Phosphorus and Sulfur, 1983, Vol. 14, pp. 267–283
0308-664X/83/1403-0267/$18.50/0
© 1983 Gordon and Breach, Science Publishers, Inc.
Printed in the United States of America

ACYL- AND ALKYLIDENEPHOSPHINES. XXI.[1] Acylphosphines and Their Derivatives with Phosphorus Atoms of Coordination Number 3, 2, and 1[†]

G. BECKER, W. BECKER and O. MUNDT

Institut für Anorganische Chemie der Universität Stuttgart
Pfaffenwaldring 55, 7000 Stuttgart 80

(*Received September 24, 1982*)

The following article summarizes our work on acylphosphines and acylphosphides as well as on alkylidene- and alkylidynephosphines, most of which were thought only thirty years ago not to exist under ordinary conditions.

COMMON ACYLPHOSPHINES

Acylphosphines contain the group $>P-\underset{|}{C}=O$ and are the phosphorus analogues of acyl amides, a class of compounds known to organic chemists since the work of Dumas in 1830.[2] In spite of the fact that, after the successful synthesis of ethylphosphine from ethyl bromide and phosphorus hydride in the presence of zinc oxide in 1871, A. W. v. Hofmann[3] had expressed the anticipation of a forthcoming preparation of acetophosphide, the analogue of acetamide, and even had made the proposal to start with the synthesis of "acetophosphile", the analogue of acetonitrile, and although other fields of phosphorus chemistry have been developed very rapidly during the last decades, only a few groups were concerned with the synthesis of acylphosphines. Probably the hesitation arose because, on one hand these compounds lie on the borderline between inorganic and organic chemistry, and on the other hand, early attempts, reviewed in reference 4, gave very disappointing results and yielded only yellow, amorphous powders, similar to solid yellow phosphorus hydride.

Apart from the isolated synthesis of acetyldiethylphosphine,[5] acylphosphines were obtained in high yields only as late as 1959 when Issleib and Priebe[4] carried out the reaction of acyl halides with element-organic alkali-metal phosphides. As reported by Polish authors,[6] some tribenzoylphosphines have been formed from phosphorus hydride and the corresponding aroyl halides in pyridine. Several publications of Kostyanovskii and coworkers[7] deal with the addition of primary and secondary phosphines to the C—C double bond of ketene; phosphorus hydride, however, does not react in the expected manner to give mono- or triacetylphosphine. Short reviews of these and different methods are given in references 8 and 9.

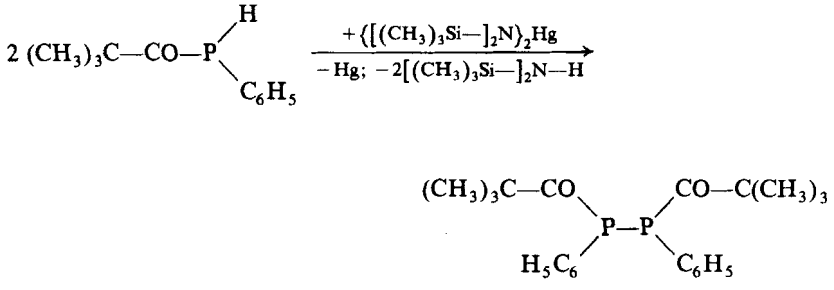
[†] Plenary Lecture, Colloque National sur la Chimie du Phosphore, Montpellier, September 22, 1982.

In 1972–73 several groups nearly simultaneously discovered that acylphosphines can best be prepared via cleavage reactions of trimethylsilylphosphines with acyl halides. Whereas, Becher, Fenske and Langer[10] as well as Rühlmann and coworker[11] studied mono(trimethylsilyl)phosphines, we were engaged in studies of compounds containing more than one Si—P bond in the molecule. For example, acetyl chloride and tris(trimethylsilyl)phosphine, a compound easily synthesized in large amounts from sodium-potassium alloy, white phosphorus and chlorotrimethylsilane in 1,2-dimethoxyethane,[12] give triacetylphosphine in very good yields[9,13] (eq. (1)).

$$[(CH_3)_3Si]_3P \xrightarrow[-3(CH_3)_3SiCl]{+3CH_3COCl} (CH_3CO)_3P \qquad (1)$$

The wide applicability of this method is also shown in reactions with trimethylsilylphosphines containing a P—H group. For example, phenyltrimethylsilylphosphine reacts with 2,2-dimethylpropionyl chloride to give 2,2-dimethylpropionylphenylphosphine.[14]

Whereas the C—N bond in acyl amides is shortened by interaction of the free electron pair at nitrogen and the (2p—2p) π-bonding system of the CO group, X-ray structure determinations of bis(2,2-dimethylpropionyl)phenylphosphine obtained from phenylbis(trimethylsilyl)phosphine and 2,2-dimethylpropionyl chloride[14] or of 1,2-bis(2′,2′-dimethylpropionyl)-1,2-diphenyldiphosphine prepared according to eq. (2)[17] as well as of other derivatives (Table I) showed the P—C(O) bond length to be



(2)

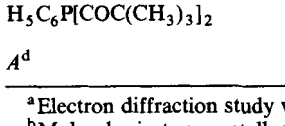
longer by about 6 pm than the standard value of 183 pm. In keeping with this observation, the nmr spectra do not give any indication of a hindered rotation of the acyl group round the P—C(O) bond. Obviously, as a consequence of the neighboring electronegative oxygen atom, the carbon atom gains more positive charge so that the polarity of the P—C bond is changed from $P^{\delta+}$—$C^{\delta-}$ as expected to $P^{\delta+}$—$C^{\delta+}$ and the bond length is elongated. A similar phenomenon is observed in trifluoromethylphosphines.[22]

ENOLIC DIACYLPHOSPHINES AND DIACYLPHOSPHIDES

Treatment of triacetylphosphine mentioned above with alcohols according to eq. (3) leads to simultaneous formation of diacetyl- and monoacetylphosphine.[23] ^1H and ^{31}P nmr spectra of the former compound confirm the existence of a keto-enol equilibrium (eq. (4)), the enol form being characterized by $^3J_{P-C-C-H}$ and $^3J_{P-C-O-H}$ coupling constants of 10.9 or of 3.3 cps as well as by a downfield shift

TABLE I

Characteristic Bond Lengths of Some Common Monoacyl- and Diacylphosphines

Acylphosphine	P—C(O) (pm)	C=O (pm)	P—C(R) (pm)	Ref.
$(H_3C)_2PCOCH_3$[a]	186.3(2)	121.9(4)	186.3(2)	7, 15
$(H_5C_6)_2PCOCHCl_2$[b]	187.3(4) 189.0(5)	119.7(5) 119.6(6)	180.3(5) to 185.0(4)	16
	189.4(3)[c]	120.9(3)[c]	184.1(3)[c]	17
$[(H_5C_6)_2PCO]_2$	187.2[c]	121.2[c]	183.3[c]	18
$\{[(H_3C)_3C]_2PCO\}_2$	188[c]	121[c]	190[c]	18
$(H_5C_6)_2PCOCH_2CHClCH_3$ ↓ $Mn(CO)_4Br$	189.0(11)	117.0(14)	179.9(8) 181.4(7)	19
$H_5C_6P[COC(CH_3)_3]_2$	189.3(4) 192.2(4)	121.7(5) 120.1(4)	183.8(4)	20
A[d]	186[c]	122[c]	[e]	21

