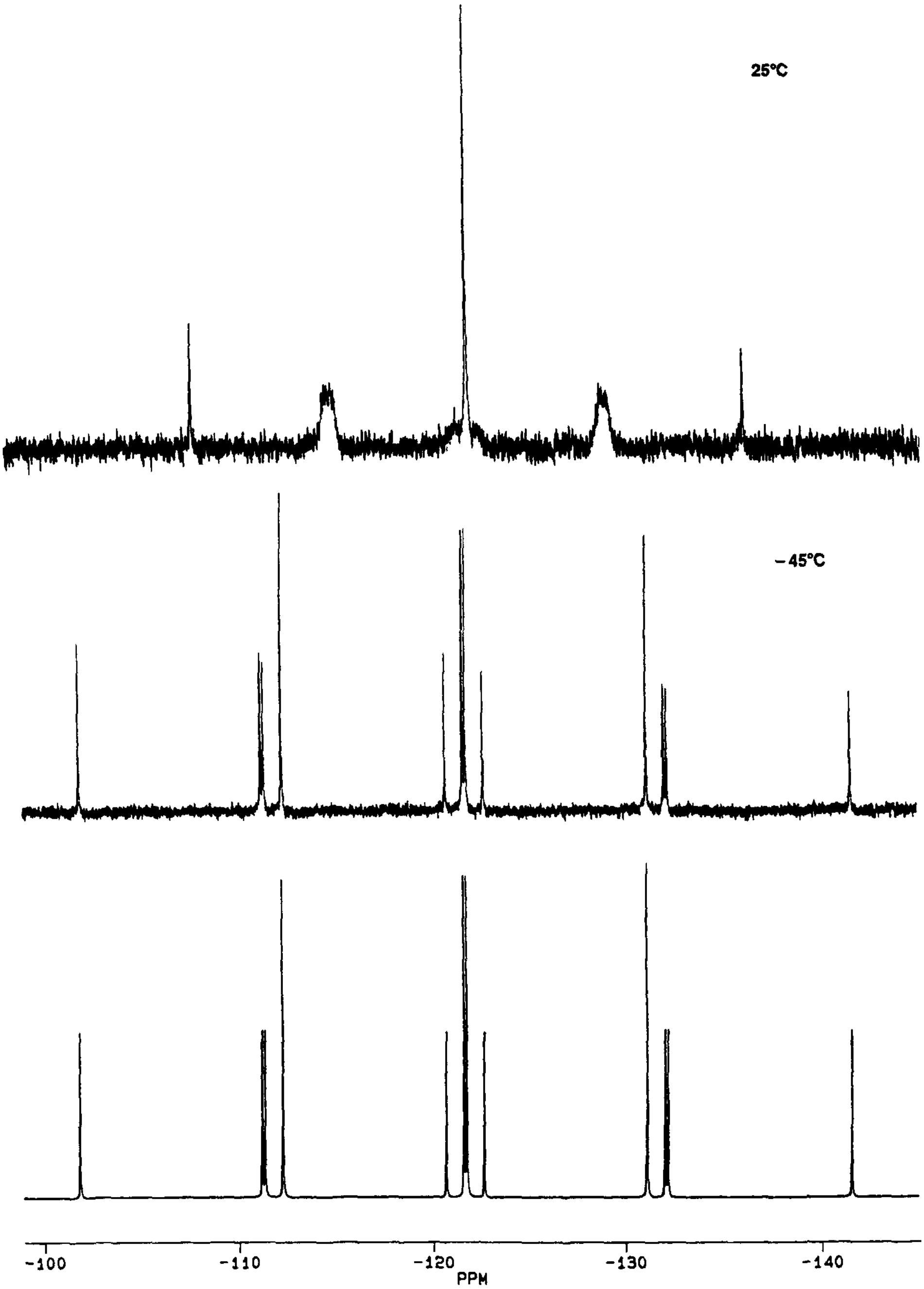


Fig. 18. Temperature-dependent ^{31}P NMR spectra of **105**. Top, ^{31}P NMR spectra of **105** at room temperature and −45°C; bottom, calculated ^{31}P NMR spectrum of **105** [128]; reprinted by permission of VCH Verlagsgesellschaft.

