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Iminophosphanes: Unconventional Compounds of Main Group Elements

By Edgar Niecke* and Dietrich Gudat

Dedicated to Professor Rolf Appel on the occasion of his 70th birthday

The large number of known stable compounds in which phosphorus has a low coordination number makes it clear that such compounds can no longer be regarded as “exotic” in main group chemistry. While the rich chemistry of P–C multiply bonded systems makes clear their affinity to their organic congeners, iminophosphanes in particular are also of increasing importance. The linkage of a phosphinidine fragment with an imine fragment via a multiple bond gives rise to a class of compounds with an unusually wide range of structural types. This in turn leads to a broad spectrum of chemical behavior which makes iminophosphanes extremely useful synthetic building blocks in organoelement chemistry.

1. Introduction

The development of the chemistry of multiply bonded systems involving elements in higher periods is generally regarded as a renaissance of main group chemistry. An extremely important role in this chemistry has been played by phosphorus compounds with low coordination numbers; although the first of these were discovered in the 1960's, either little notice was taken of them because of their low stability ($P\equiv CH^{(1)}$) or they were regarded sceptically because of the nature of their bonding (phosphacyanine) cations^[2]. The discovery of arenes of the phosphabenzene type^[3] led to a more intensive study of compounds with such “exotic” bonding systems. The preparation of acyclic imino-^[4] and methylenephosphanes^[5] marked the beginning of a rapid phase of development, in the course of which a number of compounds were prepared which are both synthetically useful and also interesting because of their bonding properties.^[6] This work culminated in the 1980's in the inclusion of heavier elements of the fourth^[7] and fifth main groups^[8] and

of boron^[9] in a stable (p–p) π -bonding system involving phosphorus.

The (3p–2p) π -P–N bonding system occupies a special place among the known compounds with twofold coordinated phosphorus because of the presence of a π -bonded fragment of high electronegativity with a “lone pair”. In contrast to the phosphorus atom, the imine nitrogen can vary its bonding state within wide limits by means of formal electron release or acceptance (“isovalent hybridization”^[10]); this manifests itself in a series of unconventional structures and gives rise to unusual reactivity patterns. The application of this potential made possible the first successful synthesis of bis(imino)phosphoranes from iminophosphanes; it has also led to the generation of a large number of new heterocycles, so that today the iminophosphanes can be regarded as important synthetic building blocks in organoelement chemistry.

The present account will attempt to provide a critical overview of the chemistry of the P=N double bond, particular attention being paid to structural and bond-theoretical aspects. We have attempted to prepare a comprehensive survey, including more recent work. As experience has shown, systems such as aminophosphonium cations^[11] or resonance-stabilized five-membered PN heterocycles of the aza-

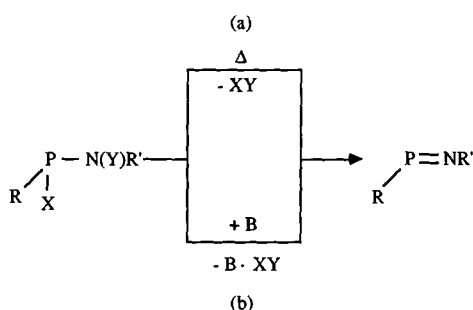
[*] Prof. Dr. E. Niecke, Dr. D. Gudat
Institut für Anorganische Chemie, Universität Bonn
Gerhard-Domagk-Strasse 1, W-5300 Bonn 1 (FRG)

phosphole type^[121] (in which P–N bonds with (p–p)π-interactions are also present) exhibit a quite different chemical behavior. These classes of compounds will thus not be included in the present discussion, and we refer the reader to relevant reviews.^[11, 12] The coordination chemistry of iminophosphanes has also not been included, since it has been covered in detail in a recent survey.^[13] We should mention that some aspects of the subject matter covered here have been discussed in earlier reviews.^[14, 15]

2. Synthetic Methods

2.1. Elimination Reactions

In analogy to the normal methods for the formation of olefins or heteroolefins (e.g. phosphalkenes, silalkenes),

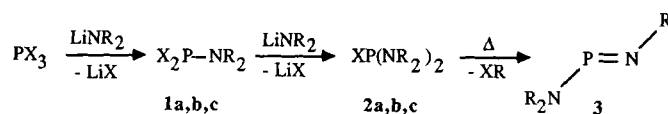


Scheme 1. Formation of the double bond in iminophosphanes by thermally-induced (a) or base-induced elimination (b).

1,2-elimination reactions form by far the most important synthetic route to iminophosphanes. The formation of the double bond by elimination of a molecule XY from aminophosphanes $\text{R}(\text{X})\text{P}-\text{N}(\text{Y})\text{R}'$ can be carried out either thermally or under the influence of a base (Scheme 1). The

preparatively most valuable methods involve thermal elimination of organohalogenosilanes ($\text{X} = \text{F}, \text{Cl}, \text{Br}$; $\text{Y} = \text{SiMe}_3$)^[16–40] or lithium halides ($\text{X} = \text{F}, \text{Cl}$; $\text{Y} = \text{Li}$)^[24, 36, 41–45] and base-induced dehydrohalogenation reactions ($\text{X} = \text{Cl}, \text{Y} = \text{H}$).^[38, 46–47]

The thermal elimination of trimethylchlorosilane from the *N*-silylated diaminohalogenophosphanes **2a–2c**, which were prepared from PX_3 via **1**, provided the first route to an isolable aminoiminophosphane **3** with a P–N–(p–p)π-bonding system^[4, 17] (Scheme 2). The synthesis of a variety of



Scheme 2. $\text{R} = \text{SiMe}_3$; $\text{X} = \text{F}$ (a), Cl (b), Br (c).

iminophosphanes has been carried out in an analogous manner via thermolysis of suitably substituted precursors; apart from *P*-alkyl or *P*-aryl substituents,^[24, 29] these can contain *P*-amino,^[16–18, 21–23, 39] *P*-hydrazino,^[19, 29, 40] *P*-diorganophosphino^[36, 37] or *P*-aryloxy substituents^[32] as well as *N*-phosphino^[26, 30] or *N*-amino^[20, 27, 28] residues. In spite of the versatility of this synthetic principle, it is limited in its generality, as the thermal stability of the precursors requires extremely drastic reaction conditions. The high temperatures required lead to the occurrence of side reactions: for example the thermolysis of diamino fluorophosphanes $\text{R}_2\text{N}(\text{F})\text{P}-\text{N}(\text{SiMe}_3)\text{tBu}$ with sterically undemanding R_2N ligands (**4e–h**) leads to elimination of R_2NSiMe_3 with formation of 1,3-di-*tert*-butyl-2,4-difluoro-1,3,2,4-diazaphosphetidine **6** rather than the expected iminophosphanes **5**^[27, 48] (Scheme 3). It is generally necessary to remove the

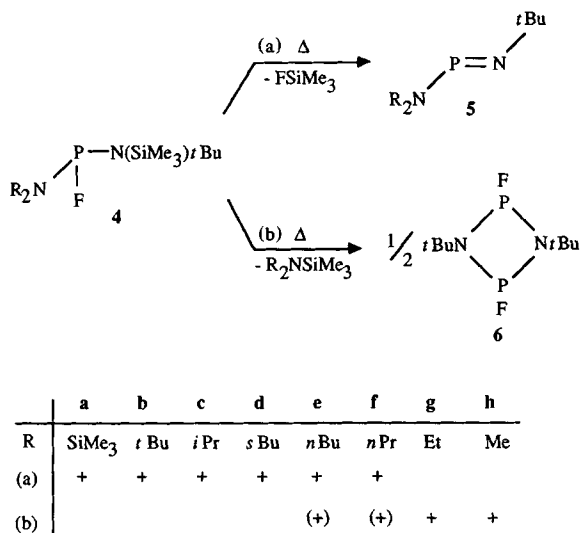


Edgar Niecke, born 1939 in Berlin, studied chemistry at the University of Göttingen, where he received his doctorate under the supervision of O. Glemser. After his habilitation in 1976 in Göttingen, he took up an appointment as Professor of Inorganic Chemistry at the University of Bielefeld, and in 1986 he was offered and accepted a professorial chair at the University of Bonn. His main fields of interest are the synthesis, structure, and reactivity of compounds of phosphorus with lower coordination numbers (phosphorus-element (p–p)π bond systems), but also phosphorus heterocycles, phosphanediyls and organometallic compounds with novel phosphorus ligands.



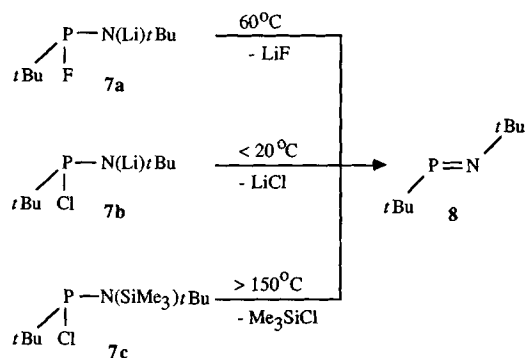
Dietrich Gudat, born 1957 in Düsseldorf, studied chemistry at the University of Düsseldorf and then at the University of Bielefeld, where he gained his doctorate under the supervision of E. Niecke. After Postdoc research at the University of Sussex (with J. F. Nixon) and at the Iowa State University (with J. G. Verkade) he accepted a post at the University of Bonn, where he has been working for his habilitation since 1989. His research interests focus on investigations of the coordination chemistry and redox properties of novel podand-like and macrocyclic phosphorus compounds as well as the applications of NMR spectroscopy, particularly for the monitoring of dynamic processes.

iminophosphanes continually from the reaction mixture in order to avoid the occurrence of further reactions, so that this method is only suited for the preparation of volatile compounds which distil without decomposition.



Scheme 3. Product formation in the thermolysis of diaminophosphanes in dependence of residue R.

It is possible to avoid high temperatures in the synthesis of iminophosphanes by using a procedure involving thermal salt elimination, since the decomposition temperature of the *N*-lithiated aminohalogenophosphane precursors is much lower than that of the *N*-silylated derivatives. Thus, the formation of **8** via elimination of LiX from **7a, b** occurs at below 20 °C (X = Cl) or at 60 °C (X = F), while the elimination of Me₃SiCl from *N*-silylated **7c** only occurs at above 150 °C^[24] (Scheme 4). The *N*-lithiated aminohalogenophos-

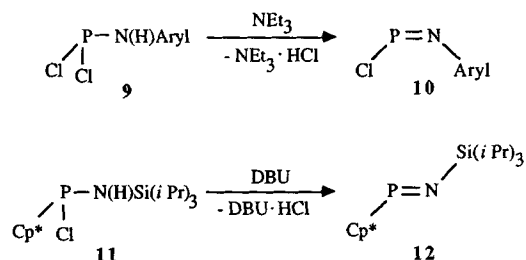


Scheme 4. Variation of reaction conditions by using lithiated aminohalogenophosphanes.

phanes can readily be prepared from the corresponding NH-substituted derivatives via Li/H exchange. Lithium amides (LiN(SiMe₃)₂, LiN(SiMe₃)*t*Bu,^[41–44] lithium di-*tert*-butylphosphide^[36, 45] or *tert*-butyllithium^[24] have been found to be particularly advantageous, as they combine a considerable basicity with a steric demand which suffices to suppress side reactions such as substitution at the phosphorus atom or addition of the organo-H compounds formed to the P=N

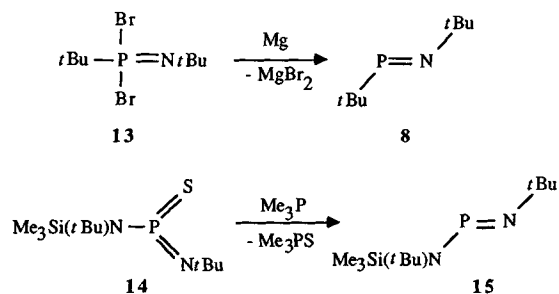
double bond. In general, as can be seen from the examples **7a, b**, the thermal stability of *N*-lithiated phosphanes decreases on going from fluoro-substituted derivatives (which are in some cases isolable and stable at room temperature) to the chloro- or bromo-substituted derivatives, so that the salt elimination can often be carried out below room temperature.

In contrast to the thermal elimination reactions, the amine-induced dehydrohalogenation of NH-substituted aminohalogenophosphanes normally leads to the formation of 1,3,2,4-diazadiphosphetidines (cf. **6**)^[49–51] or higher P,N oligomers.^[51] It has not yet been demonstrated unequivocally that unsaturated intermediates are formed.^[50] Only in a few cases has the formation of isolable P=N double bond systems in such elimination reactions been reported: thus the reaction of the aminochlorophosphanes **9** and **11** with triethylamine and DBU (1,8-diazabicyclo[5.4.0]under-7-ene) respectively yields the *P*-functionalized iminophosphanes **10**^[46, 47] and **12**^[38] (Scheme 5), the formation of which is apparently favored by the high steric demand of the substituents at nitrogen.



Scheme 5. Aryl = 2,4,6-tri-*tert*-butylphenyl, Cp* = pentamethylcyclopentadienyl.

The synthesis of iminophosphanes is in principle also feasible via 1,1-elimination reactions starting from iminophosphorane precursors, as has been shown for the reductive debromination of the dibromoiminophosphorane **13**^[52] and the desulfurization of iminothiophosphoranes such as **14** to **15** (Scheme 6).^[50, 53] Although this reaction is of theoretical

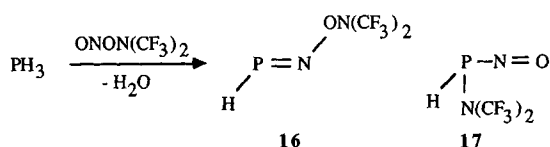


Scheme 6. Synthesis of iminophosphanes by 1,1-elimination.

interest, its preparative use has so far been only very limited, as the synthesis of the precursors was carried out starting from iminophosphanes.