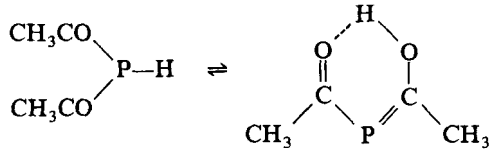
[a]Electron diffraction study with P—C(O) and P—C(R) assumed to be equal.
[b]Molecules in two crystallographically different sites.
[c]Averaged value.
[d]For formula see Table II.
[e]Value not given.

of 18.3 ppm for the O—*H*—O group and of +73 ppm for the phosphorus nucleus. Since bis(2,2-dimethylpropionyl)phosphine, synthesized from bis(trimethylsilyl)phosphine and 2,2-dimethylpropionyl chloride according to eq. (5), shows the same equilibrium,[1] diacylphosphines resemble 1,3-diketones.[24] The influence of temperature and the dielectric constant of the solvent on this equilibrium, which is typical for these purely organic compounds, has also been confirmed for diacylphosphines. For example, with bis(2,2-dimethylpropionyl)phosphine, the keto form is present only to the extent of 10% in benzene; however, when the crystalline compound is dissolved in polar acetonitrile, the keto form increases slowly up to more than 50%.[1]

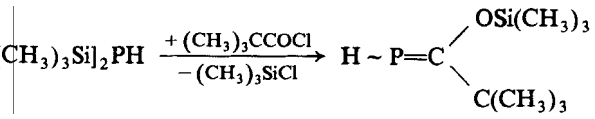
$$(CH_3CO)_3P \xrightarrow[-\,ROCOCH_3]{+\,ROH} (CH_3CO)_2P(\sim H) \xrightarrow[-\,ROCOCH_3]{+\,ROH} CH_3COPH_2$$

$$R = CH_3, C_6H_5CH_2 \qquad (3)$$

The results of an X-ray structure determination of bis(2,2-dimethylpropionyl)-phosphine[25] prove the existence of the enol form in the solid in that: the molecular symmetry is mm2; the bridging hydrogen atom of the O—H—O group has been localized on the intersecting line of both mirror planes; and bond lengths (Table II)



(4)



E and Z isomer (5)

$$\xrightarrow[-(CH_3)_3SiCl]{+(CH_3)_3CCOCl} [(CH_3)_3CCO]_2P(\sim H)$$

indicate a mesomeric system with a very short averaged oxygen–oxygen distance of 241 pm.

Bis(2,2-dimethylpropionyl)phosphine reacts with sodium bis(trimethylsilyl)amide in 1,2-dimethoxyethane (DME) to give sodium bis(2,2-dimethylpropionyl)phosphide · DME. Subsequent addition of nickel bromide leads to nickel bis[bis(2,2-dimethylpropionyl)phosphide] · DME (eq. (6))[1] in which the nickel ion is surrounded

$$2\,[(CH_3)_3CCO]_2P(\sim Na \cdot DME) \xrightarrow[-\,2\,NaBr\ -\,DME]{+\,NiBr_2} \{[(CH_3)_3CCO]_2P\}_2Ni \cdot DME \qquad (6)$$

DME = 1,2-dimethoxyethane

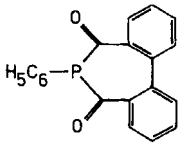
octahedrally by six oxygen atoms of two diacylphosphide ligands and one DME molecule (Fig. 1).[26] Recently, a convenient synthesis of diacylphosphides has been found in the reaction of sodium tetraphosphinoaluminate or of monolithium phosphide · DME with benzoyl chloride to give aluminum tris(dibenzoylphosphide)[28] and lithium dibenzoylphosphide · DME, respectively.[27] The latter compound has been proven to be dimeric in the solid state; the lithium ion is

TABLE II

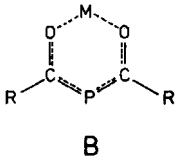
Characteristic Structural Data of Enolic Bis(2,2-dimethylpropionyl)phosphine (R = $C(CH_3)_3$; M = H) and of Diacylphosphides with the general formula *B*[a]

M	R	P···C(O) (pm)	C···O (pm)	C···P···C (°)	Ref.
H	$C(CH_3)_3$[b]	180.1(4)	129.2(5)	97.8(2)	1, 25
		179.6(4)	129.3(5)	97.5(2)	
1/2 Ni · DME[c]	$C(CH_3)_3$	178.6(3)[d]	125.2(1)[d]	103.7(2) (2x)	26
Li · DME[c]	C_6H_5[e]	181.5(3)	125.4(3)	101.8(1)	27
		179.6(3)	127.4(2)		
1/3 Al	C_6H_5	177.1(2)[d]	126.2(2)[d]	100.9(1)[d]	28

[a]For *A* see Table I.



A



B

[b]Molecules of symmetry mm2 in two crystallographically different sites.
[c]DME = 1,2-dimethoxyethane.
[d]Averaged value.
[e]Dimeric in the solid state.

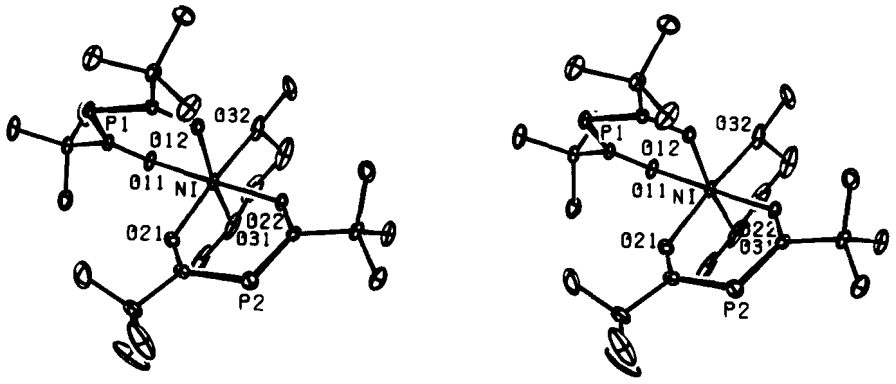


FIGURE 1 Molecular structure of nickel bis[bis(2,2-dimethylpropionyl)phosphide] · DME in stereoscopic view (diacylphosphide ligand: Ni—O 198; DME-ligand: Ni—O 212 pm; further data given in Table II; hydrogen atoms omitted for clarity).

situated above the base of a square pyramid consisting of the four oxygen atoms of the DME molecule and the dibenzoylphosphide anion as well as one oxygen atom of a neighboring C—O group. X-ray structure determinations of all these compounds show P—C distances to be shortened to 177 to 181 pm and C—O distances to be elongated up to 125 to 129 pm (Table II).