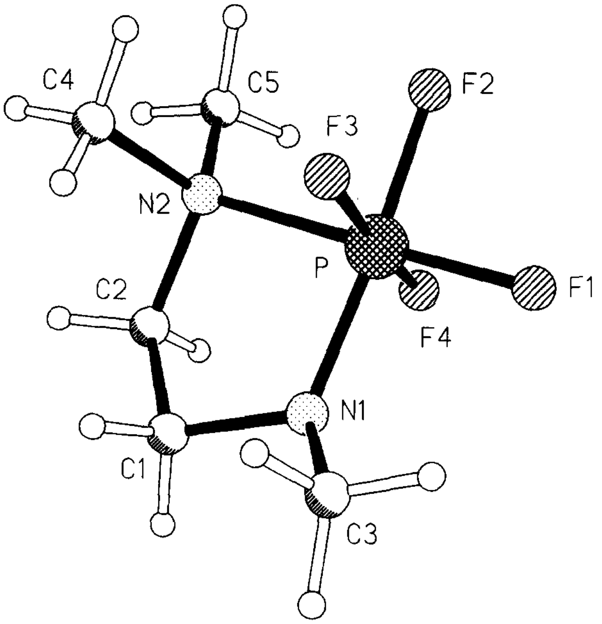


Fig. 19. The molecule of **105** in the crystal [128]; reprinted by permission of VCH Verlagsgesellschaft.

*5.7.2. Reaction of the tetrafluorophosphate **105** with phosphorus pentafluoride*

The reaction of **105** with phosphorus pentafluoride yielded the hexafluorophosphate salt **106** [129] shown in Scheme 16. In addition to the PF_6^- grouping, two magnetically inequivalent fluorine atoms were observed by ^{19}F and ^{31}P NMR spectroscopy, corresponding to two equatorial and one axial fluorine atom bonded to a trigonal bipyramidal phosphorus center. In contrast to **105**, dynamic behavior in solution at room temperature was not observed for **106**. All NMR spectra were unambiguous. The reaction of **1** with phosphorus pentafluoride did not produce **106** [129].

5.8. Reaction of dichloro(dimethylamino)difluorophosphorane with N-trimethylsilyl-N,N′,N′-trimethylethylenediamine

As described in Section 5.7, the reaction of **1** with dimethylaminotetrafluorophosphorane did not lead to the dimethylamino-substituted trifluorophosphorane by analogy with compounds **94–98** and compound **105** was formed instead (Scheme 16). The synthesis of the intramolecular complex **107** was effected in accord with Scheme 16 by reaction of equimolar amounts of the unstable dimethylaminodichlorodifluorophosphorane $Me_2NPF_2Cl_2$ [130–133] with **1** [104], involving selective scission of the two P–Cl bonds. The NMR spectroscopic investigation of **107** showed equivalence of the two fluorine atoms bonded to phosphorus contrary to expectation. Because of the magnitude of $\delta(F)$ and $^1J(PF)$, a dynamic exchange process [105] involving the two fluorine atoms at the tbp phosphorus center in **107** was assumed. This process must be fast, relative to the NMR time scale. For this reason, only a mean value for $\delta(F)$ and $^1J(PF)$ for the axially and equatorially bonded fluorine atoms could be determined [104]. Because of its ability to coordinate to phosphorus, it seemed conceivable that the chloride ion in **107** has an influence on the proposed dynamic exchange process in solution. The chloride ion was exchanged for the non-coordinating tetraphenylborate anion (Scheme 16) by reaction of **107** with sodium tetraphenylborate [134] and the NMR spectroscopic investigation of **108** led to the same results as observed for **107**. The dynamic behavior of the cations of **107** and **108** does not depend on the anion. Only when ^{19}F and ^{31}P NMR spectra were recorded at low temperature did the fluorine atoms become magnetically non-equivalent, with one axial and one equatorial fluorine atom at the trigonal bipyramidal phosphorus center [134].