A recent report^[54] has described the preparation of the *N*-aminoxy-substituted iminophosphane **16** via an elimination of water in the course of the reaction between PH₃ and

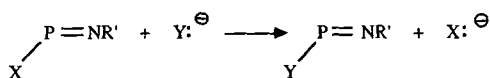
O-nitroso-*N,N*-bis(trifluoromethyl)hydroxylamine.^[54] However, the suggested structure **16** involving a P=N double bond does not follow with certainty from the spectroscopic data presented; the IR spectrum in particular supports the isomeric structure **17**.



It has in several cases been possible to use the synthetic principles described above for the preparation of homologous molecules with As=N double bonds.^[40, 42]

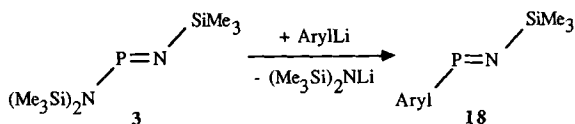
2.2. Substitution Reactions

Iminophosphanes with a nucleofugal leaving group at phosphorus can react with nucleophiles via ligand substitution, the double bond remaining unchanged (Scheme 7). The



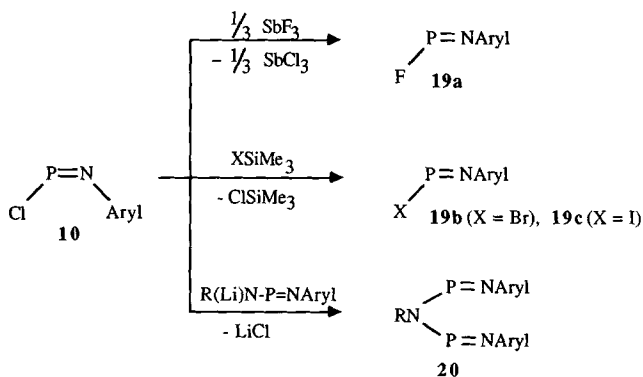
Scheme 7. Synthesis of iminophosphanes by nucleophilic substitution.

first reported preparative applications of this synthetic method involved the transamination of bis(trimethylsilyl)aminoiminophosphanes with dialkylamides^[55] and the preparation of the aryliminophosphane **18** from **3** and 2,4,6-tri-*tert*-butyllithiobenzene^[53, 56] (Scheme 8). However, only the



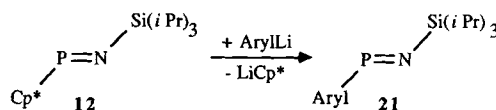
Scheme 8. Aryl = 2,4,6-tri-*tert*-butylphenyl.

recent preparations of stable *P*-chloro^[47] and *P*-phenoxy derivatives^[32] have permitted such substitution reactions to become of more general importance.^[46, 57–61] The chloroiminophosphane **10** in particular has been shown to be a key intermediate in the preparation of a large variety of new *P*-functionalized iminophosphanes^[46, 47, 58–60, 62–64] (Scheme 9). Reactions of **10** with *N*-lithiated aminoiminophosphanes should also be mentioned: these afford 1,3,5-triaza-2,4-diphosphapenta-1,4-dienes **20**^[61] (Scheme 9), which as heteroanalogues of pentadienyl anions are expected to exhibit interesting coordination properties. While in general *P*-alkyl- or *P*-aryl-substituted iminophosphanes do not undergo ligand substitution reactions, pentamethylcyclopentadienyl-substituted compounds such as **12** are a special case, as the five-membered ring can readily be exchanged in a nucleophilic manner for amino or aryl substituents (e.g. synthesis of **21**, aryl = 2,4,6-tri-*tert*-butylphenyl.^[38] An unex-



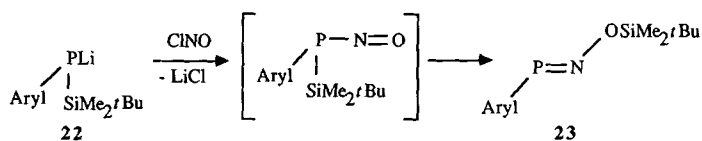
Scheme 9. Aryl = 2,4,6-tri-*tert*-butylphenyl. X can, apart from being F, Br, I also be *t*Bu₂As, *t*Bu₂P, R'RN, RO, *t*BuS, R₂C=N, Cp*, *t*BuC≡C, R₃P=N. **20a**, R = *t*Bu; **20b**, R = Aryl; **20c**, R = 2,4,6-*t*Pr₃C₆H₃.

pected substitution of the *t*Bu residue (rather than an oxidative addition at phosphorus) was also observed in the reaction of *t*BuP=NArlyl with sterically demanding halogenoamines.^[32]

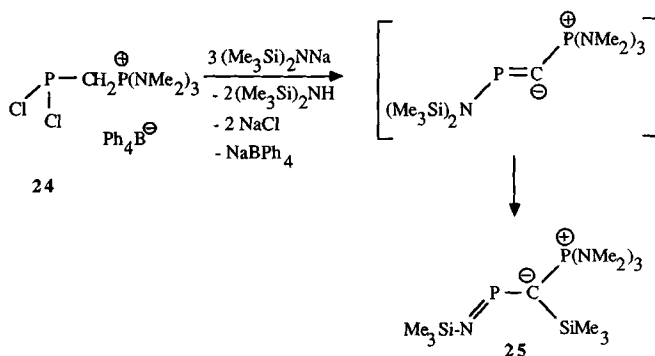


2.3. Rearrangement Reactions

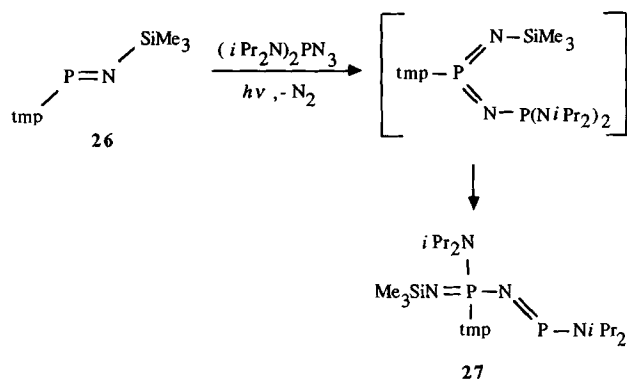
Only a few examples of syntheses of iminophosphanes via rearrangement reactions have so far been described. The formation of a P=N double bond via a [1,3] shift of a silyl group bonded to phosphorus to a doubly bonded oxygen in the α -position, a standard synthetic principle in phosphalkene chemistry, has only been verified in the preparation of the *N*-silyloxy-substituted iminophosphanes **23**.^[65] A



[1,3] silyl shift is also assumed to occur during the reaction of the phosphonium salt **24** with three equivalents of sodium bis(trimethylsilyl)amide, which affords the phosphoranylidenedimethyl-substituted iminophosphane **25**.^[66] The [1,3]

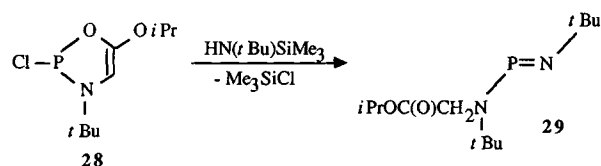


shift of a dialkylamino group has been suggested to occur in the formation of **27** by photolysis of azidobis(diisopropylamino)phosphane in the presence of the iminophosphane **26**^[67] (Scheme 10). The reaction of the 2,3-dihydro-1,3,2-



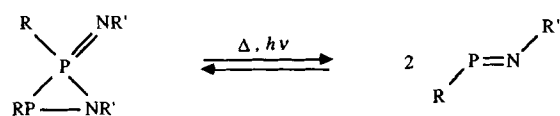
Scheme 10. tmp = 2,2,6,6-tetramethylpiperidyl.

oxazaphosphole **28** with *tert*-butyl(trimethylsilyl)amine leads via elimination of trimethylchlorosilane and [1,5] hydrogen shift to the functionalized aminoiminophosphane **29**.^[68]



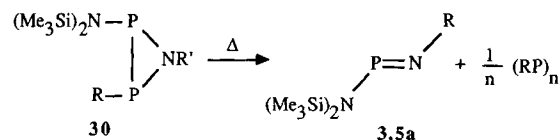
2.4. Cycloreversion Reactions

Because of the reversibility of the [2 + 1] cyclodimerization of iminophosphanes, the λ^3, λ^5 -azadiphosphiridines formed in the reverse reaction can in turn be used as precursors for iminophosphanes (Scheme 11). It is thus possible,



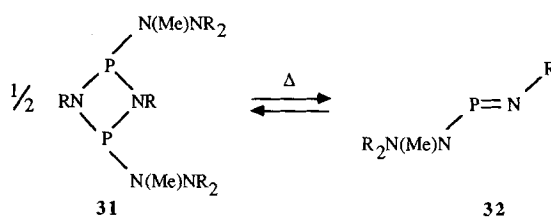
Scheme 11. Azadiphosphiridines as sources of iminophosphanes.

starting from solutions of *P*-alkyl-*N*-alkyl/aryl-substituted λ^3, λ^5 -azadiphosphiridines to generate the corresponding monomers thermally or photochemically and to characterize them spectroscopically, even though they are not stable in the pure state.^[24, 42, 44] The cycloreversion of *N*-silyl-substituted λ^3, λ^5 -azadiphosphiridines requires considerably higher temperatures; under such conditions the monomers cannot be characterized spectroscopically, but their presence has been detected by means of trapping reactions (see Section 4.3). Thermal [2 + 1] cycloreversion reactions of λ^3, λ^5 -azadiphosphiridines have been observed in the case of **30**; they lead to the formation of the aminoiminophosphanes **3** and **5** as well as to cyclopolyphosphanes $(RP)_n$ ^[69, 70] (Scheme 12).

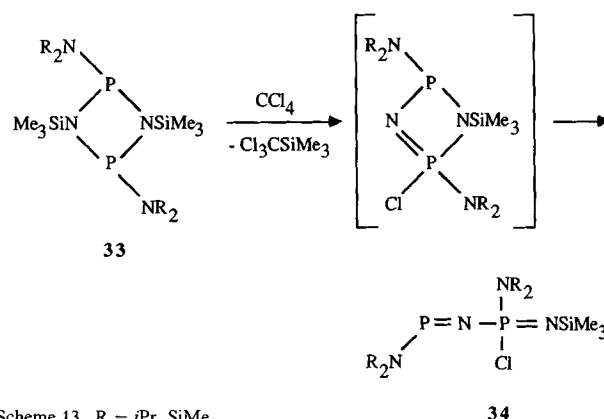


Scheme 12. R = *i*Pr, *t*Bu; R' = SiMe₃, *t*Bu.

There are very few examples of the formation of iminophosphanes via retroreactions starting from four-membered or larger rings. The diazadiphosphetidine **31** (R = SiMe₃) is in equilibrium with the aminoiminophosphane **32** (R = SiMe₃)^[20] while the formation of iminophosphoranes and alkoxyphosphoranes in the course of reactions of the cyclotetramers $(Me_3C_6H_2PNtBu)_4$ with diethylamine and alcohols respectively has been explained as resulting from reactions of the iminophosphane formed from the eight-membered ring by cycloreversion.^[51] Electro-



cyclic ring-opening of an intermediate didehydrodiazadiphosphetidine has been postulated to be involved in the formation of the phosphoranyl-substituted iminophosphanes **34** via oxidation of the diazadiphosphetidine **33** with CCl_4 ^[67, 71] (Scheme 13).



Scheme 13. R = *i*Pr, SiMe₃.

3. Structural and Bonding Considerations

3.1. Theoretical Studies

According to ab initio calculations the parent system $HP=NH$ resembles diimine in having a planar bent structure, the (*E*)-conformation being slightly more stable than the (*Z*)-conformation.^[72-79] Participation of d orbitals in the double bond system can be neglected.^[80] The comparison with structural parameters calculated at the SCF level^[76]

(see Fig. 1) shows that the transition from (*E*)- to (*Z*)-HP=NH is accompanied by a shortening of the P–N bond and an increase in the bond angles P and N. The inversion barrier at the nitrogen atom is considerably lower than that in diimine and corresponds to approximately one-third of the activation energy for a rotation about the π bond. According to these calculations, the (*E*)/(*Z*)-isomerization involves a transition state in which the PNH geometry is almost linear^[73, 76] (Fig. 1). The low value of the nitrogen inversion barrier can be regarded as the reason why it has so far not been possible to detect the existence of (*E*)/(*Z*) isomer pairs in iminophosphanes.

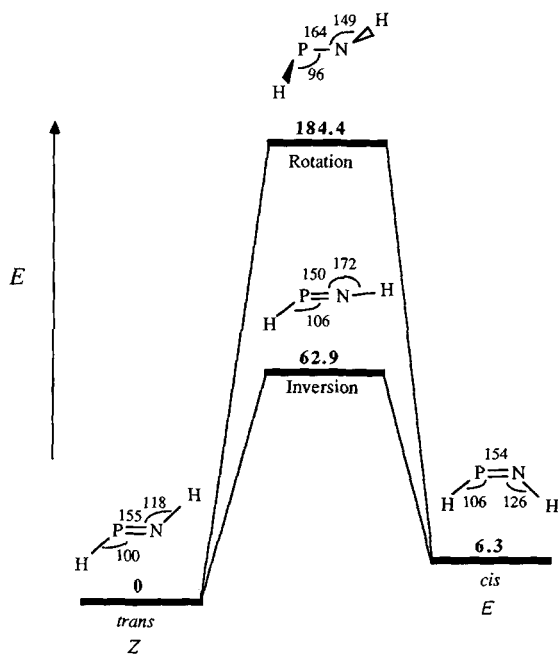


Fig. 1. SCF equilibrium geometries and relative energies for HP=NH (bond lengths in pm, bond angles in degrees, energies in kJ mol⁻¹; after [76]).

