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λ^3-Phosphinocarbenes λ^5-phosphaacetylenes

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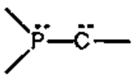
ABSTRACT

The title compounds were the first representatives of stable compounds having properties approaching those of real carbenes. Theoretical as well as spectroscopic studies suggest a multiply bonded formulation and a singlet ground state. The dual nature of the phosphinocarbenes (carbene and phosphorus–carbon multiple bond) is demonstrated by their chemical reactivity. All presently available data concerning the title compounds are reported.

1. INTRODUCTION

In the literature, two definitions for carbenes can be found: (i) "Carbenes are divalent carbon compounds with two non-bonding electrons on one carbon atom" [1]; (ii) "carbenes are two-coordinate carbon compounds that have two non-bonding electrons and no formal charge on the carbon" [2]. Stable compounds featuring monocoordinated carbon with oxidation state II are well exemplified by carbon monoxide and isonitriles. In contrast, the challenge of preparing compounds having properties approaching those of real carbenes, consistent with the criteria of the second definition, has only recently been met. The first representative type of stable carbenes **A** is the subject of this review, the second type being the imidazol-2-ylidenes **B** reported by Arduengo et al. [2,3]. Both compounds have subtle electronic structures and the reason for their stability, apparent from their long lifetimes (weeks to years at room temperature), is not evident: this is a combination of electronic and steric effects.

A



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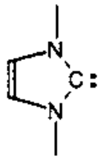
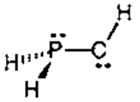


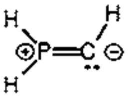
Returning to the definition of carbenes, a two-coordinate carbon is a true carbene if the valence at the carbon is genuinely two. Problems arise in determining the valence of the carbon if the substituents are capable of non-traditional bonding. If the ligating atoms belong to the first or second period, the problem is usually simple. As examples, F_2C: is a pure carbene [4], while the carbon atom of nitrile oxide is much better described as a triply bonded carbon than as a carbene substituted by a nitroso group [5]. If the ligand atoms are from the third period or higher, there is the possibility of the ligand having more bonds than expected from the normal Lewis counting rules. Seppelt compounds (F_3C–C–SF_3 [6a–c] and F_5S–C–SF_3 [6d]) and phosphinocarbenes belong to this category. For this reason, several theoretical studies have been carried out for the phosphinocarbenes, and we first summarize the conclusions of the calculations. Then, the synthesis of stable and transient phosphinocarbenes is presented. In section 4, the spectroscopic data are discussed, as well as the results of the only known X-ray analysis. The intramolecular and intermolecular reactivity of neutral and cationic phosphinocarbenes is the subject of the last part of this review.

2. THEORETICAL STUDIES

The first study by Hegarty and co-workers [7] examined the singlet and triplet structural isomers of CH_3P. For the singlets, the calculations predicted a number of stationary points on the potential energy surface including local minima for phosphinocarbene $H_2P–CH$, phosphaethylene $HP{=}CH_2$, and methylenephosphinidene $CH_3–P$, plus saddle points connecting these isomers. At the MP4SDQ/6-31++G*//HF/3-3-21G* level plus zero point energy contributions, the most stable form is the phosphaethene $HP{=}CH_2$, lying 43 and 60 kcal mol^{-1} below singlet methylphosphinidene and phosphinocarbene respectively. Of particular interest for our purpose, this paper concluded that for H_2PCH, the phosphorus vinyl ylide form **II** is the most stable structure. Its geometric parameters are given in Fig. 1. The phosphinocarbene with a pyramidal phosphorus centre **I** is neither a minimum nor a saddle point but the result of inversion of the phosphorus centre with an energy barrier of only 4 kcal mol^{-1}. The λ^5-phosphaacetylene structure **III** is the transition structure corresponding to the inversion at carbon with an energy barrier of 10.3 kcal mol^{-1}.