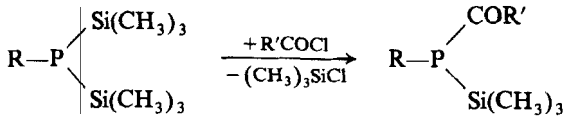
By working out synthetic methods for diacylphosphines and diacylphosphides, very unexpectedly we have succeeded in preparing compounds of dicoordinated phosphorus. According to the double-bond rule, which controlled the chemistry of main group elements for many years, these phosphines should not be stable under ordinary conditions. But even at the beginning of this research, several exceptions such as phosphamethincyanines,[29] λ^3-phosphorines,[30] 1,2,3-diazaphospholes and other compounds[31a] with an extended conjugated bonding system were known.

ALKYLIDENEPHOSPHINES[31]

As initially found with the synthesis of triacetylphosphine (eq. (1))[9,13] and as already demonstrated in eq. (5) describing the formation of bis(2,2-dimethylpropionyl)phosphine, alkylidenephosphines with an *isolated* P=C bond occur as intermediate products during the preparation of acylphosphines. In the meantime, compounds have been prepared by one of the following methods in such a considerable number that already reasons for their surprisingly high thermal stability can be discussed:

[*1-(Trimethylsiloxy)alkylidene*] *phosphines*

When in bis(trimethylsilyl)phosphines as well as in tris(trimethylsilyl)phosphine one trimethylsilyl group is replaced by the acyl moiety, acyl trimethylsilylphosphines with a P—C single and a C=O double bond are formed (eq. (7)). ^{1}H, ^{31}P, ^{13}C, and ^{29}Si nmr-spectroscopic studies, however, show these compounds to be thermally unstable and to rearrange via a 1,3-migration of the second trimethylsilyl group from

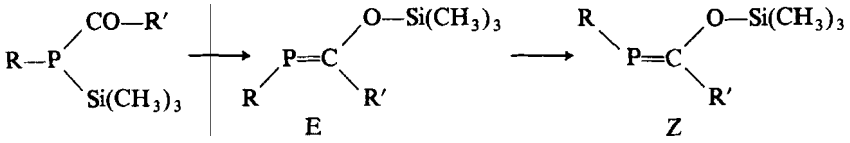


(7)

$R' = C(CH_3)_3$; R = alkyl or aryl,[32] $Si(CH_3)_3$,[33] H[34]

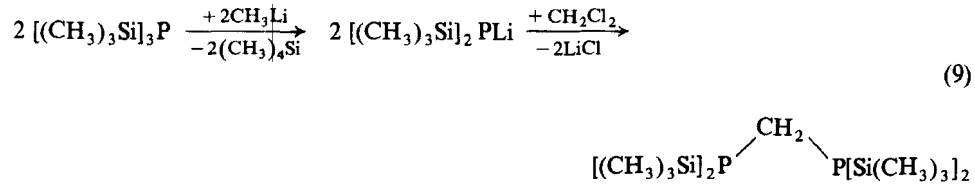
$R' = C_6H_5$; R = alkyl or aryl[35]

phosphorus to oxygen giving [1-(trimethylsiloxy)alkylidene]phosphines. In many cases, initially the E-, and later the Z-isomers can be detected (eq. (8)).[36] Obviously, the formation of a silicon–oxygen bond, which is much stronger than the weak silicon–phosphorus bond, favors the observed 1,3-rearrangement. Reactions with 2,2-dimethylpropionyl chloride are easiest to investigate; the corresponding [2,2-dimethyl-1-(trimethylsiloxy)propylidene]phosphines are obtained in nearly quantitative yields.



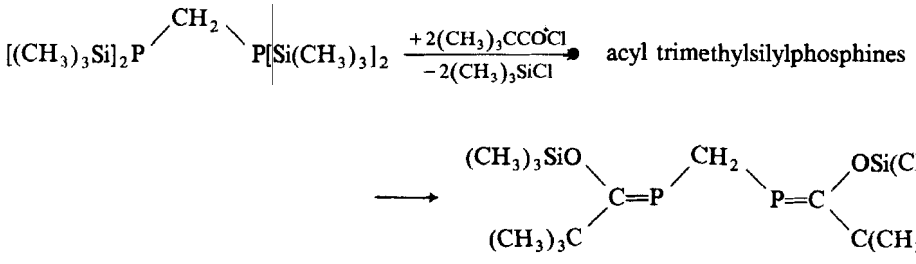
(8)

The constitution of these compounds has been confirmed by an X-ray structure determination of a diphosphanomethane derivative[37] synthesized from tris(trimethylsilyl)phosphine by the following route (eq. (9))



(9)

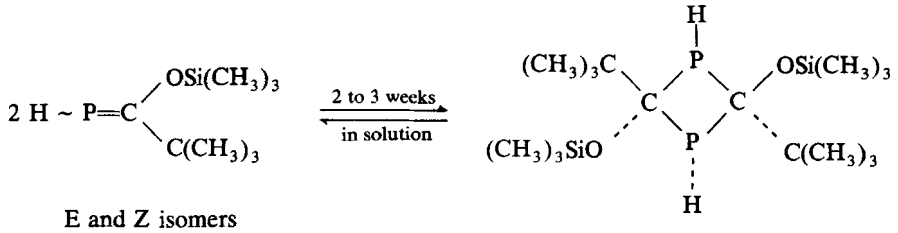
via bis[bis(trimethylsilyl)phosphino]methane[38] (eq. (10)).



(10)

The trimethylsilyl groups of bis[2,2-dimethyl-1-(trimethylsiloxy)propylidenephosphino]methane are both found to be bound to oxygen. Compared with the typical value of a single bond, the P=C distance has shortened from 185 to 169 pm. The C—O distance of 135 pm deserves some special remarks in that it is as short as in the esters of carboxylic acids. Whether or not this length indicates an interaction of a free electron pair at oxygen with the (3p—2p) π-bond of the P=C group remains still open to question.

In order to elucidate factors responsible for the high thermal stability of the phosphines obtained so far, especially to test the shielding effect of bulky groups, [1-(trimethylsiloxy)alkylidene]phosphines with small substituents R and R′ were synthesized according to eqs. (7) and (8). For example, when unsubstituted bis(trimethylsilyl)phosphine is treated with 2,2-dimethylpropionyl chloride,* after the transient formation of a thermally rather stable acyl trimethylsilylphosphine, a mixture of E- and Z-isomeric [2,2-dimethyl-1-(trimethylsiloxy)propylidene]phosphine can be isolated. Both isomers scarcely differ in their nmr shift values, but do so strongly in the coupling between phosphorus and the corresponding nucleus. The larger value always is found when the substituent under consideration and the free electron pair at phosphorus are on the same side of the P—C double bond.[34] Keeping the mixture of E- and Z-isomer for two or three weeks at room temperature in diffuse daylight, leads slowly to a precipitate of large, well shaped crystals (eq. (11)). One important structural feature of the 1,3-diphosphetane formed is the endocyclic P—C distance of about 190 pm (Table III). As a result of strong intramolecular interactions, the ring system is strained to such an extent that in solution rapid decomposition to the mixture of E- and Z-isomer occurs.[39]



(11)

We also came across thermally unstable [1-(trimethylsiloxy)alkylidene]phosphines when 2,2-dimethylpropionyl chloride with its bulky *tert*-butyl group was replaced by benzoyl chloride. As the P=C group of E- and Z-[1-phenyl-1-(trimethylsiloxy)methylidene]phosphine, formed according to eq. (8), is insufficiently shielded by the rather small substituents, these compounds are unstable and dimerize to diphosphetanes.