*5.8.1. X-ray crystal structure analysis of the 1,1,3-trimethyl-1,3,2λ^5-diazaphospholidin-1-ium salt **108***

The structure of the cation of **108** in the solid state was confirmed by a single-crystal X-ray structure determination [134] (Fig. 20), revealing a trigonal bipyramidal geometry for the phosphorus center, with N(1) (of the NMe_2 group of the chelate ring) and F(1) in the axial position. The ethylenediamine ring is attached axially/

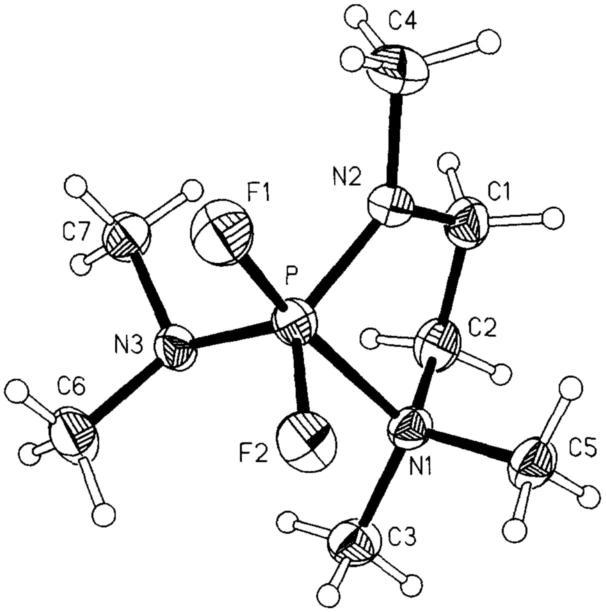


Fig. 20. Structure of the cation of **108** in the crystal [134]; reprinted by permission of Gordon and Breach Science Publishers.

equatorially at the trigonal bipyramidal phosphorus center. The coordinative P–N(1) bond [198.7(1) pm] is very long [134].

6. CONCLUSIONS AND PROSPECTS

The introduction of the *N,N′,N′*-trimethylethylenediamine substituent at silicon and, especially, at phosphorus has given rise to a wealth of new chemistry and unusual compounds, by virtue of its ability to coordinate intramolecularly to the central atom. The trimethylethylenediamine substituent was found to coordinate intramolecularly ($Me_2N \rightarrow Si$) to silicon, leading to an increase in the coordination number of silicon from 4 to 5 (λ^5Si). P(III)–$N(Me)CH_2CH_2NMe_2$ systems have been studied in detail. The trimethylethylenediamine substituent group was found to coordinate spontaneously ($Me_2N \rightarrow P$) in a number of cases, with the formation of intramolecular $Me_2N \rightarrow P$ complexes. In other cases the formation of such complexes could be induced by Lewis acids, e.g. $AlCl_3$. Despite the $Me_2N \rightarrow P$ coordination, reactions typical of P(III) were observed for the trivalent phosphorus atoms exhibiting acceptor properties. $Me_2NCH_2CH_2N(Me)$-substituted P(III) compounds were evaluated with regard to their ligand qualities towards transition metals, e.g. Cr(0), Mo(0), Fe(0) and Pt(II). It was found that $Me_2NCH_2CH_2N(Me)$-substituted P(III) compounds may function solely as P(III) donors or as chelating ligands, coordinating either via P(III) and the nitrogen atom of the Me_2N group, or via both nitrogen atoms.

The trimethylethylenediamine substituent bonded to tetra- and pentacoordinate phosphorus was also studied for some representative examples. Whereas spontaneous intramolecular $Me_2N \rightarrow P$ coordination was not observed for trimethylethylenediamine-substituted fluorophosphoranes, $Me_2N \rightarrow P$ coordination could be induced on their treatment with PF_5 as an F^- acceptor. In many cases X-ray crystal structure determinations served to establish the $Me_2N \rightarrow P$ (and, in one representative case, the $Me_2N \rightarrow Si$) coordination in trimethylethylenediamine-substituted compounds of phosphorus (and silicon). Bond lengths typical of $N \rightarrow P$ (and $N \rightarrow Si$) coordinative bonds were observed.

The introduction of the trimethylethylenediamine group as a substituent at main group centers has opened up a new area of chemistry which can be expected to develop in several directions. Clearly, the studies focusing previously on phosphorus should be extended to other Group 15 elements, e.g. arsenic and, perhaps, antimony, and to neighboring elements of Groups 14 and 16. Other substituents, related to the trimethylethylenediamine group (including compounds with other donor atoms, e.g. sulfur) should be attached to the same elements. The transition metal chemistry of intramolecular trimethylethylenediamine–P(III) complexes, and also that of their acyclic precursors, should be studied in detail, and are expected to hold much promise.

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