I



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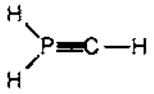


III

For the triplet states, the methylphosphinidene is the most stable isomer lying 30 and 53 kcal mol^{-1} below phosphaethylene and phosphinocarbene respectively. The optimized geometry of triplet phosphinocarbene is summarized in Fig. 1. It can be noted that these calculations predicted a triplet–singlet separation in H_2PCH of only 3 kcal mol^{-1} in favour of the singlet state. The recently formulated multiconfiguration-based unitary coupled electron pair approximation (UCEPA) has been used to study the parent phosphinocarbene [8]. The singlet was predicted to be planar, while the triplet was calculated to be non-planar with C_s symmetry (Fig. 1). The results of this study corroborate Hegarty's prediction [7] that the singlet is more stable than the triplet, but favour a somewhat larger gap (10 kcal mol^{-1}).

A third study [9] examined the role of silicon substitution at carbon (SiH_3) and of amino groups at phosphorus. Both singlet and triplet structures were considered. For the singlet state, the presence of an additional heteroelement at carbon with empty d-orbitals results in a larger angle at carbon with a slightly shortened C–Si bond. Replacement of the hydrogens by amino groups at phosphorus led to a shortening of the P–C and C–Si bonds, and the P–C–Si angle becomes almost linear. Thus, the structure of the singlet is essentially that expected for a λ^5-phosphaacetylene (Fig. 1). At the PMP-4 level, the singlet states of H_2PCSiH_3 and $(NH_2)_2PCSiH_3$ are 5.6 and 13.9 kcal mol^{-1} respectively, below the triplet, which presents a long P–C bond and a pyramidal phosphorus centre (Fig. 1).

The most recent study by Ahlrichs and co-workers [10] deals with diphosphino and (phosphino)(phosphonio)carbenes with amino or even diisopropylamino groups at phosphorus. These SCF and MP2 calculations were performed with the program system Turbomole [11]. The symmetric bis[(diamino)phosphino]carbene with two short P–C single bonds (1.719 Å) and a P–C–P bond angle of 131.4°, which is in line with a singlet carbene, represents only a saddle point of the energy hypersurface. Removing the symmetry restrictions leads to a minimum structure of C_1 symmetry, with a short (1.533 Å) and a long (1.765 Å) P–C bond, and a large P–C–P angle 160.5° (Fig. 1). The atomic charges indicate that the short bond is a strong double bond plus Coulomb attractions, while an inspection of the MOs revealed a slight delocalization of the carbon lone pair into the low-lying orbitals of the two phosphorus atoms. The "distortion" from the symmetrical structure can be viewed as a second-order Jahn–Teller effect.

The (phosphino)(phosphonio)carbene was studied for both the amino and the diisopropylamino derivatives with similar results. At the SCF level, one P–C bond is short (1.531 Å) with a planar phosphorus atom, the other P–C bond is long (1.674 Å), and the P–C–P angle is large (162°). However, at the MP2 level, structural optimization affords a much smaller bond angle of 135.7°, while the bond lengths have not been significantly lengthened (0.02–0.04 Å) (Fig. 1). As for the (phosphino)(silyl)carbene and the bis(phosphino)carbene, there is a degree of "back donation" of the carbene lone pair into low lying phosphorus orbitals.

In summary, all calculations done so far predict that phosphinocarbenes present a planar phosphorus atom and a short P–C distance with high atomic charges, and thus are best regarded as phosphorus–vinyl ylides.

3. SYNTHESIS

Two types of precursor have been used for the generation of phosphinocarbenes, namely P-halogenomethylenephosphoranes and α-diazophosphines. However, stable carbenes have only been obtained starting from diazo derivatives.