Replacement of the hydrogen atom at phosphorus in HP=NH by either more electronegative or more electropositive substituents (π -acceptors/donors) results in the former case in an appreciable strengthening and in the latter in a corresponding weakening of the double bond. At the same time the (*Z*)-configuration becomes more stable with respect to the (*E*)-configuration, while the inversion barrier is decreased.^[81] Exactly opposite effects have been forecast for the influence of corresponding substituents at nitrogen,^[81] the greatest changes being observed for donor-acceptor ("push-pull")-substituted model compounds.^[37, 81] A weakening of the double bond with concomitant formation of a delocalized 4-electron-3-center π -bond system is caused by the introduction of substituents with pronounced π -donor properties (e.g. NH₂) at the phosphorus or nitrogen atoms.^[72, 81, 82] The inductive effect of the ligands is either weakened (by *P*-substitution) or strengthened (by *N*-substitution).^[81]

An analysis of the frontier orbitals of (*E*)-HP=NH shows that the HOMO is a non-bonding orbital which is mainly localized at phosphorus, while the LUMO is an antibonding π^* orbital. The π (P=N) orbital lies directly below the

HOMO in energy.^[72, 83–85] The formation of a delocalized π -bonding system in H₂N–P=NH is accompanied by a strong destabilization of the π (P=N) energy level, so that the energy difference between the two highest occupied orbitals is minimal in this case.^[72, 82] On the basis of these calculations it was predicted that HP=NH would preferentially undergo [*n* + 1] addition reactions^[86] (oxidative addition at phosphorus, "carbene-analogous reaction behavior"), while in the case of H₂N–P=NH [*n* + 2] additions to the double bond should be favored^[72] (see Section 4.3).

3.2. Electron Spectroscopic and Electrical Measurements

The UV/visible spectra of iminophosphanes show two characteristic absorption bands, which can be identified on the basis of their differing intensities as arising from the expected *n*– π^* and π – π^* transitions of the P/N chromophore.^[87, 88] In the He(I) photoelectron (PE) spectra the double bond system manifests itself in the form of a series of ionization bands at low energies in addition to the undifferentiated bands which result from the ionization of the skeletal MO's.^[84, 87, 88] An assignment of these bands to ionization from *n*(P) or π (P=N) orbitals can be made on the basis of the observed linear correlation (Fig. 2) between the

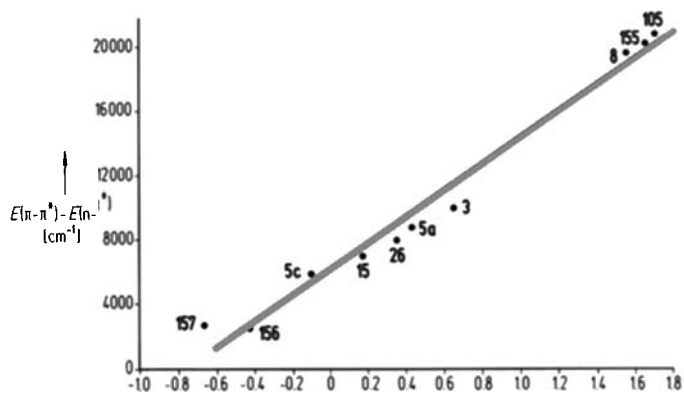


Fig. 2. Correlation between the difference in electron excitation energies $[\Delta E(\pi-\pi^*) - \Delta E(n-\pi^*)]$ and vertical ionization potentials $[I(\pi) - I(n)]$ for alkyl- and amino-substituted iminophosphanes (after [88], 155: *t*BuP=NCEt₃, 156: *t*BuP=N-TMP; 157: *t*Bu-P=N-NMe₂).

ionization energy differences and the corresponding optical excitation energies^[27, 87] and is further supported by the comparison with calculated adiabatic ionization potentials.^[88] In the case of *P*-alkyl substituted iminophosphanes the first ionization potential corresponds to an ionization from the *n* orbital, while for *N*-aminoiminophosphanes and *P*-(dialkylamino)iminophosphanes it involves an ionization from the π -orbital. Assuming the validity of *Koopmans'* theorem^[89] the bonding situation corresponds in the first case to that of the parent system (*E*)-HP=NH [$\varepsilon(n_p) > \varepsilon(\pi_{P=N})$], while in the second case there is a crossover of the orbital sequence [$\varepsilon(n_p) < \varepsilon(\pi_{P=N})$].

The measurement of dipole moments for iminophosphanes and a comparison with those measured for other P–E multiply bonded systems made possible the determination of

a double bond increment ($p_{P=N} = 2.2 \pm 0.2$ D) and thus demonstrates the high polarity of the double bond.^[90] Electrooptical measurements with the help of the Kerr effect made it possible to determine the anisotropy of the polarizability of the P–N bond ($3.5\text{--}4.0$ Å³) as well as to carry out studies on the geometrical orientation of substituents.^[91]

3.3. Molecular Structures

A large number of crystallographic investigations on iminophosphanes have been carried out recently (Table 1). While in most cases the double bond was found to have an (*E*)-configuration, a (*Z*)-configuration or even a nearly linear P–N–R geometry was observed in a few cases. Thus, it is now possible to discuss the nature of the P–N bond not only on a theoretical but also on an experimental basis.

Structural studies on iminophosphanes with a C–P=N–C skeleton, which can be considered as homologues of the unknown parent compound (*E*)-HP=NH, have so far been limited to two examples. The experimentally determined double bond distances in **44**^[97] and **47**^[96] agree well with the

results of SCF calculations for (*E*)-HP=NH, while the relative increases in the bond angles at phosphorus and nitrogen are apparently due to the steric bulk of the substituents.

Aminoiminophosphanes have been the subject of intensive study, and in almost all cases an (*E*)-configuration at the double bond was determined. The amine nitrogen generally has a planar coordination geometry, while the R₂N and the PNR' units are coplanar; this indicates the formation of a delocalized π -electron system. The P–N bond distances lie within the expected ranges: 167 ± 3 pm (P–N_{amine}) and 156 ± 2 pm (P–N_{imine}). In the azomethine-substituted derivatives **45** and **51** the large values for the bond angles at the azomethine nitrogen (\angle PN'C, **45**: 167.5°, **51**: 165°) and the short P–N_{azomethine} bond distances (r_{P-N} ; **45**: 159.5 pm, **51**: 161.4 pm) indicate the existence of a high degree of s-character in this P–N' bond. The R₂C=N- and Aryl N=P- units exhibit an almost orthogonal arrangement (\angle N'PNC/NCR₂, **45**: 87.5°, **51**: 87.9°), also indicating the formation of a 4 π -electron system delocalized across the N–P–N sequence rather than of a theoretically possible heterobutadiene system.

Table 1. Selected structural data for compounds R–P=N–R' [a]. Bond lengths [pm], bond angles [°].

Cpd.	R	R'	P=N	R-P=N	P=N-R'	Torsion angle R-P-N-R'	Ref.
35	<i>t</i> Bu ₂ P	N(SiMe ₃) ₂	161.9(2)	95.8(1)	124.1(2)	176.3(2)	[37]
36	tmp	N(SiMe ₃) ₂	159.8(5)	107.7(2)	107.1(3)	175.3	[28]
37	(SiMe ₃) ₂ N	[<i>t</i> Bu ₂ (Me)P] [⊕]	159.1(2)	107.5(1)	128.3(1)	177.7(1)	[92]
38	<i>t</i> Bu ₂ P	Aryl	157.8(2)	105.8(1)	119.9(1)	164.8	[36, 82]
39	(Me ₃ Si) ₂ N	<i>t</i> Bu ₂ P(S)	157.5(5)	106.5(2)	120.2(2)	174.2(4)	[93]
40	Aryl (H)N	Aryl	157.3(8)	103.8(5)	126.1(7)	[b]	[43]
41	(Me ₃ Si) ₂ N	Aryl	156.6(2)	109.3(1)	117.6(2)	177.6(2)	[94]
42	Cp*(CO) ₂ Fe	Aryl	156.4(12)	115.4(5)	119.8(9)	180 [c]	[95]
43	(SiMe ₃) ₃ N ₂	Aryl	155.8(4)	107.3(2)	115.3(3)	–177.8(3)	[96]
25	(Me ₂ N) ₃ P=C(SiMe ₃)	SiMe ₃	155.8(4)	108.4(2)	138.8(3)		[66]
		NiPr ₂					
27	<i>i</i> Pr ₂ N	P=N(SiMe ₃)	155.8(3)	107.2(1)	118.2(2)	–174.0(1)	[67]
		tmp					
44	Aryl	<i>t</i> Bu	155.6(5)	100.6(3)	122.7(5)	179.0(7)	[97]
45	<i>t</i> Bu ₂ C=N	Aryl	155.5(3)	107.3(1)	123.4(2)	–175.6(3)	[59]
46	<i>i</i> Pr ₂ N	Aryl	155.5(2)	105.6(1)	129.6(2)	179.9(3)	[98]
50 [d]	<i>t</i> BuS	Aryl	155.4(4)	109.1(2)	131.7(3)	0 [c]	[96]
			154.9(2)	109.0(1)	131.3(2)	1.5(2)	[99]
47	Cp*	Aryl	155.2(6)	105.9(4)	125.9(4)	178.7(7)	[96]
51	Fl=N	Aryl	154.7(3)	114.6(2)	137.2(2)	1.8(4)	[59]
48	<i>t</i> Bu ₂ P(SiMe ₃)N	<i>t</i> Bu ₂ P	154.6(9)	106.4(4)	114.0(5)	178.0(8)	[100]
52	<i>t</i> Bu(H)N	Aryl	154.5(6)	110.4(3)	128.0(4)	0 [c]	[96]
15	<i>t</i> Bu(SiMe ₃)N	<i>t</i> Bu	154.4(4)	104.9(2)	124.4(2)	180 [c]	[101]
3	(SiMe ₃) ₂ N	SiMe ₃	154.5(2)	108.4(1)	129.9(1)	179.0	[101]
62	(Ph ₂ C=N) ₂ P(Aryl)N	Aryl	153.9(6)	107.4(3)	135.2(5)	178.6(6)	[102]
53	Me ₂ N	Aryl	153.9(3)	115.9(3)	140.7(4)	–4.9(7)	[98]
49	(Me ₃ Si) ₃ Si(Me)P(Aryl)N	Aryl	153.7(2)	111.2(1)	152.3(3)	–153.7(3)	[96]
54	Me ₃ SiO	Aryl	152.9(3)	115.8(2)	144.4(2)	–1.3(5)	[96]
20a	<i>t</i> Bu(ArylN=P)N	Aryl	152.7(5)	106.0(2)	125.8(3)	177.6(4)	[61]
			152.9(4)	109.4(2)	120.3(3)	–177.8(3)	
56	2,6- <i>t</i> Bu ₂ -4-MeC ₆ H ₂ O	Aryl	150.0(1)	110.3(1)	173.7(1)	86.3(8)	[103]
19b	Br	Aryl	149.9(6)	112.6(3)	161.0(6)	0 [c]	[96]
55	2-MeC ₆ H ₄ O	Aryl	149.7(2)	111.8(1)	164.1(1)	–0.5(4)	[104]
10 [d]	Cl	Aryl	149.5(4)	112.4(2)	154.8(4)	0 [c]	[46]
			150.9(2)	111.4(1)	146.5(2)	[b]	[105]
58	<i>t</i> Bu ₂ HCO	Aryl	149.1(5)	109.5(2)	179.1(4)	0 [c]	[96]
57	<i>t</i> Bu ₃ CO	Aryl	148.6(4)	109.9(2)	175.4(4)	13(5)	[96]
19c	I	Aryl	148.0(3)	118.0(1)	172.5(3)	–140(2)	[96]
12	Cp*	Si <i>i</i> Pr ₃	153.3(3)	–	153.3(2)	–	[38]
59	<i>t</i> Bu ₂ PS ₂	Aryl	148.7(3)	–	169.7(3)	–	[96]
60	<i>t</i> Bu ₂ PSe ₂	Aryl	149.3(1)	–	169.1(11)	–	[106]
61	AlCl ₄	Aryl	147.5(8)	–	177.0(7)	–	[46]

[a] Abbreviations: Cp* = pentamethylcyclopentadienyl; Fl = fluorenyl; Aryl = 2,4,6-tri-*tert*-butylphenyl; TMP = 2,2,6,6-tetramethylpiperidyl. [b] No literature value available. [c] Due to crystallographic symmetry. [d] Different modification.

A surprisingly short P–N bond distance of 153.7 pm and a torsion of 26° about the double bond have been observed for the sterically hindered derivative **49**. The expected weakening of the π bond caused by the twisting is apparently more than compensated by the considerable increase of the bond angle at the imine nitrogen (152°).^[96] The comparatively long P–N_{amine} and short P–N_{imine} distances in the 1,3,5-triaza-2,4-diphosphapenta-1,4 diene **20a**, the P/N skeleton of which is (*S*)-configured, can be explained in terms of a delocalized 5-center-6-electron π system.^[61] The *N,P*-diaminoiminophosphane **36** has two amine ligands in 1,2-position: only the amine residue at nitrogen has the geometry necessary for an effective π conjugation. The (SiMe₃)₂N residue at the imine nitrogen is in contrast orthogonal to the plane of the π system; this leads to a decrease of the angle at the imine nitrogen (107.1°) and an increase in the P–N bond length to 159.8 pm.^[28]

An almost planar P–N–NR₂ arrangement, which indicates a conjugation between the double bond and an (SiMe₃)₂N group at nitrogen, has been found for the *N*-amino-*P*-phosphinoiminophosphane **35**. The π -electron delocalization makes itself apparent in the short N–N bond distance (138.1 pm) and the particularly long P–N bond (161.9 pm).^[37]

Until now a (*Z*)-configuration of the double bond has only been found for iminophosphanes which bear a tris(*tert*-butyl)phenyl group at nitrogen. The aryl ligand is orthogonal to the plane of the P=N double bond, due no doubt to steric effects. In the pairs of compounds (*E*)-*t*Bu₂C=N–P=N–Aryl (**45**)/(*Z*)-Fl=N–P=N–Aryl (**51**),^[59] and (*E*)-*i*Pr₂N–P=N–Aryl (**46**)/(*Z*)-Me₂N–P=N–Aryl (**53**),^[98] which contain substituents with comparable steric and electronic properties, a comparison of the bonding parameters confirms the expected larger bond angles and shortening of the P–N bond distances in the (*Z*)-isomers. The observed correlation between the P–N bond length and the valence angle at nitrogen is remarkable: in the halogen-, aryloxy-, or alkoxy-substituted iminophosphanes **10**, **19c**, **56–58** in particular it is found that extremely short P–N bond distances (148–151 pm) are accompanied by an almost linear arrangement of the P–N–C_{aryl} fragment (Table 1). The P–O bonds in **54–58**, which vary between 159 pm (**54**)^[96] and 166 pm (**55**),^[104] lie within the range expected for single bonds (164 pm^[107]).