With careful studies on the benzyl or isopropyl derivative, the rate of rearrangement was shown to be strongly increased by traces of acid from the acyl halide.[35] Using ordinary distilled benzoyl chloride, the Z-isomer is formed very rapidly so that there is enough time for the dimerization of this compound (Fig. 2). An X-ray

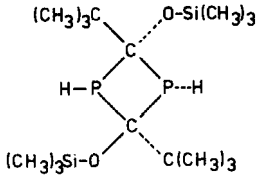
*In a molar ratio of 1 : 1.

TABLE III

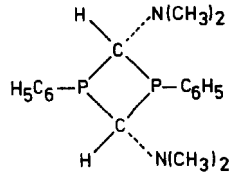
Characteristic Bond Lengths and Angles in 1,2- and 1,3-Diphosphetanes

Compound[a]	Endocyclic P—C (pm)	P—P (pm)	C—C (pm)	∢ at P (°)	∢ at C (°)	Exocyclic P—C (pm)	Ref.
C	189.6(2) 190.3(2)	—	—	87.3(1)	92.7(1)		39
D	187.2(3) to 191.4(3)	—	—	83.5(1) 84.9(1)	93.4(1) 92.3(1)	183.9(3) 183.4(3)	44
E	187.3(2) to 191.2(3)	—	—	86.7(3) 84.7(3)	90.3(3) 90.2(3)	183.5(3) 184.0(4)	43
F	185.2(2) 182.8(2)	—	—	81.2(1)	98.8(1)	183.9(2)	46
G[b]	183.8(3) to 186.2(3)	—	—	81.8(1) (2x)	98.2(1) (2x)	186.1(3) 186.0(3)	46
H	191.8(3) 193.0(3)	220.4(1)	158.9(4)	77.2(2) 76.9(2)	94.2(3) 93.9(3)	184.5(3) 185.5(4)	40
I[c]	193.1(12) to 196.7(12)	222.1(4) 222.8(5)	157.7(17) 161.0(15)	75.9(3) to 77.5(3)	92.9(8) to 94.1(6)	185.3(14) to 187.1(15)	40
K	188.7(6) 195.0(6)	222.8(2)	157.0(9)	77.3(2) 76.4(2)	96.8(4) 93.8(4)	[d]	47
L	185.1(4) 177.7(3)	221.9(1)	[e]	79.0(1) 73.5(1)	105.0(3) 102.2(3)	186.0(4) 188.7(4)	45

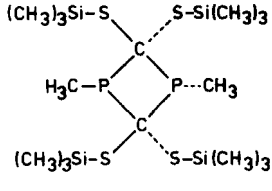
[a]



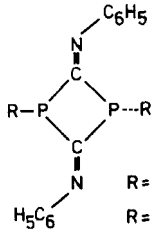
C



D

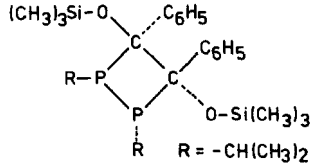


E



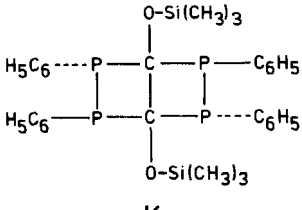
R = $-CH_2-CH_3$ F

R = $-CH_2-C_6H_5$ G

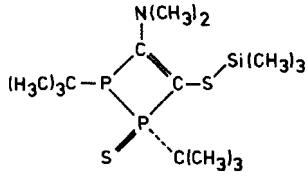


R = $-CH(CH_3)_2$ H

R = $-CH_2-C_6H_5$ I



K



L

[b] Molecules of symmetry $\bar{1}$ in two crystallographically different sites.
[c] Molecules in two crystallographically different sites.
[d] Values not given.
[e] Double bond 136.0(5) pm.

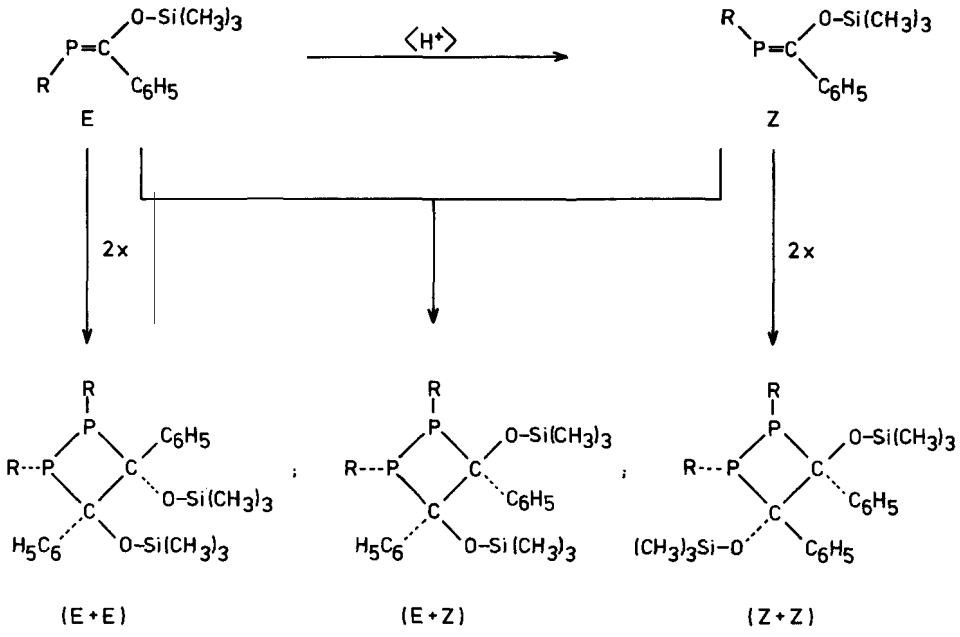


FIGURE 2 Dimerization of E and Z isopropyl- or of E and Z benzyl[phenyl(trimethylsiloxy)methylidene]phosphine.

structure determination of the product formed (Fig. 3) gave three important results:[40] Not a 1,3- but a 1,2-diphosphetane with a direct phosphorus–phosphorus bond has been formed. The configuration of the monomer can still be recognized in the dimer. With the structure shown it is clear that these 1,2-diphosphetanes decompose to give (E)-1,2-bis(trimethylsiloxy)-1,2-diphenylethene and cyclopolyphosphines.

If the benzoyl chloride used is carefully freed from acid impurities by distillation with triethylamine, the rearrangement of the E to the Z alkylidenephosphine is retarded and a competitive dimerization reaction can occur. Finally, one isolates a mixture of two other diphosphetanes marked with (E + E) and (E + Z) in Fig. 2.