3.1. α,β-Elimination from P-halogenomethylene phosphoranes

In 1981, Appel postulated the transient formation of (diphenylphosphino)(trimethylsilyl)carbene **2** to explain the formation of phosphaalkene **3**, in the thermolysis

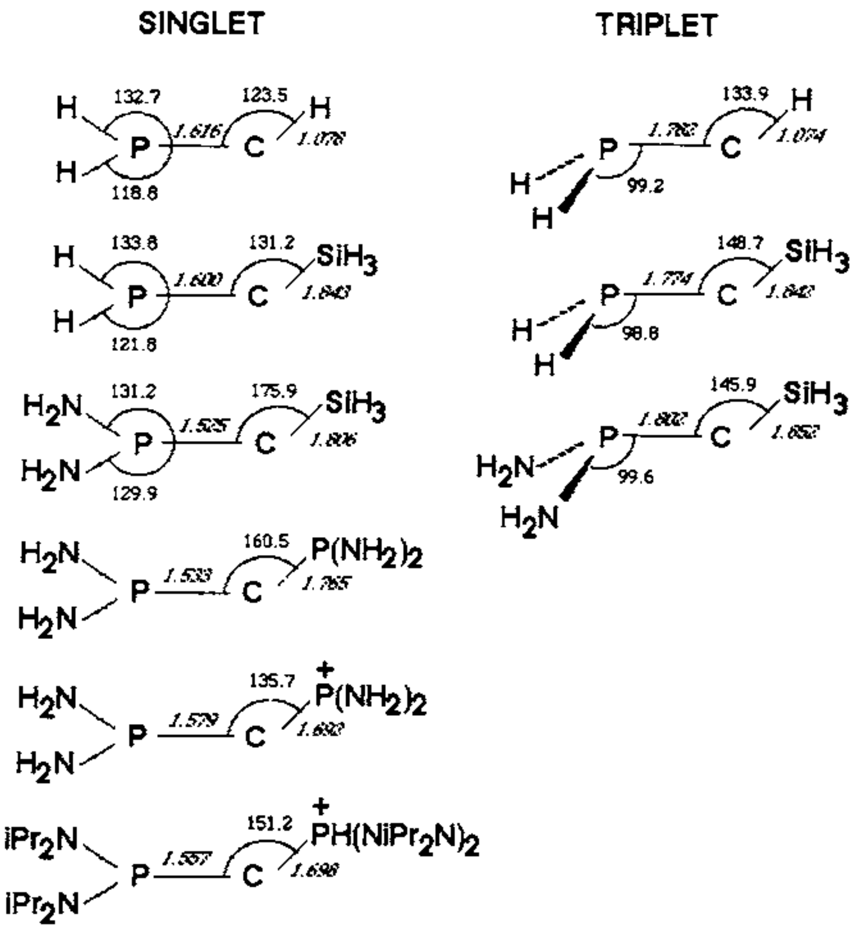
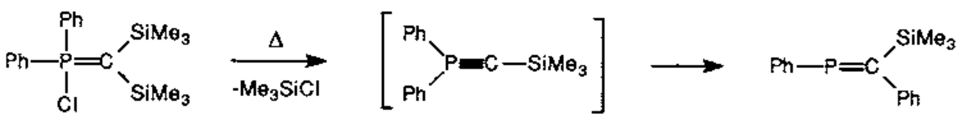


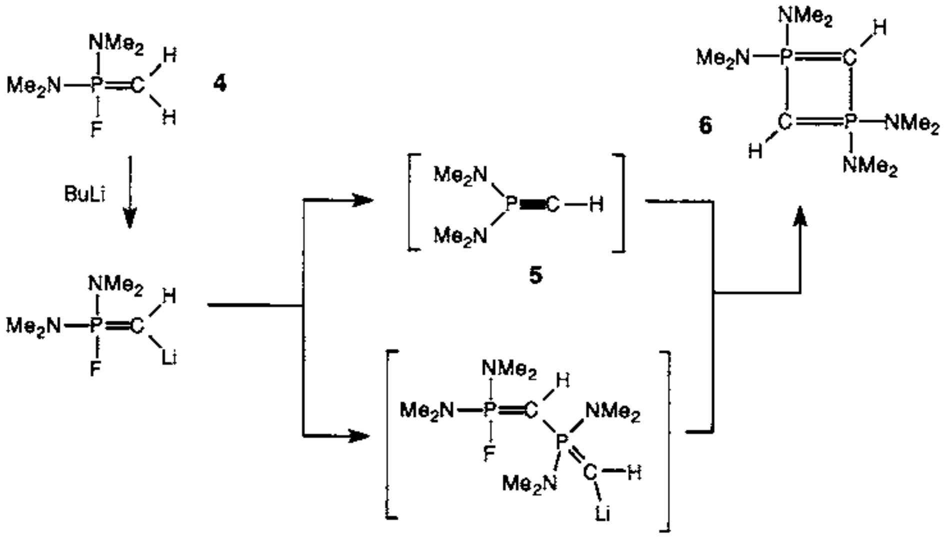
Fig. 1. Calculated geometric parameters for singlet and triplet phosphinocarbenes [7–10].