Interesting structural effects are shown by the *P*-halogenoiminophosphanes **10** and **19b,c**, the bis(chalcogeno)-phosphinato-substituted derivatives **59** and **60**, and the (C₅Me₅)-substituted derivative **12**. In those modifications of **10** which have been studied there is a significant difference in the valence angle at the imine nitrogen, although the other bonding parameters remain almost unchanged (Table 1). This indicates that the P–N–R unit can very readily undergo deformation, a fact which can be interpreted in terms of the prediction of a low inversion barrier at nitrogen.^[81]

The phosphorus–halogen bonds in **10** ($r_{\text{P-Cl}} = 214.2$ pm,^[46] 212.7 pm^[105]) and **19b** ($r_{\text{P-Br}} = 233.5$ pm^[96]) are significantly longer than in the trihalides PX₃ ($r_{\text{P-X}} = 204$ pm (X = Cl); 222 pm (X = Br)); this can be interpreted in terms of an n(N) → $\sigma^*(\text{PX})$ charge transfer.^[108] This effect is even more pronounced in the iodo compound **19c** ($r_{\text{P-I}} = 289.5$ pm^[96] vs. 252 pm in PI₃^[107]). In this case the increasing polarization of the *P*-halogen bond is accompanied by the presence of a short intermolecular P–I contact

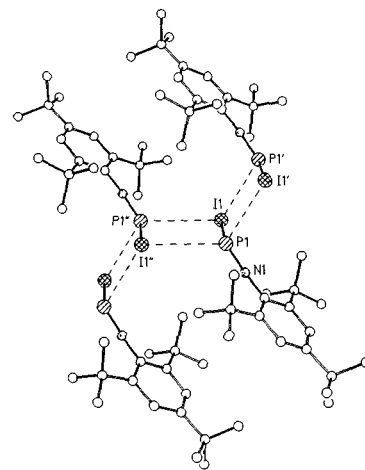


Fig. 3. Crystal structure of **19c**. Bond lengths: P1–I1 289.5(1) pm, P1–I1' 322.4 pm. The additional intermolecular contact P1–I1'' (360.5 pm) lies within the range of the sum of the van der Waals' radii and does not correspond to a bonding interaction (after [46]).

(322 pm), so that a transition to a biomolecular donor-acceptor complex is already indicated in the crystal (Fig. 3).

A bonding situation comparable to that in **19c**, in this case in the form of an intramolecular donor-acceptor interaction, can be found in **59**, which has two weak phosphorus–sulfur bonds of different lengths ($r_{\text{P-S}} = 244.2$ and 273.9 pm).^[96] The two phosphorus–chalcogen bond lengths are less divergent in the selenium derivative **60** ($r_{\text{P-Se}} = 263.6$ and 278.8 pm), so that in this case a description of the bonding situation can include the participation of a contact ion pair of the type [R₂PSe₂][⊖][PNAr][⊕] as a resonance hybrid.^[106] Complete separation into a cation and an anion is realized in the case of **61**, where the extremely short P–N bond distance and the almost linear arrangement of the P–N–C_{aryl} fragment justify a description in terms of a phosphanetriammonium ion with partial triple bonding between P and N.^[46]

The molecular structure of the iminophosphane **12** can be interpreted as an intramolecular π -complex between [Me₅C₅][⊖] and [R₃SiNP][⊕] (Fig. 4); in contrast to **47** the

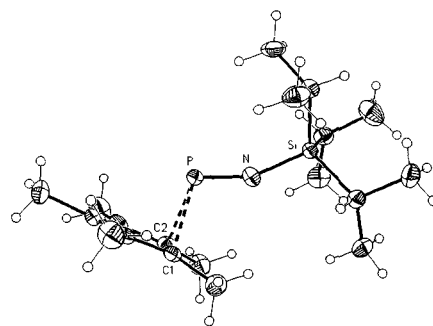


Fig. 4. Crystal structure of **12**. Bond lengths: P–Cl 216.8(4) pm, P–C2 212.2(4) pm, P–N 153.3(3) pm; bond angle P–N–Si 153.3(2)° (after [38]).

cyclopentadienyl ligand is coordinated in a “non-classical” η^2 manner. Important arguments for this description are provided by the almost equal bond distances, the (pseudo)-planar geometry in the five-membered ring, the increase in the length of the P–C bonds ($r_{\text{P-C}} = 212.2$ and 216.8 pm)

and in the valence angle at the imine nitrogen, and the shortening of the P–N bond (see Table 1) in comparison to that in 47.^[38]

3.4. NMR Spectroscopic Investigations

The chemical shift range for the ³¹P resonance of iminophosphanes covers the wide range between $\delta = 87$ for **19a** and $\delta = 787$ for **42** (see Table 2). The ³¹P-NMR data

Table 2. ³¹P-NMR chemical shifts for selected iminophosphanes of the type R–P=N–R' [a, b].

R	$\delta(^{31}\text{P})$	Ref.	R	$\delta(^{31}\text{P})$	Ref.
<i>R' = Aryl</i>			<i>R' = <i>t</i>Bu</i>		
42 Cp*(CO) ₂ Fe(<i>E</i>)	787	[95]	8 <i>t</i> Bu	472	[24]
63 <i>t</i> Bu ₂ As	644	[47]	5a (Me ₃ Si) ₂ N	330	[18]
38 <i>t</i> Bu ₂ P(<i>E</i>)	570	[45]	67 tmp	314	[21]
64 <i>t</i> Bu	490	[33, 42]	68 Cp*	283	[41]
65 Aryl	396	[47]	<i>R' = SiMe₃</i>		
66 <i>t</i> BuSe	315	[47]	18 Aryl	476	[55]
50 <i>t</i> BuS(<i>Z</i>)	314	[47]	3 (Me ₃ Si) ₂ N	325	[4]
40 ArylNH(<i>E</i>)	272	[43]	26 tmp	303	[25]
46 <i>i</i> Pr ₂ N(<i>E</i>)	268	[98]	69 Cp*	140	[36]
19c 1	218	[46]	<i>R' = N(SiMe₃)₂</i>		
52 <i>t</i> BuNH (<i>Z</i>)	210	[47]	35 <i>t</i> Bu ₂ P(<i>E</i>)	428	[37]
53 Me ₂ N (<i>Z</i>)	203	[34]	70 <i>t</i> Bu	378	[27]
47 Cp*(<i>E</i>)	194	[47]	36 tmp (<i>E</i>)	364	[28]
45 <i>t</i> Bu ₂ C=N(<i>E</i>)	179	[59]	71 Cp*	323	[38]
54 Me ₃ SiO (<i>Z</i>)	157	[47]	<i>R' = N(SiMe₃)₂</i>		
19b Br (<i>Z</i>)	153	[46]	35 <i>t</i> Bu ₂ P(<i>E</i>)	428	[37]
10 Cl(<i>Z</i>)	135	[46]	70 <i>t</i> Bu	378	[27]
51 Fl=N (<i>Z</i>)	124	[59]	36 tmp (<i>E</i>)	364	[28]
19a F	87	[47]	71 Cp*	323	[38]

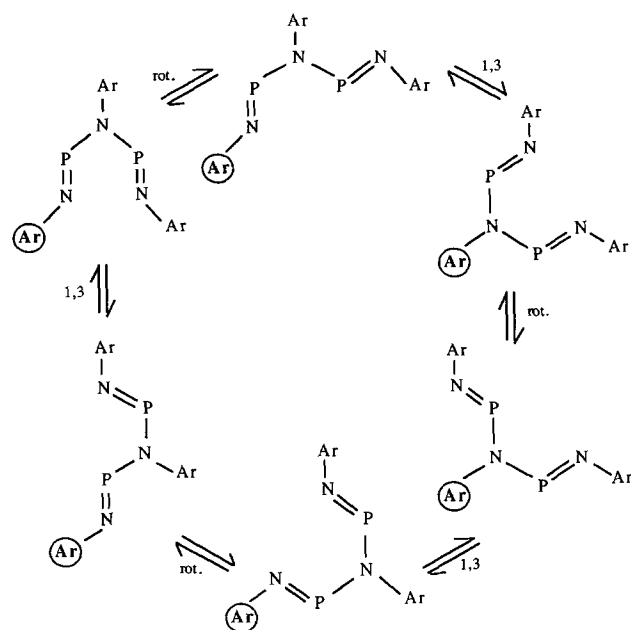
[a] (*E*)/(*Z*): *E* or *Z* double bond geometry in the crystalline state; no data = structure not known. [b] For abbreviations see footnote [a] of Table 1.

published up to mid-1985 have been reviewed.^[15] Although a theoretical or empirical treatment of the large chemical shift differences generally observed for compounds in which phosphorus has a coordination number of two is extremely difficult,^[109] the shifts in iminophosphanes can be explained to a good approximation in terms of the stereoelectronic effects of the substituents at phosphorus and nitrogen. Thus, for a series of compounds of the type R–P=NAr there is a linear correlation between $\delta^{31}\text{P}$ and the $n\text{--}\pi^*$ electron excitation energy; this indicates that the paramagnetic term makes a dominant contribution to the shielding tensor.^[88] According to this postulate, substituents R with strong σ -donor properties (C₅Me₅(CO)₂Fe, *t*Bu₂As, *t*Bu₂P) which cause a red shift of the $n\text{--}\pi^*$ band will lead to deshielding, while ligands with π -donor and/or σ -acceptor properties (R₂C=N, R₂N, RO, halogen) will induce a shielding of the phosphorus nucleus. A geometrical effect on the chemical shift, which is well documented for (*E*)/(*Z*) isomer pairs of diphosphenes or phosphalkenes, is also apparent in the iminophosphane system. Thus, in the pairs **45/51**, **40/52**, and **46/53**, for which the substituents at phosphorus have comparable steric and electronic effects, the (*E*)-configured iminophosphanes **45**, **40** and **46** show a significant deshielding ($\Delta\delta^{31}\text{P}$ 60 ± 5 ppm, see Table 2).

Although in the case of phosphalkenes ¹³C-NMR spectroscopy acts as an additional probe for studying the nature

of the double bond, the unfavorable magnetic properties of the isotopes ¹⁴N and ¹⁵N are an extreme handicap to such studies on iminophosphanes. ¹⁴N/¹⁵N-NMR studies on iminophosphanes have thus so far been carried out in only a few cases,^[110] so that it is not at present possible to discuss the data in a systematic manner.

Apart from the interpretation of chemical shifts and coupling constants, NMR can be used for studying dynamic processes and thus provides a further tool for probing the nature of the P=N double bond. Thus in a series of aminoiminophosphanes R'(R)N–P=NR' (R = SiMe₃, R' = SiMe₃ (**3**), *t*Bu (**15**); R = H, R' = Aryl (**40**)) it has been possible to detect degenerate sigmatropic [1,3] shifts involving either protons or trimethylsilyl groups; these correspond to chemical exchange between the amino and imino positions in the molecule.^[4, 17, 43] The 1,3,5-triaza-2,4-diphosphapenta-1,4-diene **20b** undergoes an analogous rearrangement in which the shift of a P=NAr group and a P–N bond rotation lead to a complete equilibration of all three nitrogen positions^[61] (Scheme 14).



Scheme 14. Schematic representation of the dynamic structure of **20b**; labeled aryl residue passes through all possible positions (after [61]). rot. = rotation about a P–N single bond, 1,3 = [1,3] shift of an arylN=P group. Ar = Aryl.

“Ring whizzing”, i.e. a series of very fast [1,5] sigmatropic ring shifts, is observed for *P*-(pentamethylcyclopentadienyl)-substituted iminophosphanes. Since the observed processes are still fast with respect to the NMR time scale even at low temperatures, it can be concluded that the activation energy is considerably lower than in the corresponding $\lambda^3\sigma^3$ phosphorus compounds.^[38, 41]

A remarkable temperature dependence is observed in the ³¹P- and ⁷⁷Se-NMR spectra of the iminophosphane *t*Bu₂P^ASe₂P^BNAr^{yl} **60**. While the coupling constants ²J(P^A, P^B) and ¹J(P^B, Se) are detectable at –80 °C, they disappear when the temperature is raised, although ¹J(P^A, Se) remains almost unchanged. At the same time the signal correspond-

ing to the phosphorus atom of the double bond undergoes a significant low-field shift. An explanation of these results is possible on the basis that the structure in the crystalline state (see Section 3.3), which involves the presence of contact ion pairs $[R_2PSe_2]^{\ominus}[PNAr]^{\oplus}$, is maintained at low temperatures in solution; the partial disappearance of the couplings when the temperature is increased corresponds to an increasing dissociation into single ions.^[47, 106]

4. Reactivity

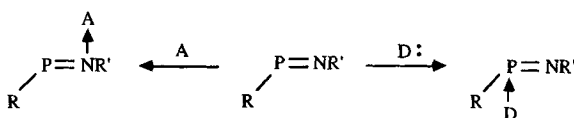
4.1. Addition Reactions

Product formation in many reactions of iminophosphanes can be understood on the basis of a complex reaction mechanism whose first step is an addition to the P=N double bond. Such an addition can in principle involve either an increase of the coordination number of phosphorus (oxidative 1,1 addition) or a 1,2 addition; the observed regioselectivities indicate a complex dependence on the nature of the substrate. Thus 1,1 additions at phosphorus are preferred in reactions of halogens and halogen derivatives of electronegative elements, while the alkyl and halogen derivatives of electropositive elements undergo 1,2 addition with the formation of a very stable element–nitrogen bond.