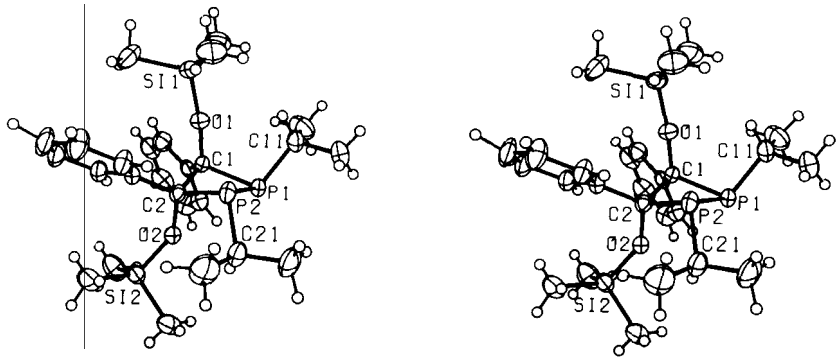
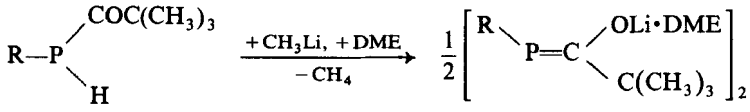


FIGURE 3 Molecular structure of 1,2-diisopropyl-3,4-diphenyl-3,4-bis(trimethylsiloxy)-1,2-diphosphetane in stereoscopic view (characteristic bond lengths and angles given in Table III).

Their nmr-spectra confirm the formation of 1,2-diphosphetanes, but at this time we can not yet distinguish between the stereoisomers shown here and two different ones with the alkyl groups at phosphorus placed on the same side of the four-membered ring.[35]

Lithium acylphosphides

As a result of nmr spectroscopic studies, dimeric lithium acylphosphides prepared from acylphosphines and methyllithium according to eq. (12) must also be described as alkylidenephosphines with the ether-complexed lithium atom bound to oxygen. An X-ray structure determination of a characteristic compound is planned.

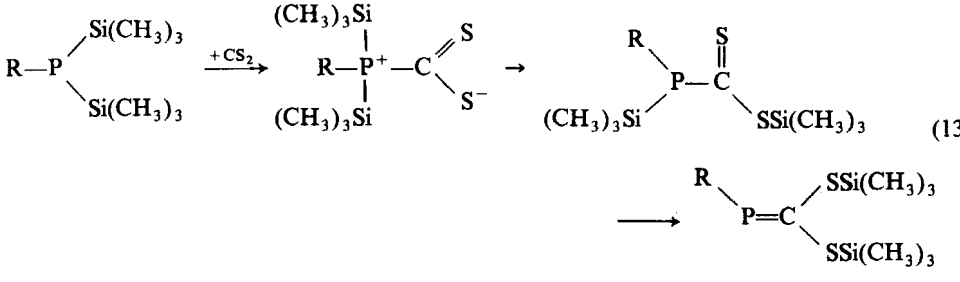


(12)

R = C_6H_5,[14] H[34]

[Bis(trimethylsilylsulfano)methylidene]phosphines

Alkyl- or arylbis(trimethylsilyl)phosphines react with carbon disulfide to give the corresponding [bis(trimethylsilylsulfano)methylidene]phosphines (eq. (13)). As in the case of trialkylphosphines, an initial red color indicates the formation of an adduct; later on the trimethylsilyl groups successively migrate from phosphorus to the sulfur atoms.[41] The constitution of the compounds formed has been proven by an X-ray structure analysis of the phenyl derivative (Fig. 4).[42] Again, the length of the P—C double bond has been determined to be 170 pm; all other parameters deviate only slightly from standard values. In the case of the methyl derivative, the dimer only was isolated in nearly quantitative yields.[43] Characteristic bond lengths and angles of this 1,3-diphosphetane are compiled together with those of other compounds in Table III.



(13)

[Dimethylaminomethylidene]- and [Diphenylmethylidene]phosphines

When carbonyl compounds like dimethylformamide or benzophenone are treated with alkyl- or arylbis(trimethylsilyl)phosphines, [dimethylaminomethylidene]- or [diphenylmethylidene]phosphines and hexamethyldisiloxane are produced probably via

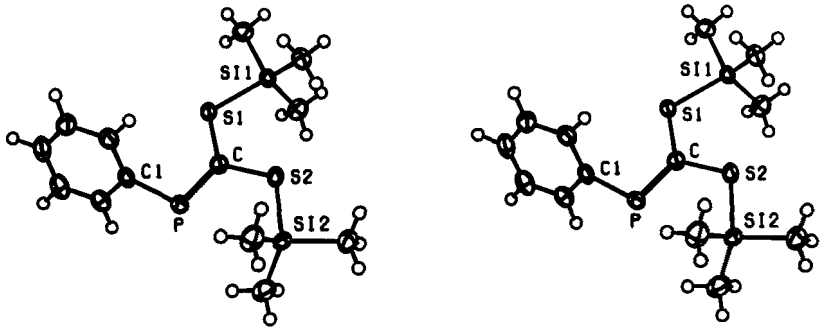
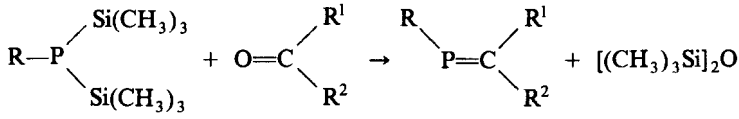


FIGURE 4 Molecular structure of phenyl[bis(trimethylsilylsulfano)methylidene]phosphine in stereoscopic view (P=C 170.0(2); P—C 1 183.1(2); C—S 176.1; S—Si 218.6 pm; C—P—C 1 106.7(1); C—S—Si 111.1°).

addition and subsequent elimination (eq. (14)). Here, too, the formation of strong Si—O bonds must be taken to be the driving force of these reactions. In some cases lithium trimethylsilylphosphides[48a] as well as the corresponding arsenides[48b] have been used. The nmr data of [dimethylaminomethylidene]phosphines, if compared

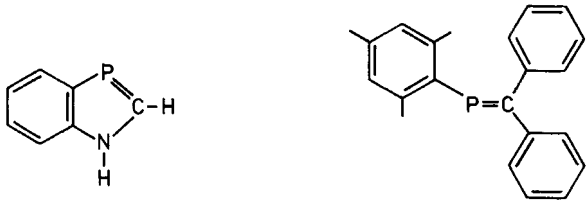


(14)

R = alkyl, aryl; R^1 = H; $R^2 = N(CH_3)_2$ [8,48a]

$R^1 = R^2 = C_6H_5$ [48a]

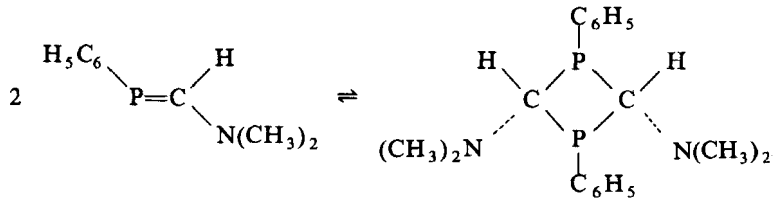
e.g. with those of benzazaphospholes,[49] (Fig. 5), clearly indicate these compounds to have the E-configuration with the substituent at phosphorus and the dimethylamino group being placed on different sides of the P=C bond. For the P=C—H moiety, nearly no difference is found in ^{31}P and ^{13}C chemical-shift values, but a great difference is observed in the $^2J_{PH}$-coupling constants—about 15 and 40 cps for the former and latter compounds, respectively.