of P-chloromethylenephosphorane **1** [12]. Note that at that time, the authors did not recognize the carbene character of **2**, and simply named the intermediate λ^5-



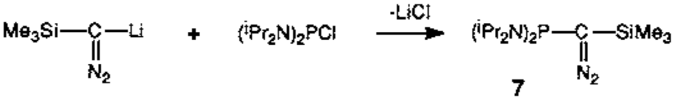
1 **2** **3**

phosphaalkyne. In 1985, Fluck and co-workers reported that treatment of methylenebis(dimethylamino)fluorophosphorane **4** with two equivalents of butyllithium at −95°C gave 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete **6** in 33.9% yield [13]. The formation of this four-membered ring could result from 2+2 head-to-tail dimerization of transient λ^5-phosphaalkyne **5**. However, an alternative mechanism, with intramolecular LiF elimination is also possible, and does not involve the transient formation of **5**.



3.2. *Nitrogen-elimination from α-diazophosphines*

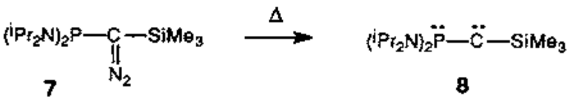
In contrast to diazo λ^5-phosphorus derivatives, which have been known for a long time [14], the synthesis of the first α-diazophosphine was reported in 1985 [15]. This compound, namely the [bis(diisopropylamino)phosphino](trimethylsilyl)-diazomethane **7**, was obtained by treatment of the lithium salt of trimethylsilyldiazomethane with a stoichiometric amount of bis(diisopropylamino)chlorophosphine.



$$\mathrm{Me_3Si{-}}\underset{\underset{\textstyle N_2}{\|}}{\mathrm{C}}\mathrm{{-}Li} + (^i\mathrm{Pr_2N})_2\mathrm{PCl} \xrightarrow{-\mathrm{LiCl}} (^i\mathrm{Pr_2N})_2\mathrm{P{-}}\underset{\underset{\textstyle N_2}{\|}}{\mathrm{C}}\mathrm{{-}SiMe_3}$$

7

We first recognized that photolysis of **7**, in the presence of a variety of trapping agents, led to products resulting from the transient formation of phosphaacetylene **8** [15]. It was only in 1988 that we discovered that flash thermolysis of **7** at 250°C under vacuum afforded the desired species **8** in 80% yield. Compound **8** is a red oily material, stable for several weeks at room temperature in benzene solution, which can be purified by quick distillation (bp 75–80°C under 10^{-2} mmHg) [16]. It should

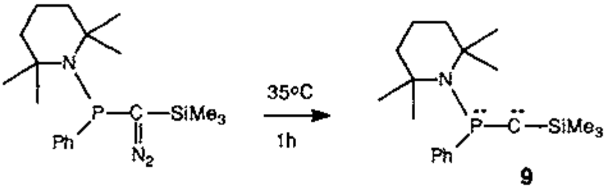


$$(^i\mathrm{Pr_2N})_2\mathrm{P{-}}\underset{\underset{\textstyle N_2}{\|}}{\mathrm{C}}\mathrm{{-}SiMe_3} \xrightarrow{\Delta} (^i\mathrm{Pr_2N})_2\ddot{\mathrm{P}}\mathrm{{-}}\ddot{\mathrm{C}}\mathrm{{-}SiMe_3}$$