Because of the high polarity of the P–N bond we can assume that most addition reactions occur via a two-step mechanism, the initial step of which involves attack of a Lewis acid or base at the double bond. The interaction of iminophosphanes with Lewis acids/bases, which can in this sense be regarded as “incomplete additions”, is thus of great importance in understanding the reactivity of these compounds.

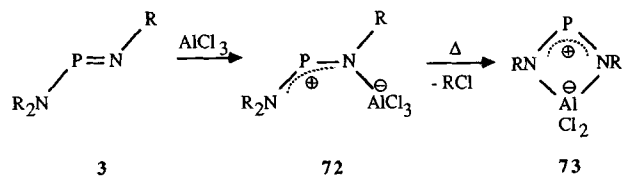
4.1.1. Attack by Lewis Acids and Bases

Theoretical treatments of the electron density distribution in the P=N double bond of iminophosphanes lead us to expect that Lewis acids will attack preferably at nitrogen and Lewis bases at phosphorus^[74] (Scheme 15). Although such



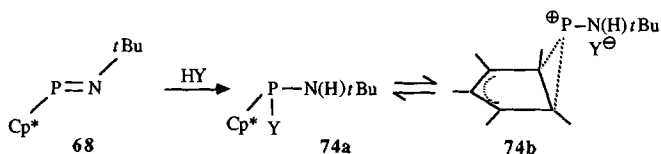
Scheme 15. A = Lewis acid, D = Lewis base.

acid/base adducts are very difficult to study because of their extreme readiness to undergo further reactions, an experimental confirmation of the expected behavior was possible in several cases. Thus the complex **72** was isolated from the reaction of **3** with aluminum trichloride; on raising the temperature this complex decomposed with the formation of the heterocyclic product **73**^[111] (Scheme 16). Addition of trifluoroacetic acid to the iminophosphane **68** yielded a product which according to NMR studies is the phosphonium ion **74b** (formed via *N*-protonation of **68**) in dynamic equilibrium



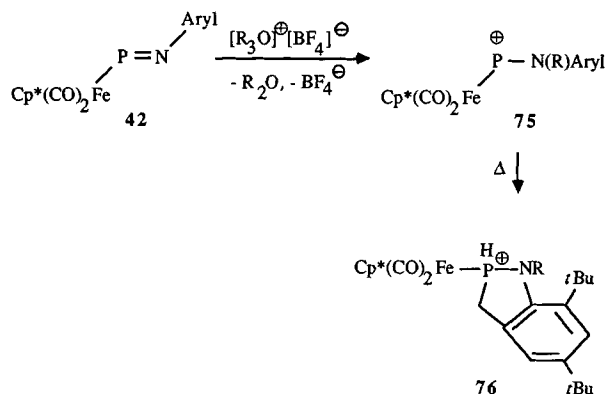
Scheme 16. R = SiMe₃.

um with the aminophosphane **74a**^[112] (Scheme 17). In an analogous reaction, treatment of the ferriiminophosphane **42** with Meerwein's salt initially yields an isolable cationic



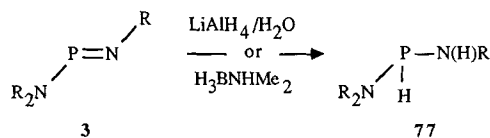
Scheme 17. Y = CF₃SO₃.

phosphinidene complex **75**, which undergoes thermal rearrangement to give the phosphane complex **76** (Scheme 18).^[113]

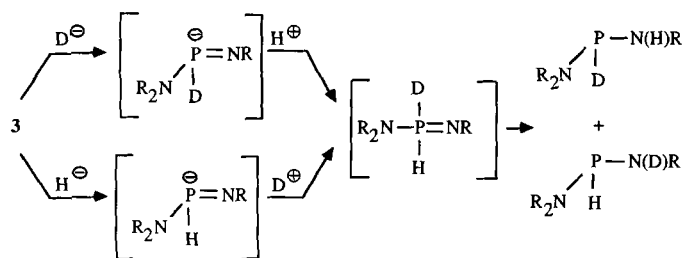


Scheme 18. R = Me, Et; Aryl = 2,4-di-*tert*-butylphenyl.

The intermediate formation of iminophosphoranide anions in the course of the formation of **77** (R = SiMe₃) from **3** (R = SiMe₃) and LiAlH₄ (after hydrolysis) was confirmed

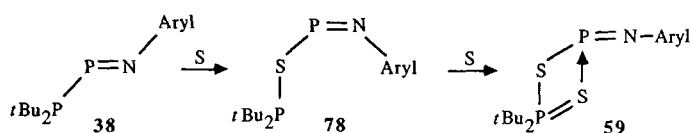


by means of isotopic labeling studies (Scheme 19).^[114] A similar process has been suggested for the analogous methylation with MeLi/MeI,^[114] however, the mechanism of formation of **77** (R = SiMe₃) in the reaction of **3** (R = SiMe₃) with H₃BNHME₂, which formally involves the transfer of both a hydride ion and a proton, could not be clarified.^[115] The dithiophosphinic acid derivative **59**, which was formed

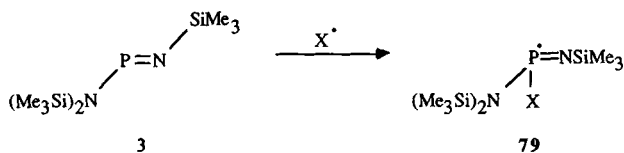


Scheme 19. Isotope labeling experiments for the reduction of **3**. R = SiMe₃.

by double sulfurization from **38** via **78**, has the structure of an *intramolecular* iminophosphane/Lewis base complex.^[47] Similar *intermolecular* donor-acceptor interactions in the solid state have been detected in the case of the

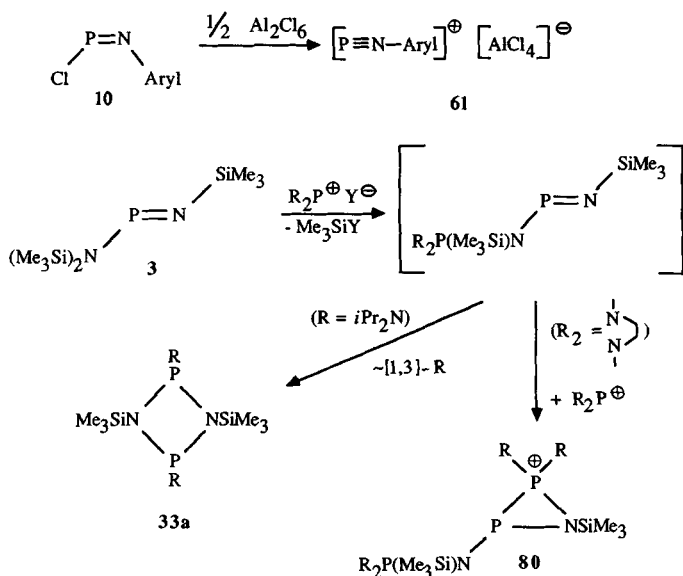


halogenoiminophosphane **19c**.^[106] The formation of iminophosphoranyl radicals **79** from **3** and suitable alkyl, alkoxy or acyl radicals can also be considered as an attack of a Lewis base at twofold coordinated phosphorus^[116] (Scheme 20).



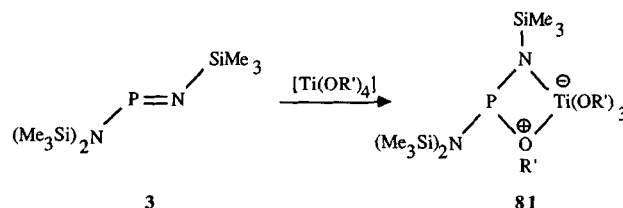
Scheme 20. X = R, RO, RCO.

An alternative mechanism for the interaction of an iminophosphane with a Lewis acid was observed in the reaction of the *P*-chloroiminophosphane **10** with aluminum



Scheme 21. Y = CF₃SO₃.

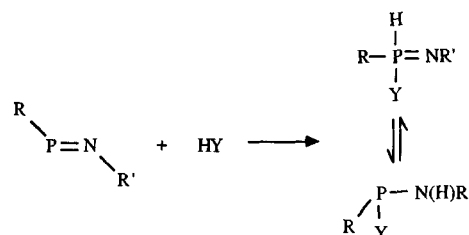
trichloride. Attack of the Lewis acid at the chlorine atom, followed by ligand abstraction, led to formation of the first known phosphanetriammonium ion^[46]. In contrast, the reaction of diaminophosphonium ions with **3** occurred in the expected manner; the formation of the final products **33a** and **80** was explained on the basis of an undetectable iminophosphane/Lewis acid complex^[117] (Scheme 21). Treatment of the aminoiminophosphane **3** with titanium



alkoxides led to the occurrence of double Lewis acid/base reactions, giving heterocyclic products which contain two donor-acceptor bonds.^[118]

4.1.2. Addition of Reagents with Acidic Hydrogens

The relatively polar iminophosphane double bond reacts readily with compounds containing acidic hydrogens to form either correspondingly substituted aminophosphanes (formal 1,2 addition) or the tautomeric iminophosphoranes (formal 1,1 addition) (Scheme 22). Since the tautomeric equi-

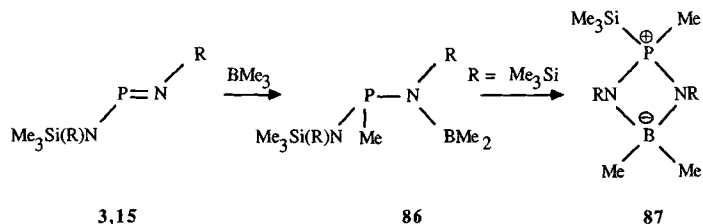


Scheme 22. Reactions of iminophosphanes with H-acidic compounds.

librium reaction must be assumed to be fast,^[119] the observed constitution of the reaction products, and not the differing regioselectivities for the two addition reactions, will reflect the relative thermodynamic stabilities of the two forms. The phosphane form is generally found to be of lower energy, so that additions of hydrogen halides^[47], alcohols,^[30, 31, 120, 121] thiols,^[120, 121] amines,^[30, 122] phosphanes,^[123] and some other compounds with acidic hydrogens^[36] to P=N double bond systems lead in most cases to the formation of the corresponding aminophosphanes as the sole products. Stabilization of the hydridophosphorane form requires not only the presence of a trimethylsilyl group at the imino position but also further substituents at phosphorus which increase its basicity. Thus, reactions of (Me₃Si)₂N-P=NSiMe₃ with sterically less demanding alkyl alcohols and amines lead to the selective formation of the corresponding iminophosphoranes^[120-122] while in the reactions with phenol, *tert*-butyl alcohol, and adamantanol the

products are in each case an equilibrium mixture of the two tautomers.^[120, 121]

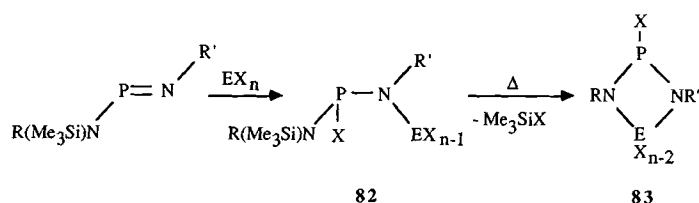
The addition of substrates with acidic hydrogens to iminophosphanes occurs even in the absence of additional bases; however, asymmetric induction was recently observed during the addition of achiral alcohols to iminophosphanes in the presence of chiral tertiary amines, thus indicating a possible base catalysis of the addition reaction.^[124]



Scheme 24. R = SiMe₃, *t*Bu.

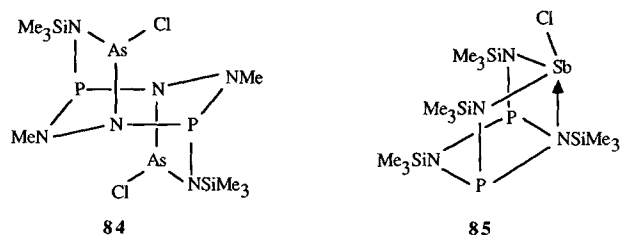
4.1.3. Halometalation and Organometalation Reactions

The readiness of phosphorus halides and redox-stable halides of more electropositive elements to react with iminophosphanes depends on their Lewis acidity; the initial formation of Lewis acid–iminophosphane adducts (see Section 4.1.1) is followed by a 1,2 shift of a halogen to give aminohalogenophosphanes **82** (Scheme 23). While such



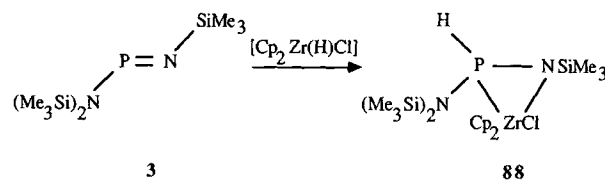
Scheme 23. E = B, Si, P, As; R, R' = SiMe₃, *t*Bu.

products are stable in the case of complete alkyl substitution (R = R¹ = R² = alkyl),^[123] *N*-silylated derivatives are subject to further reaction steps; the most favored of these is an intramolecular 1,3 elimination of halogenosilanes to give the four-membered heterocycles **83**.^[125–129] However, an intermolecular condensation reaction has also been detected in a few cases, for example in the formation of the hexazadiphosphadiarsatricyclodecane derivative **84** from arsenic trichloride and the iminophosphane (Me₃Si)₂N–N(Me)–P=NSiMe₃.^[130] Multiple addition of an iminophosphane to an element halide was observed in the reaction of **3** with antimony trichloride, which affords the tricyclic compound **85**.^[131]