Benzazaphosphole [Diphenylmethylidene]-mesitylphosphine

FIGURE 5

At first, the synthesis of a variety of [dimethylaminomethylidene]phosphines was complicated by long reaction times. For example, *tert*-butylbis(trimethylsilyl)phosphine and dimethylformamide had not yet reacted completely after one year. When, however, small pieces of solid sodium hydroxide are added to the ethereal solution, the reaction rate is increased considerably and the batch can be worked up after one or two days. Compounds with a *tert*-butyl or a mesityl group at phosphorus remain monomers, whereas the methyl and phenyl derivative form dimers within days. An X-ray structure determination[44] shows the dimeric phenyl compound to be a 1,3-diphosphetane with the configuration shown in eq. (15). An endocyclic P—C



(15)

distance of 189 pm indicates a strained ring system. In keeping with this observation, the compound dissociates to some extent when stored in solution for a longer time.

By the same type of reaction (eq. (14)), the mechanism of which has already been discussed elsewhere,[48a] mesityl-, phenyl- or isopropylbis(trimethylsilyl)phosphine and benzophenone give the corresponding [diphenylmethylidene] derivatives. The structure of the stable mesityl compound (Fig. 5), prepared in 1978 by Bickelhaupt and coworkers[50] in a different way, has been confirmed by X-ray structure determinations;[51,52] the structural parameters obtained are compared with those of unsubstituted benzazaphosphole in reference 52. The phenyl- and isopropyl derivative were identified at low temperature by their ^{31}P nmr signals which are characteristically shifted to very low field. With increasing temperature, these alkylidenephosphines dimerize to compounds, which as a result of nmr spectroscopic studies, are most probably 1,2-diphosphetanes.[53]

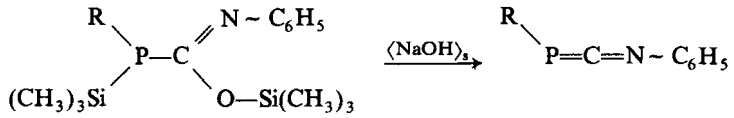
Thermal Stability of Alkylidenephosphines

The thermal stability of the enol tautomers of diacylphosphines and of diacylphosphides must be attributed to the existence of an extended conjugated bonding system. In contrast to these compounds [2,2-dimethyl-1-(trimethylsiloxy)propylidene]- and probably [bis(trimethylsilylsulfano)methylidene]phosphines gain their stability mainly from a shielding of the P=C double bond by bulky substituents. In [dimethylaminomethylidene]phosphines, however, an interaction between the free electron pair at nitrogen and the π-bonding system of the P—C group quite obviously contributes also to the stability of these compounds. The temperature dependent ^{1}H and ^{13}C nmr spectra indicate a hindered rotation of the dimethylamino group. The free energy of activation $\Delta G^{\ddagger}$ calculated from the temperature of coalescence is found to be about 60 kJ/mol, a value somewhat lower than that for the corresponding amidines.[48a]

In our view, the strong influence of an amino group at the P=C double bond on the stability of alkylidenephosphines can clearly be demonstrated with the considerable number of similar compounds synthesized by other groups. In addition to [dimethylaminomethylidene]phosphines obtained nearly simultaneously by us[8] and by Oehme, Leissring and Meyer,[54] the preparation of similar phosphines with one trimethylsilyl group at nitrogen has been published by Issleib,[55] Appel[56] and coworkers. [Diaminomethylidene] derivatives have been obtained from carbodiimides and bis(trimethylsilyl)phosphines;[57] cyanophosphinidenebenzoimidazolines are described by Schmidpeter and others.[58]

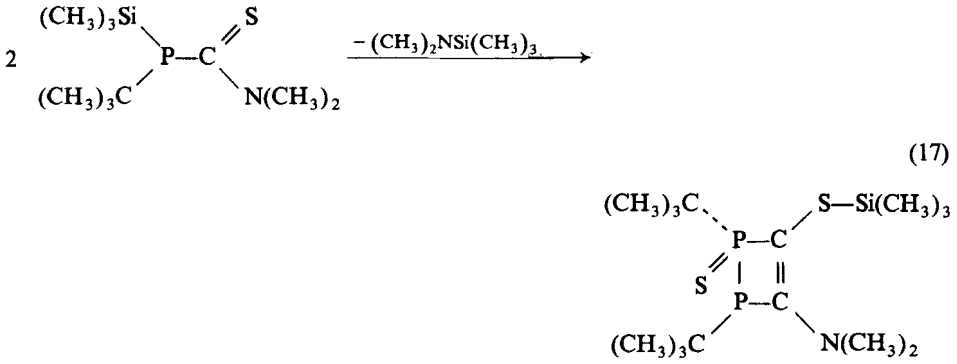
Current Research on [Iminomethylidene]- and [Aminosulfanomethylidene] phosphines

In contact with small amounts of solid sodium hydroxide, adducts prepared from alkyl- or arylbis(trimethylsilyl)phosphines and phenyl isocyanate[59] or phenyl isothiocyanate eliminate hexamethyldisiloxane (eq. (16)) or bis(trimethylsilyl)sulfane, probably to give very unstable [(phenylimino)methylidene]phosphines first, which dimerize immediately to 2,4-bis(phenylimino)-1,3-diphosphetanes (Fig. 6, Table III).[46]



(16)

From lithium *tert*-butyltrimethylsilylphosphide and N,N-dimethylthiocarbamoyl chloride, the corresponding thiocarbamoylphosphine has been obtained. In solution the unstable compound eliminates dimethyltrimethylsilylamine and gives 1,2-di(*tert*-butyl)-3-dimethylamino-4-trimethylsilylsulfano-1,2-diphosphetene-1-sulfide (eq. (17)). The constitution of this unexpected product was elucidated by an X-ray structure determination (Table III); [(dimethylaminotrimethylsilylsulfano)methylidene]phosphines could not be isolated.[45]



(17)

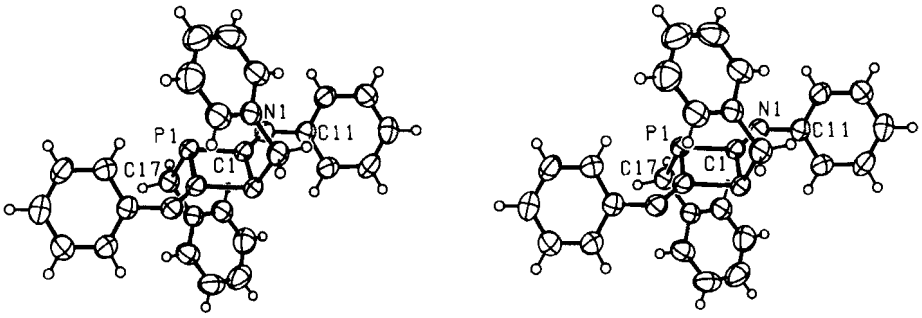


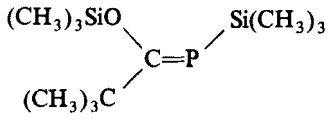
FIGURE 6 Molecular structure of 1,3-dibenzyl-2,4-bis(phenylimino)-1,3-diphosphetane in stereoscopic view (C 1—N 1 126.6; N 1—C 1 1 142.2 pm; C 1—N 1—C 1 1 121.1°; further data given in Table III).