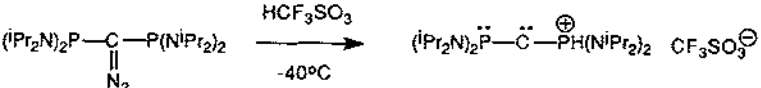
7 **8**

be noted that the synthesis of **8** is not trivial. The experimental conditions used are drastic (250°C under vacuum), and the utilizable range for the thermolysis is very narrow. Below 240°C compound **7** is not decomposed, and above 260°C the carbene inserts into a CH bond of a diisopropylamino substituent. Under photolytic conditions, the diazo derivative **7** led to the carbene **8** in very poor yield (less than 10%), along with CH insertion products.

Since that time, a number of transient λ^5-phosphaacetylenes bearing various substituents at phosphorus and carbon have been synthesized by thermolysis or photolysis of α-diazophosphines. Their reactivity is presented in Section 5. However, only a few stable phosphanylcarbenes are known, and the influence of the substituents on their stability merits comment. All stable phosphinocarbenes feature two amino groups at phosphorus and a trimethylsilyl group at carbon with only two exceptions: (i) the [2,2,6,6-tetramethylpiperidino)(phenyl)phosphino](trimethylsilyl)carbene **9** [17], which is stable for 1 day in solution at room temperature, but for weeks at −20°C; (ii) the [bis(diisopropylamino)phosphino][bis(diisopropylamino)-phosphonio]carbene **10** [18] which is stable for years in the solid state.



9



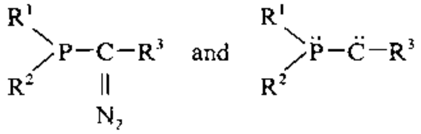
$(^iPr_2N)_2P{-}C(=N_2){-}P(N^iPr_2)_2 \xrightarrow[-40°C]{HCF_3SO_3} (^iPr_2N)_2\ddot{P}{-}\ddot{C}{-}\overset{\oplus}{P}H(N^iPr_2)_2\ CF_3SO_3^{\ominus}$

10

The stabilizing effects of amino groups at phosphorus and a silyl group at carbon can be rationalized taking into account the vinyl ylide structure predicted by calculations (Section 2). In other words, the positive charge at phosphorus and the negative charge at carbon are delocalized into the amino and silyl groups respectively. Since silyl and phosphonio groups are isoelectronic, the stability of **10** is not surprising. Of course, bulky substituents also stabilize the carbenes, but interestingly, during the course of our study, we realized that the stability of the carbenes is often inversely proportional to the stability of the starting diazo compounds [17], as illustrated in Table 1. Lastly, it should be mentioned that the [bis(cyclohexylamino)phosphino](trimethyl-silyl)carbene [19] is the only stable phosphinocarbene cleanly accessible by photolysis.

TABLE 1

Stability of the carbenes and of the diazo precursors



R^1	R^2	R^3	Diazo stability	Carbene stability
Pr^i_2N	Pr^i_2N	$\mathrm{SiMe_3}$	bp 85–90°C, 10^{-2} mmHg	bp 75–80°C, 10^{-2} mmHg, stable several weeks at 25°C
Tmp	Pr^i_2N	$\mathrm{SiMe_3}$	Few minutes at 25°C	Several weeks at 25°C
Tmp	$\mathrm{Me_2N}$	SiPr^i_3	Several days at 25°C, 1 h at 35°C	Several weeks at 25°C
Tmp	$\mathrm{Me_2N}$	$\mathrm{SiMe_3}$	Several days at 25°C, 1 h at 35°C	Several weeks at 25°C
Tmp	Ph	$\mathrm{SiMe_3}$	Few minutes at 25°C	Few hours at 25°C
c-$\mathrm{Hex_2N}$	c-$\mathrm{Hex_2N}$	$\mathrm{SiMe_3}$	Stable 24 h at 70°C	Several weeks at 25°C
Pr^i_2N	Pr^i_2N	$\mathrm{PR_2H}^{+}$[a]	Not observed at 25°C	Indefinitely at 25°C

[a] R = Pr^i_2N.