In analogy to the halides, alkyl compounds of electropositive elements also add at the P=N double bond. Thus, reaction of **3** with BMe₃ smoothly affords the 1,2-addition product **86**, while the partly alkylated aminoiminophosphane **15** reacts further via a [1,2] trimethylsilyl shift and ring closure to give the heterocycle **87** (Scheme 24). Analogous products are also formed on reaction of **3** or **15** with Al₂Me₆.^[132] An unstable organometallic compound which decomposes with

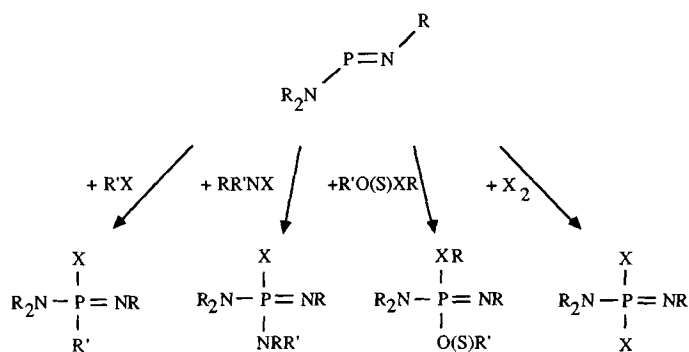
reductive elimination of mercury can be assumed as intermediate in the formation of diamino(silyl)phosphanes by reaction of aminoiminophosphanes with bis(trimethylsilyl)mercury.^[133] A reaction similar to the hydrosilylation of



olefins was observed in the reaction of **3** with [Cp₂Zr(H)Cl], which affords, via 1,2 addition and subsequent intramolecular complexation, the heterocycle **88**.^[134]

4.1.4. Oxidative Additions

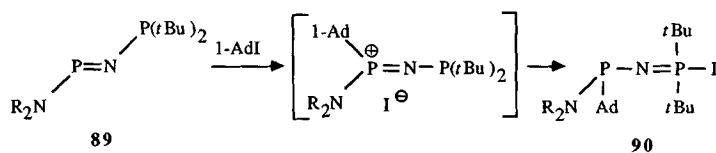
In contrast to the types of reaction discussed above, iminophosphanes react with alkyl halides and halogen derivatives of electronegative elements such as halogenoamines, alkyl hypohalites, arylchlorosulfanes or with halogens themselves via 1,1 addition to give the corresponding iminophosphoranes^[4, 25, 31, 125, 126, 135–141] (Scheme 25). The addition products thus obtained from reactions of



Scheme 25. R = SiMe₃; X = Cl, Br.

aminoiminophosphanes with (*N*-trimethylsilyl)halogenoamines are important intermediates in the synthesis of aminobis(imino)phosphoranes (see Section 4.2). A free radical mechanism has been suggested for most of the oxidative addition reactions which have been studied,^[126] although an alternative ionic mechanism has been discussed for the addition of CCl₃Br to aminoiminophosphanes.^[25] An interesting special case is provided by the reaction of the *N*-phosphi-

noiminophosphane **89** with iodoadamantane; in this case a 1,3 addition of the alkyl halides with concomitant 1,2 shift of the double bond is observed, apparently as the result of steric effects^[142] (Scheme 26). Oxidative chlorination with the for



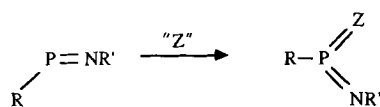
Scheme 26. R = SiMe₃; Ad = adamantyl.

mation of a dihalogenophosphorane and an element subhalide was found to occur when tin tetrachloride was allowed to react with **3**.^[126]

4.2. Reactions involving the Formation of Diylides R-P(=Z)=NR'

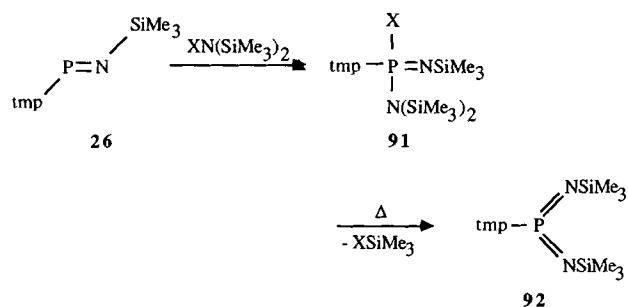
Iminophosphanes play a central role in the preparation of diylidic iminophosphoranes R-P(=Z)=NR' (Z = O, S, Se, "PR"). Systems of this type, in which a trigonal planar coordinated phosphorus(v) atom forms part of a delocalized (p-p) π -bond system, are not only of considerable theoretical interest but also offer interesting synthetic possibilities. Although the formation of these products can formally be regarded as an oxidative addition to iminophosphanes, experimental studies have shown that various reaction mechanisms are in fact involved.

Thus reactions of iminophosphanes with ozone, sulfur or selenium appear to involve a direct oxidative addition; no intermediates could be detected in the formation of either the iminochalcogenophosphoranes (Scheme 27) or the [2 + 2] cyclodimerization products resulting from them.^[17, 18, 143 - 145] Evidence for a formal oxidative trans-



Scheme 27. Z = O, S, Se, "PR".

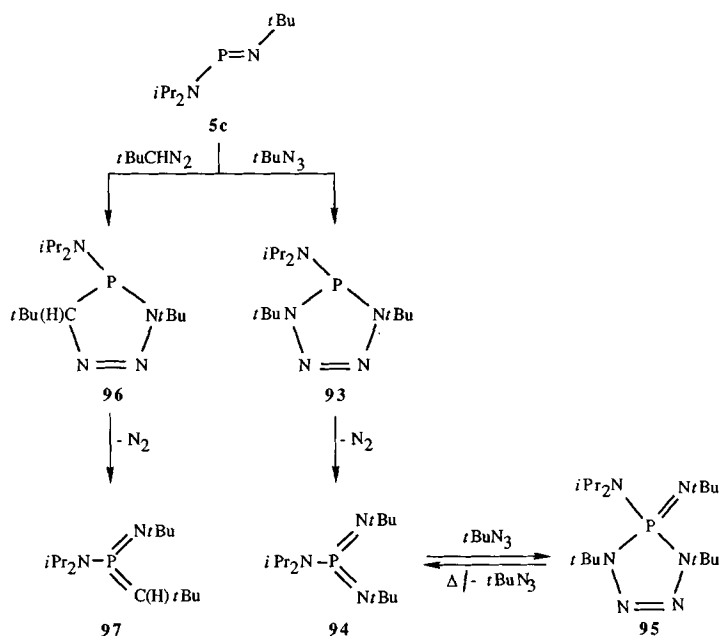
fer of a phosphanediyl "RP" to an iminophosphane with formation of an imino- λ^3, λ^5 -diphosphene was recently presented.^[146] Bis(imino)phosphoranes such as **92** can be ob-



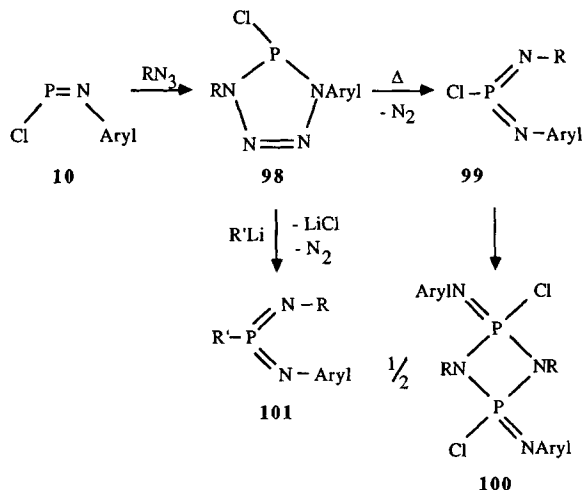
Scheme 28. X = Cl, Br; tmp = 2,2,6,6-tetramethylpiperidyl.

tained in good yields via oxidative addition of chloro(silyl)amines to iminophosphanes such as **26** to **91** with subsequent chlorosilane elimination^[25, 135] (Scheme 28).

In contrast to chalcogenation, alternative reaction mechanisms have been detected in some cases in reactions of iminophosphanes with azides or diazoalkanes, which lead to the formation of iminomethylene- or bis(imino)phosphoranes via a formal oxidative addition of a carbene or a nitrene.^[25, 44, 47, 67, 147 - 154] Thus reaction of the aminoiminophosphane **5c** with alkyl *tert*-butylazide and diazo-neopentane led via [2 + 3] cycloaddition to formation of the heterocycles **93**^[155] and **96** respectively; these underwent thermal or photolytic elimination of nitrogen to give the corresponding diylides **94** and **97** respectively.^[149 - 151] Un-

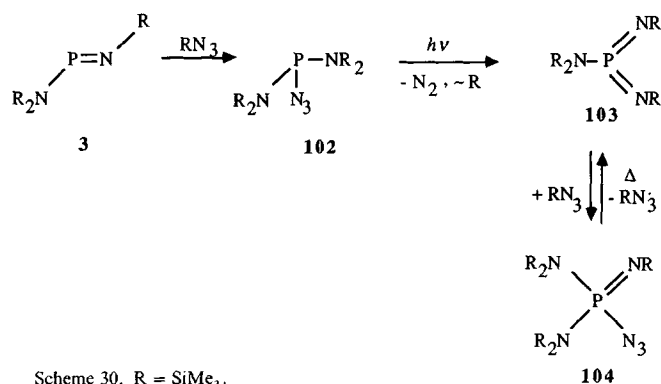


der the reaction conditions the bis(imino)phosphorane **94** can add excess azide to give **95**, from which the diylide can be re-formed by vacuum thermolysis.^[151] The chloroiminophosphane **10** reacts in a similar manner via [2 + 3]

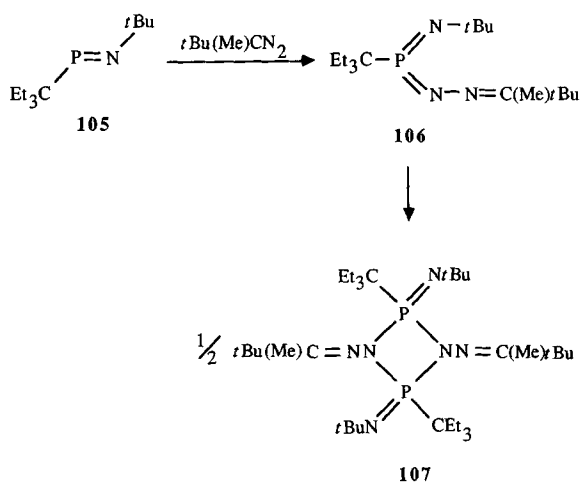


Scheme 29. R = *t*Bu, Et₃C, 1-adamantyl; R' = *n*-Bu, C₅Me₅, Aryl NH, Aryl O, *t*BuS.

cycloaddition to afford the heterocycles **98**; thermolysis of the latter leads to elimination of nitrogen to give the diazadiphosphetidines **100** via the unstable bis(imino)phosphoranes **99**. In the presence of suitable organolithium derivatives, **98** undergoes nucleophilic substitution to give the stable bis(imino)phosphoranes **101** (Scheme 29).^[154] A 1,2 addition analogous to the halometalation was observed in the reaction of **3** with trimethylsilyl azide; the unstable azidophosphane **102** thus formed undergoes nitrogen elimination and a Curtius-type rearrangement to afford the bis(imino)phosphorane **103**, which can add reversibly to excess azide to form **104**^[149] (Scheme 30).



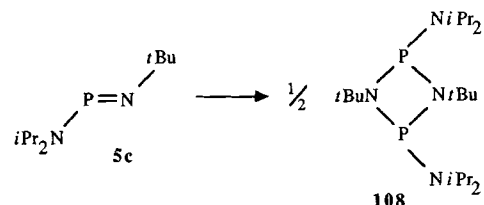
It was possible to detect an oxidative addition of an azoalkane to the P=N double bond in the reaction of the *P*-alkylated iminophosphane **105** with 2-diazobutane-3,3-dimethyl. In analogy to the Staudinger reaction between tertiary phosphanes and azides, the primary product is the spectroscopically detectable adduct **106**, which undergoes stabilization via a [2 + 2] cycloaddition to give the isolable diazadiphosphetidine **107**.^[144] In contrast, the reaction of



(Me₃Si)₂N-P=N-SiMe₃ **3** with diazomethane occurs spontaneously with the uptake of two methylene groups to give the corresponding λ⁵-iminophosphirane; in this case it was not possible to observe the formation of a diylide intermediate.^[156]

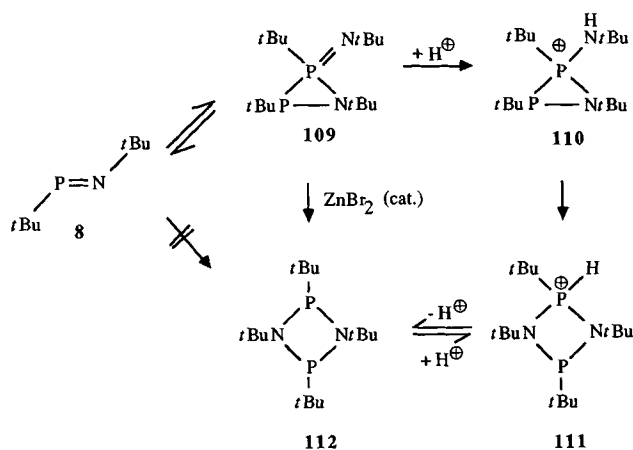
4.3. Oligomerization Reactions

The low kinetic stability of the double bond in iminophosphanes causes them to undergo cyclodimerization, a reaction typical of other "non-classical" double bond systems. However, in the case of the iminophosphanes a structure-dependent regioselectivity is observed, a phenomenon which is unknown for other heteroolefin systems. Thus *P*-alkyl- and *P*-aryl-substituted iminophosphanes react via a reversible [2 + 1] cycloaddition to give λ³,λ⁵-azaphosphiridines^[24, 43-45] (see Scheme 11), while π-donor-substituted aminoiminophosphanes and (*N*-amino)iminophosphanes undergo (with one known exception) irreversible [2 + 2] cycloaddition with the formation of 1,3,2,4-diazadiphosphetidines **5c** → **108**^[20, 23, 38] (for exception see Section 2.3). This observed duality correlates well with theoretical predictions, according to which the reactivity is due to different frontier orbital interactions between the reactants^[45, 72, 87] (see Section 3.1).