ALKYLIDYNEPHOSPHINES

Alkylidynephosphines have been known since 1961, when Gier obtained very unstable methylidynephosphine H—C≡P together with acetylene and ethylene from an electric discharge reaction between phosphorus hydride and the carbon electrode material.[60] In 1976 Nixon and coworkers[61] began their reports on the thermally or base-induced elimination of hydrogen halides from alkyl halophosphines or from (haloalkyl)phosphines. In the course of 1981, Appel, Maier and coworkers published the syntheses of phenyl- and trimethylsilylmethylidynephosphine; these compounds were prepared from chloro[(phenyltrimethylsilyl)methylidene]- or chloro[bis(trimethylsilyl)methylidene]phosphine, respectively, by a thermally induced elimination of chlorotrimethylsilane at high temperatures.[62,63]

Owing to the reaction conditions, very often only impure compounds could be isolated; they were characterized, particularly by Kroto, Nixon and coworkers,[61] with microwave, sometimes with photoelectron[64] and nmr spectra; a short summary of the literature is given in reference 65. Beyond doubt the further development of this field was retarded by the very low thermal stability and the difficult preparation of these compounds.

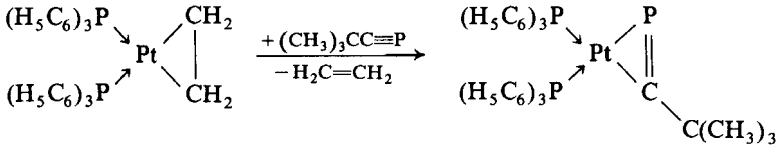
As a result of the aforementioned sodium hydroxide-promoted elimination of hexamethyldisiloxane, we had a new method of access to alkylidynephosphines. In the presence of this catalyst, [2,2-dimethyl-1-(trimethylsiloxy)propylidene]trimethylsilylphosphine, which is easily available from tris(trimethylsilyl)phosphine and 2,2-dimethylpropionyl chloride according to eqs. (7) and (8) and thermally stable up to +150°C, gives 2,2-dimethylpropylidynephosphine (eq. (18)).[65] In contrast to other alkylidynephosphines mentioned above, this compound does not decompose at room temperature so that it could be fully characterized. IR and Raman spectra show strong lines near 1530 cm^{-1} which must be attributed to the P≡C stretching



$$\xrightarrow[+25°C]{\langle NaOH\rangle_s} (CH_3)_3CC{\equiv}P + [(CH_3)_3Si]_2O \qquad (18)$$

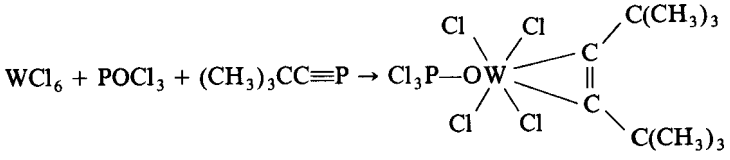
mode. Its structural proof was given by Oberhammer, Tübingen, by means of a combined electron diffraction and microwave spectroscopic analysis. With the calculated value of 153.6 pm, we are faced with the shortest P—C bond ever found for a thermally stable phosphine.[66]

In spite of the fact that the chemistry of alkylidynephosphines still remains to be developed, some results have already been obtained. As shown by Appel, Maier and coworkers, phenylmethylidynephosphine adds hydrogen chloride step-by-step to give benzyldichlorophosphine.[62] In a successful revision of our synthesis, Kroto, Nixon and coworkers[67] carried out the reaction of 2,2-dimethylpropylidynephosphine with ethylenebis(triphenylphosphine)platinum(0) and were able to replace the olefin and to isolate an alkylidynephosphine complex with the ligand bound side-on to the transition metal (eq. (19)). At 167 pm, the endocyclic P—C bond length is remarkably long and is reminiscent of a value typical for a P—C double bond.



(19)

We have treated 2,2-dimethylpropylidynephosphine with tungsten hexachloride in phosphorus oxychloride expecting the formation of compounds analogous to nitrene complexes.[68] However, a complicated redox reaction took place and we obtained only a complex with the di(*tert*-butyl)acetylene ligand bound side-on to the WCl_4 moiety (eq. (20)).[69] Further work on transition metal compounds is in progress.



(20)

ACKNOWLEDGEMENTS

We thank Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg and Fonds der Chemischen Industrie, Frankfurt a.M. for financial support.

REFERENCES

1. XX: G. Becker, M. Rössler and G. Uhl, *Z. Anorg. Allg. Chem.*, in press.
2. J. Dumas, *Ann. Chim. Phys.*, 2. Ser. **44**, 129 (1830).
3. A. W. v. Hofmann, *Ber. Deut. Chem. Ges.* **4**, 430 (1871).
4. K. Issleib and E. Priebe, *Chem. Ber.* **92**, 3183 (1959).
5. H. Albers, W. Künzel and W. Schuler, *Chem. Ber.* **85**, 239 (1952).
6. R. Tyka and E. Plazek, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **9**, 577 (1961); *C.A.* **60**, 4182a (1964).
7. R. G. Kostyanovskii, Yu. I. El'natanov and L. M. Zagurskaya, *Isv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 901; and previous publications.