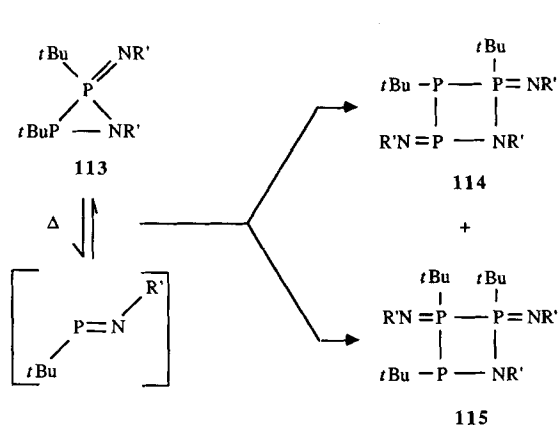
The factors which determine the course of the [2 + 1]-cycloaddition are the degree of kinetic stability and the temperature. Thus metastable iminophosphanes have a significantly longer lifetime at lower temperatures,^[24, 42] while for derivatives of the type Me_{3-n}Et_nC-P=N*t*Bu (n = 0-3) the dimerization rate decreases with increasing steric demand of the substituent at phosphorus.^[33]

Apart from these effects, there is also a remarkable susceptibility of the self-addition to the influence of Lewis acids. For example (Me₃Si)₂N-P=N-SiMe₃, which dimerizes only very slowly in the pure state, undergoes a fast [2 + 2] cycloaddition in the presence of catalytic amounts of Lewis acid.^[157] An apparent change in the regioselectivity was observed in the case of **8**; under the influence of Lewis or Brønsted acids the azadiphosphiridine **109** formed in a reversible [2 + 1] cycloaddition underwent rearrangement to



give the diazadiphosphetidine **112**, which is formally the product of a [2 + 2] cycloaddition. The course of the reaction of **109** with trifluoromethanesulfonic acid could be confirmed by isolation of the intermediates **110** and **111**.^[52]

An interesting special case of an iminophosphane oligomerization is the thermolysis reaction of the azadiphosphiridine **113**, which affords a mixture of the isomeric azatriphosphetidines **114** and **115**. The reaction has been pos-



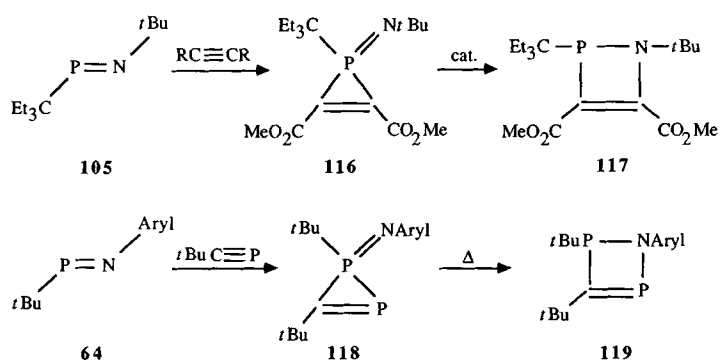
Scheme 31. R' = SiMe₃.

tulated to involve an oxidative insertion of monomeric iminophosphane, formed in an initial [2 + 1] cycloreversion of **113**, into the P–N single bonds of excess starting material (Scheme 31).^[158]

4.4. Cycloaddition Reactions

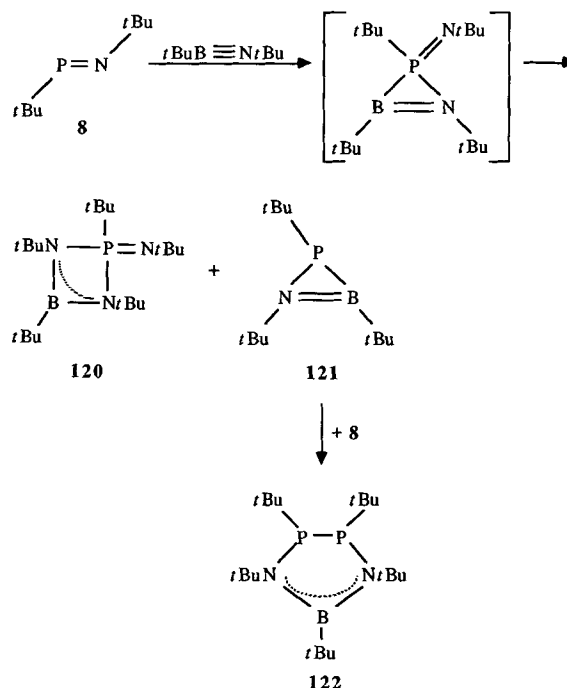
4.4.1. [2 + 1] Cycloadditions

The *P*-alkylated or arylated iminophosphanes **64** and **105** react readily with activated alkynes or *tert*-butylphosphalkyne via a [2 + 1] cycloaddition to give the corresponding λ⁵-phosphirenes **116** or the λ³, λ⁵-diphosphirenes **118** respectively (Scheme 32); in the presence of Lewis acids (and in the case of **118** also on heating) these undergo a rearrangement similar to the ring expansion reaction of λ³, λ⁵-azadiphosphiridines to form the four-membered heterocycles **117** and **119** respectively.^[44, 159, 160] A [2 + 1] cycloaddition leading to an azaphosphaboridine isoelectronic to **116** was postulated as

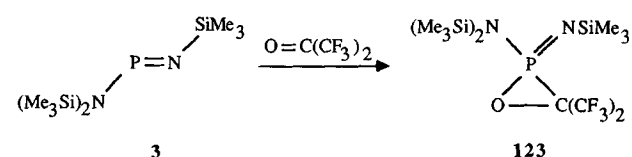


Scheme 32. [2 + 1] Cycloadditions. R = CO₂Me, Aryl = tri-*tert*-butylphenyl.

the initial step of the reaction of **8** with the acetylene isostere *tert*-butyl(*tert*-butylimino)borane. However, the product cannot be detected and undergoes a spontaneous disproportionation to give the 1,3,2,4-diazadiphosphaboretidine **120** and the azaphosphaborirene **121**, which in turn reacts via the insertion of a further molecule of **8** to form the final product **122**.^[161]

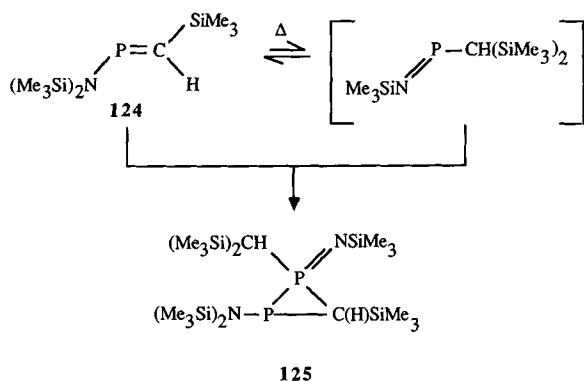


The silyl-substituted aminoiminophosphane **3** reacts very readily with hexafluoroacetone via a [2 + 1] addition to give the 1,2λ⁵-oxazaphosphirane **123**.^[162] The unusual regioselectivity observed – reactions of aminoiminophosphanes with double-bond systems normally occur via a [2 + 2]

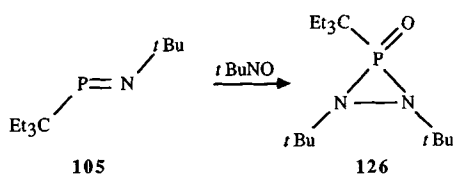


cycloaddition (see Section 4.4.2) – can be understood in terms of the frontier orbital model if a crossover between the n(PN) and π(P=N) energy levels is assumed; such a crossover is predicted by quantum-mechanical calculations and confirmed by spectroscopic studies.^[72, 87]

The formation of the λ⁵, λ³-iminodiphosphirane **125** in the thermolysis of from **124**^[163] can also be explained on the basis of a [2 + 1] cycloaddition of an iminophosphane to the P=C double bond of excess starting material; the iminophosphane, the existence of which could not be detected, is formed from **124** via a [1,3] silyl shift. The λ³, λ³-azadiphosphiridines obtained in the reaction of aminoiminophosphanes with *t*Pr₂NPCl₂ and magnesium can also formally be regarded as products of a [2 + 1] cycloaddition of a phosphanediyl at a P=N double bond; in this case the reaction mechanism is

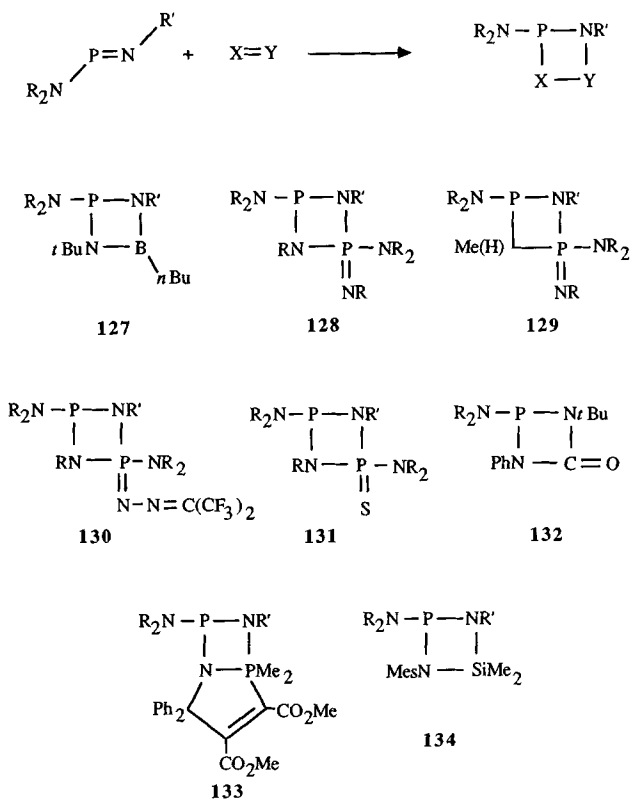


unknown.^[170] The reaction between *t*BuNO and the iminophosphane **105** to give the diazaphosphinidine **126**^[164] involves [2 + 1] cycloaddition with subsequent isomerization.



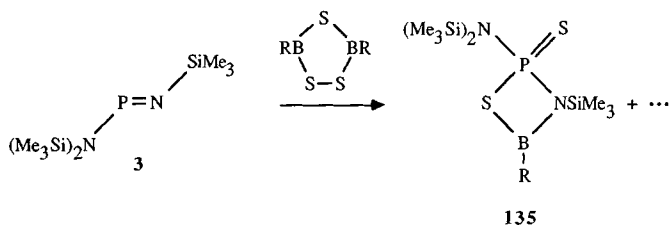
4.4.2. [2 + 2] Cycloadditions

Theoretical studies (see Section 3.1) have led to the prediction that reactions of aminoiminophosphanes with polar multiple bond systems should occur preferentially via [2 + 2] cycloaddition;^[172] they should thus differ from reac-



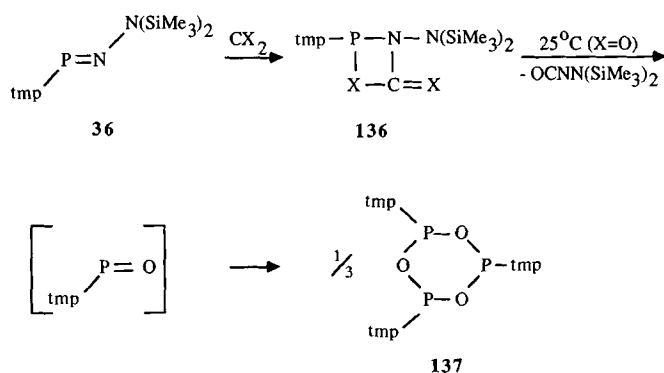
Scheme 33. R = SiMe₃, *i*Pr; R' = SiMe₃, *t*Bu.

tions of *P*-alkyl- and *P*-aryl-substituted derivatives. The synthesis of a large number of four-membered heterocycles such as **127–129**, **132**, **133** was indeed possible by reacting **3** or **5a, c** with multiply-bonded systems such as butyl(*tert*-butylimino)borane,^[165] phenyl isocyanate,^[166] substituted λ⁵-azaphospholes^[167] or diylides (Me₃Si)₂N-P(=Z)=NSiMe₃, (Z = NSiMe₃, CHMe)^[148, 168] (Scheme 33). In analogy, the formation of **130**, **131** and **134** was postulated to involve the trapping of unstable bis(imino)phosphorane, iminothiophosphorane or silandiylamine intermediates via a [2 + 2] cycloaddition with **3**,^[169, 170] while [2 + 2] cycloaddition of the iminophosphane and an RBS unit has been suggested to be the key step in the synthesis of **135** from **3** (or **5a, c**) and trithiaborolanes^[171] (Scheme 34).



Scheme 34. R = Me, Et, Bu, Ph, Mes, Me₂N, Et₂N; the dots denote oligocondensates.

Fast [2 + 2] cycloaddition of the 2-phosphatetrazene **36** to CO₂ or CS₂ afforded the heterocycles **136a, b**, of which **136a** decomposes at room temperature to give the oxaphosphinane **137**.^[128] The formation of the latter (and the generation of (*i*Pr₂NPO)₃ from **5c** and SO₂^[172]) has been suggested to involve a retroreaction of the original cycloadduct with the formation of an unstable oxophosphane, which then trimerizes (Scheme 35).



Scheme 35. X = O (a), S (b).

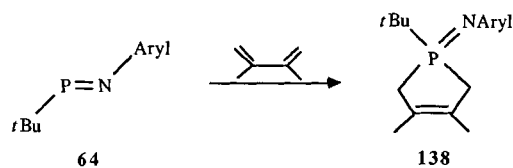
4.4.3. [2 + 3] Cycloadditions

The importance of this reaction type has already been referred to in the discussion of the reaction between iminophosphanes and alkyl azides or diazoalkanes (see Section 4.3).

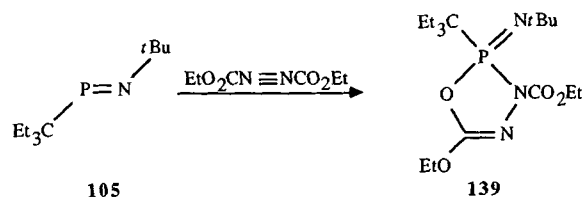
4.4.4. [4 + 1] Cycloadditions

Whereas phosphalkenes react cleanly with butadiene derivatives to give products formed in [4 + 2] cycloadditions

of the Diels-Alder type,^[5] *P*-alkyl-*N*-aryl-substituted iminophosphanes react under comparable conditions via oxidative [4 + 1] cycloaddition with formation of dihydro- λ^5 -phospholenes such as **138**^[159, 173]; they react with 1,2-



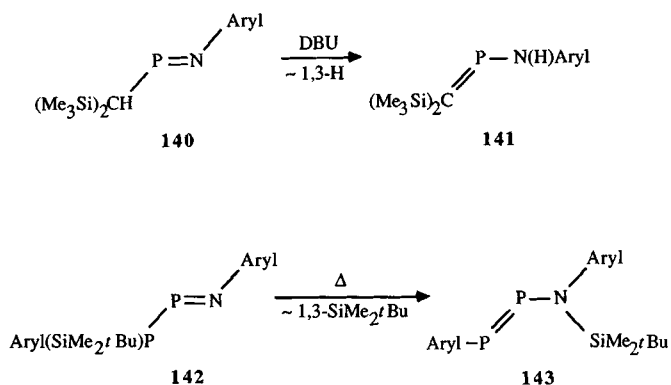
diketones to give analogous dihydro-1,3,2-dioxaphospholes.^[44, 162] The dihydrooxadiazaphosphole **139**, which results from the reaction of **105** with diethyl azodicarboxylate, can also formally be regarded as deriving from a [4 + 1]



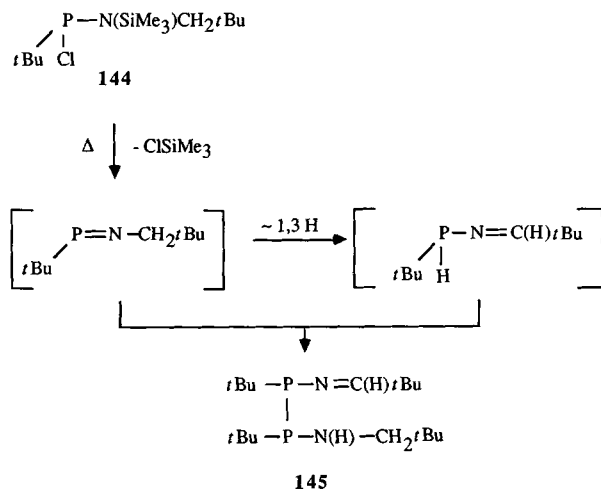
cycloaddition; however, a multistep reaction mechanism cannot be excluded with certainty in this case.^[44]

4.5. Rearrangement Reactions

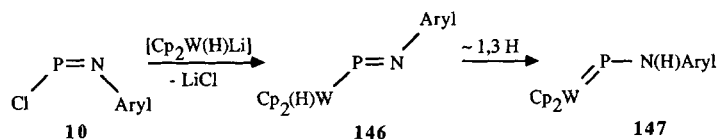
A 1,3 Shift of an α -hydrogen or of a trimethylsilyl group with the formation of a new phosphorus-element double bond was observed in the thermal or base-catalyzed isomerization of the iminophosphanes **140** and **142** to the phosphalkene **141** and the diphosphene **143** respectively^[36, 60].



A rearrangement of this type has also been suggested to occur in the synthesis of aminophosphaalkenes and -diphosphenes via the reaction of suitable iminophosphanes with either alkylolithiums^[174, 175] or trimethylsilyl-^[176] and lithio(*tri-tert*-butylphenyl)phosphane^[177] and for the formation of the diphosphane **145** in the thermolysis of **144**;^[42] however, it was not possible to detect the corresponding

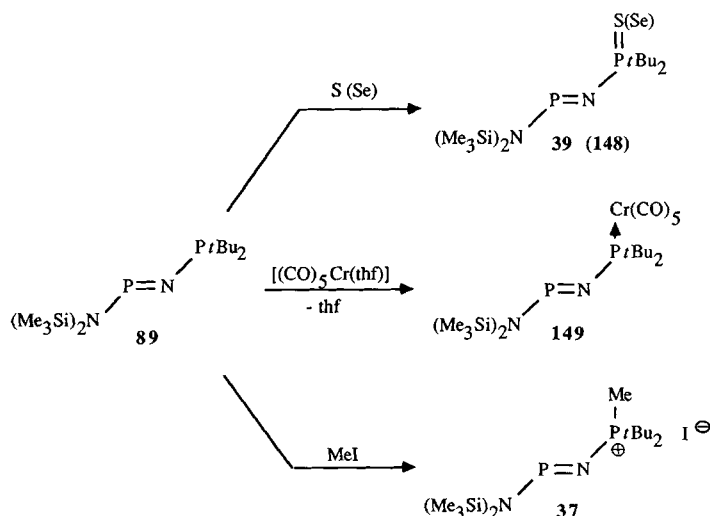


iminophosphane intermediates in these cases. The formation of the terminal phosphinidene complex **147** from **146** via a 1,3 hydrogen shift can be followed spectroscopically.^[95]



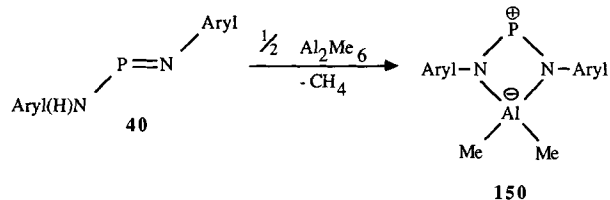
4.6. Reactions at Peripheral Groups

Although a number of iminophosphanes are known which contain further functional groups the extreme reactivity of the latter has so far prevented the discovery of many examples of reactions in which the former underwent transformations while the P=N double bond remained unchanged. Reactions of **89** with chalcogens (**38**, **148**) methyl iodide (**37**) and [(CO)₅Cr(thf)] lead to selective derivatization of the

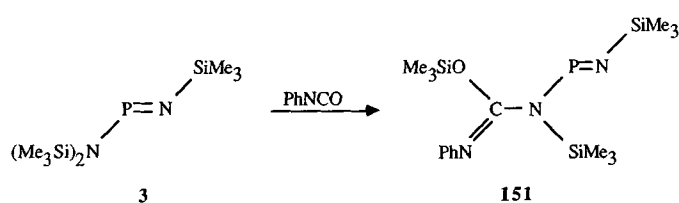


threefold coordinated phosphorus with retention of the iminophosphane structure; this indicates that the twofold coordinated phosphorus atom has a relatively low basicity in these cases^[26, 142]. The NH-functionalized compound **40**

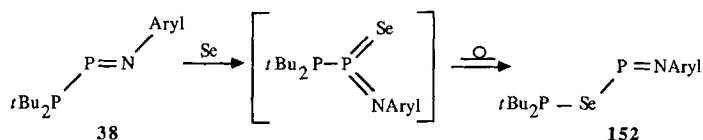
and Al_2Me_6 do not give the expected organometalation but rather a condensation product in which the low coordination number remains unchanged; the zwitterionic structure of the product **150** results from a nucleophilic attack of the imine nitrogen at aluminum.^[178]



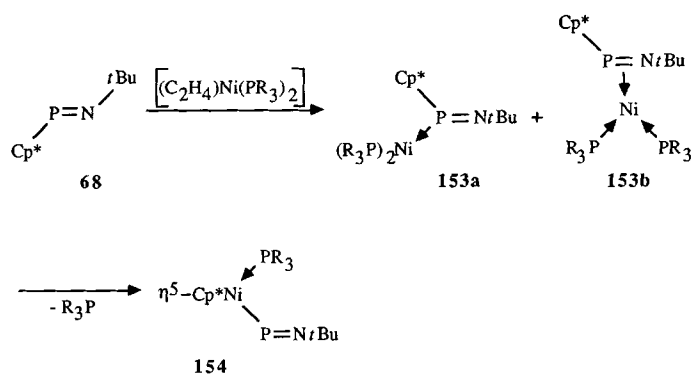
The formation of functionalized iminophosphanes such as **151** via insertion of phenyl isocyanate or tetrafluoropropyl cyanate into an Si–N bond of **3** occurs without formal participation of the double bond.^[179, 180] However, a more exact



study of the reaction with phenyl isocyanate indicated the presence of a multi-step reaction in which the product is generated via an electrophilic addition of the substrate at the imine nitrogen followed by a 1,5 silyl shift.^[166] Participation of the double bond has also been suggested for the selection of **38**; the formation of the *P*-selenoiminophosphane **152** was explained on the basis of rearrangement of a selenoiminophosphorane intermediate arising from oxidative selenation.^[106]



The reactions of **68** with nickel complexes of the type [(olefin)Ni(PR₃)₂] to give the metal-substituted derivatives **154** (Scheme 36) are related to nucleophilic substitution reac-



Scheme 36. Bu (a), Et (b), Ph (c).

tions. The detection of the intermediates **153 a, b**, from which **154** is generated via a 1,2 shift of the cyclopentadienyl residue, also indicates that the double bond system is involved in the reaction. The analogous generation of a metalloiminophosphane and its subsequent [2 + 1] addition to excess starting material was formulated to explain the formation of a spirocyclic $\lambda^3\lambda^5$ -azadiphosphiridine from $\text{Me}_5\text{C}_5\text{-P=NtBu}$ and $(\text{MeCN})_3\text{Mo}(\text{CO})_3$.^[41]

5. Future Prospects

The present survey shows that the chemistry of the iminophosphanes has undergone a very rapid development in the last few years; the mutual stimulation of theory and experiment has played an important role in making possible such rapid progress. In the initial phase the synthesis of aminoiminophosphanes and their transformation into (from the point of view of bonding theory) “unusual” compounds with $\sigma^3\lambda^5$ -phosphorus formed the focus of interest; new applications in catalysis have very recently been reported for the latter.^[182] Later studies dealt with “carbene-like” properties of the *P*-alkylated derivatives, which afforded routes to new types of phosphorus heterocycles. The recent synthesis of *P*-halogenated derivatives has made possible the preparation of a broad spectrum of functionalized iminophosphanes, including metalloiminophosphanes and a phosphanetriylammonium ion; the extreme bonding situation in the latter compounds is made clear by their in part extremely unusual crystal structures.

What can we expect in the future? Since the parent system (*E*)-HP=NH has so far resisted all attempts at its detection, one important goal is the generation of further small, highly reactive iminophosphanes and the study of their reactivity in the gas phase or in a matrix. New phospho-analogs of cumulene systems, such as diazo- and azido-compounds, are of both theoretical and synthetic interest. A further aspect which will certainly continue to be of great interest is the study of the coordination chemistry of known or still unknown phosphorus–nitrogen systems; the synthesis of phospho-analogs of pentadienes mentioned above (Section 2.2) has certainly provided an initial impulse in this direction. The generation of optically active iminophosphanes and products derived from them, and a study of their chemistry, would certainly be of great promise both from the synthetic point of view and as a tool for carrying out detailed mechanistic studies.

While until now all attempts have been directed towards the study of monomeric products, the high reaction potential of the double bond of iminophosphanes suggests that the latter are capable of serving as useful precursors in polymer chemistry. In this respect it would be extremely attractive to verify the existence of a phosphandiylimide $[\text{RP}=\text{N}]^\ominus$; such a system could be used in the construction of polyiminophosphanes $(\text{PN})_x\text{R}_y$, and together with the known iminophosphane system $\text{RP}=\text{NR}'$ could also serve as a model compound for the study of ionic polymerization and the generation of “living polymers”. The possible role of iminophosphanes as precursors for an as yet unknown $(\text{PN})_x$ polymer or corresponding copolymers formed from

iminophosphane and phosphazene units also remains to be studied.

My grateful thanks go to all those co-workers whose enthusiastic collaboration has contributed to the advancement of this area of chemistry, from the initial phase to the present time; many of the most recent results can as yet only be found in doctoral theses, but the names of all involved can be found in the list of references. Thanks are also due to Prof. Dr. W. W. Schoeller (Bielefeld) for many intensive and fruitful discussions, and to Mrs. D. Purschke for her skilful and patient help in the preparation of this manuscript. Much of the work cited here was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

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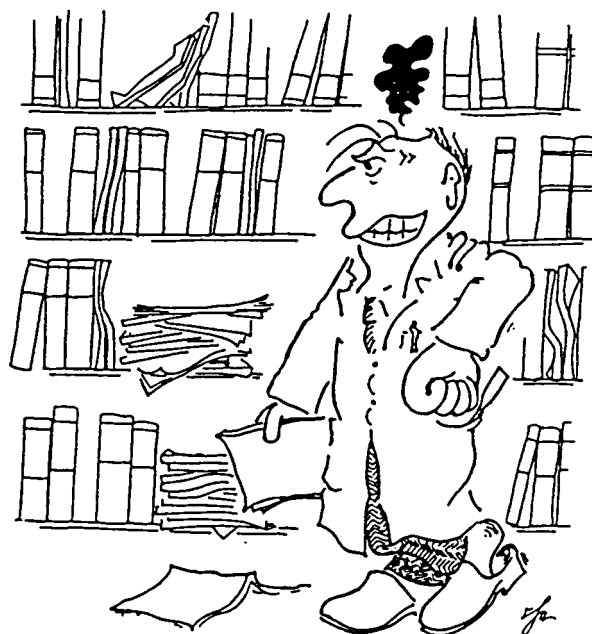
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