8. G. Becker and O. Mundt, *Z. Anorg. Allg. Chem.* **462**, 130 (1980).
9. G. Becker, *Z. Anorg. Allg. Chem.* **480**, 21 (1981).
10. H.-J. Becher, D. Fenske and E. Langer, *Chem. Ber.* **106**, 177 (1973).
11. H. Kunzek and K. Rühlmann, *J. Organomet. Chem.* **42**, 391 (1972).
12. G. Becker and W. Hölderich, *Chem. Ber.* **108**, 2484 (1975).
13. G. Becker, *Allg. Prakt. Chem.* **23**, 73 (1972).
14. G. Becker, M. Rössler and E. Schneider, *Z. Anorg. Allg. Chem.* **439**, 121 (1978).
15. L. S. Khaikin, L. G. Andrutskaya, O. E. Grikina, L. V. Vilkov, Yu. I. El'natanov and R. G. Kostyanovskii, *J. Mol. Struct.* **37**, 237 (1977).
16. E. Lindner, M. Steinwand and S. Hoehne, *Angew. Chem.* **94**, 395 (1982); *Chem. Ber.* **115**, 2181 (1982).
17. G. Becker, O. Mundt and M. Rössler, *Z. Anorg. Allg. Chem.* **468**, 55 (1980).
18. H.-J. Becher, D. Fenske, E. Langer and H. Prokscha, *Monatsh. Chem.* **111**, 749 (1980).
19. E. Lindner, M. Steinwand and S. Hoehne, *Chem. Ber.* **115**, 2478 (1982).
20. G. Becker, M. Birkhahn, W. Massa, O. Mundt and E. Schneider, unpublished results.
21. D. Fenske, private communication.
22. C. J. Marsden and L. S. Bartell, *Inorg. Chem.* **15**, 2713 (1976).
23. G. Becker, *Z. Anorg. Allg. Chem.* **480**, 38 (1981).
24. A. I. Kol'tsov and G. M. Kheifets, *Russ. Chem. Rev.* **40**, 773 (1971).
25. G. Becker and H. P. Beck, *Z. Anorg. Allg. Chem.* **430**, 77 (1977).
26. G. Becker, O. Mundt and M. Rössler, to be published.
27. G. Becker, M. Birkhahn, W. Massa and W. Uhl, *Angew. Chem.* **92**, 756 (1980).
28. G. Becker and H. P. Beck, *Z. Anorg. Allg. Chem.* **430**, 91 (1977).
29. K. Dimroth, *Fortschr. Chem. Forsch.* **38**, 1 (1973).
30. G. Märkl, *Phosphorus and Sulfur* **3**, 77 (1977); A. J. Ashe, III, *Acc. Chem. Res.* **11**, 153 (1978).
31. (a) E. Fluck, *Top. Phosphorus Chem.* **10**, 193 (1980); (b) P. Jutzi, *Angew. Chem.* **87**, 269 (1975); *Chemie in unserer Zeit* **15**, 149 (1981); (c) R. Appel, F. Knoll and I. Ruppert, *Angew. Chem.* **93**, 771 (1981).
32. G. Becker, *Z. Anorg. Allg. Chem.* **423**, 242 (1976); cf. G. Becker and G. Gutekunst, *Z. Anorg. Allg. Chem.* **470**, 131 (1980); **470**, 144 (1980); **470**, 157 (1980).
33. G. Becker, *Z. Anorg. Allg. Chem.* **430**, 66 (1977).
34. G. Becker, M. Rössler and W. Uhl, *Z. Anorg. Allg. Chem.* **473**, 7 (1981).
35. G. Becker, W. Becker, G. Eichler and W. Uhl, to be published.
36. G. Becker, O. Mundt and W. Uhl, to be published.
37. G. Becker and O. Mundt, *Z. Anorg. Allg. Chem.* **443**, 53 (1978).
38. G. Fritz and W. Hölderich, *Z. Anorg. Allg. Chem.* **422**, 104 (1976); **431**, 76 (1977).
39. G. Becker and W. Uhl, *Z. Anorg. Allg. Chem.* **475**, 35 (1981).
40. G. Becker, W. Becker, M. Birkhahn, G. Eichler, W. Massa and W. Uhl, to be published.
41. G. Becker, G. Gresser and W. Uhl, *Z. Anorg. Allg. Chem.* **463**, 144 (1980), and unpublished results.
42. G. Becker, O. Mundt and G. Uhl, to be published.
43. G. Becker, W. Massa, R. Schmidt and G. Uhl, to be published.
44. G. Becker, W. Massa, O. Mundt and R. Schmidt, *Z. Anorg. Allg. Chem.* **485**, 23 (1982).
45. G. Becker, W. Becker and G. Uhl, to be published.
46. G. Becker, J. Härer, H. Riffel, G. Uhl and H.-J. Wessely, unpublished results; cf. R. Appel and B. Laubach, *Tetrahedron Lett.* **21**, 2497 (1980).
47. R. Appel, V. Barth, M. Halstenberg, G. Huttner and J. v. Seyerl, *Angew. Chem.* **91**, 935 (1979).
48. (a) G. Becker, W. Uhl and H.-J. Wessely, *Z. Anorg. Allg. Chem.* **479**, 41 (1981); (b) G. Becker, A. Münch and H.-J. Wessely, *Z. Naturforsch.* **36b**, 1080 (1981).
49. K. Issleib and R. Vollmer, *Z. Anorg. Allg. Chem.* **481**, 22 (1981).
50. Th. C. Klebach, R. Lourens and F. Bickelhaupt, *J. Amer. Chem. Soc.* **100**, 4886 (1978).
51. F. Bickelhaupt, private communication.
52. G. Becker, M. Birkhahn, W. Massa, O. Mundt, W. Uhl and C. Witthauer, to be published.
53. G. Becker and W. Becker, unpublished results.
54. H. Oehme, E. Leissring and H. Meyer, *Tetrahedron Lett.* **21**, 1141 (1980); cf. *Z. Chem.* **21**, 407 (1981).
55. K. Issleib, H. Schmidt and H. Meyer, *J. Organomet. Chem.* **160**, 47 (1978).
56. R. Appel, H. Förster, B. Laubach, F. Knoll and I. Ruppert, *Angew. Chem.* **94**, 460 (1982); and previous publications.
57. K. Issleib, H. Schmidt and H. Meyer, *J. Organomet. Chem.* **192**, 33 (1980).
58. A. Schmidpeter, W. Gebler, F. Zwaschka and W. S. Sheldrick, *Angew. Chem.* **92**, 767 (1980).
59. G. Becker and O. Mundt, *Z. Anorg. Allg. Chem.* **459**, 87 (1979).
60. T. E. Gier, *J. Amer. Chem. Soc.* **83**, 1769 (1961).
61. M. J. Hopkinson, H. W. Kroto, J. F. Nixon and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.* 513 (1976); J. C. T. R. Burckett-St. Laurent, H. W. Kroto, J. F. Nixon and K. Ohno, *J. Mol. Spectrosc.* **92**, 158 (1982); and previous publications.

62. R. Appel, G. Maier, H. P. Reisenauer and A. Westerhaus, *Angew. Chem.* **93**, 215 (1981).
63. R. Appel and A. Westerhaus, *Tetrahedron Lett.* **22**, 2159 (1981).
64. B. Solouki, H. Bock, R. Appel, A. Westerhaus, G. Becker and G. Uhl, *Chem. Ber.*, **115**, 3747 (1982).
65. G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch.* **36b**, 16 (1981).
66. H. Oberhammer, G. Becker and G. Gresser, *J. Mol. Struct.* **75**, 283 (1981).
67. J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto and J. F. Nixon, *J. Chem. Soc., Chem. Commun.* **1981**, 1141; cf. J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, M. F. Meidine and J. F. Nixon, *J. Organomet. Chem.* **238**, C82 (1982).
68. U. Weiher, K. Dehnicke and D. Fenske, *Z. Anorg. Allg. Chem.* **457**, 105 (1979).
69. G. Uhl, E. Hey, G. Becker, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, in press.