4. SPECTROSCOPIC DATA AND X-RAY ANALYSIS

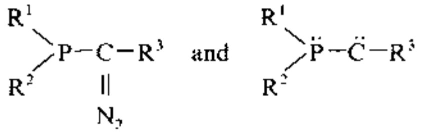
In solution, multinuclear NMR spectroscopy is by far the most informative technique to analyse the structure and bonding of phosphinocarbenes. In fact, before the synthesis and single-crystal X-ray analysis of the (phosphino)(phosphonio)carbene **10**, NMR spectroscopic data represented the only evidence for the formation of carbenes.

4.1. NMR spectroscopy

Table 2 lists all of the pertinent chemical shifts and coupling constants for the (phosphino)(silyl)carbenes and their respective diazo precursors. These carbenes are all characterized by high field chemical shifts for phosphorus (−24 to −40 ppm) and silicon (−3 to −21 ppm), and low field chemical shifts for carbon (120 to 143 ppm) with large couplings to phosphorus. What do these numbers mean? Classical shielding arguments would indicate an electron-rich phosphorus atom, or equally an increase in coordination number. The silicon atom would also be electron rich and the carbon has a chemical shift in the range expected for a multiply bonded species. This leads to a problem, as little is known about the effects of a carbene centre on chemical shifts. The cyclic imidazole carbenes of Arduengo have chemical shifts in the range of 210 ppm [2,3], but we still do not have a database for comparison. In addition, the coupling constant data are difficult to rationalize, as

TABLE 2

Pertinent chemical shifts and coupling constants for the phosphanylcarbenes and their diazo precursors



R^1	R^2	R^3	Diazo	Carbene		
			$\delta^{31}P$	$\delta^{31}P$	$\delta^{13}C$ $(J_{PC})^a$	$\delta^{29}Si$ $(J_{PSi})^a$
Pr^i_2N	Pr^i_2N	$SiMe_3$	+56.1	−40.0	142.7 (159)	−19.7 (59)
Tmp	Pr^i_2N	$SiMe_3$	+88.0	−49.7	145.5 (203)	−21.3 (70)
Tmp	Me_2N	$SiMe_3$	+83.8	−24.1	133.5 (147)	−13.2 (52)
Tmp	Me_2N	$SiPr^i_3$	+88.7	−27.8	120.7 (181)	−2.8 (47)
Tmp	Ph	$SiMe_3$	+25.0	−38.1	136.9 (147)	−17.0 (27)
c-Hex_2N	c-Hex_2N	$SiMe_3$	+58.0	−31.4	139.3 (160)	−19.7 (59)
Pr^i_2N	Pr^i_2N	$PR_2H^{+\,b}$	–[c]	+27.1	+98.9 (157)	–[d]

[a]Coupling constants in hertz; [b]$R = Pr^i_2N$; [c]not observed; [d]$J_{PP} = 120.8$ Hz.

we cannot predict the influence of orbital, spin–dipolar, Fermi contact, nor higher order quantum mechanical contributions on the magnitude of the coupling constants. Let us say that from the NMR data, classical interpretation indicates that these compounds have multiple bond character.

Replacement of the trimethylsilyl group by an isoelectronic phosphonio substituent produces a carbene with similar NMR spectroscopic characteristics (Table 2). Of particular interest are the coupling constant data. These values are almost identical and a quick comparison of the reduced $^2K_{PP}$ and $^2K_{PSi}$ coupling constants indicate that these values are also similar. The isopropylamino groups are equivalent on the NMR time-scale for the σ^3-phosphorus centres of both compounds, which is unusual. Thus the similarity of these two carbenes in solution is evident.

4.2. Solid state structure

The great advantage of the (phosphino)(phosphonio)carbene **10** over the silyl derivatives is that it can be crystallized, and since we have seen that these two types

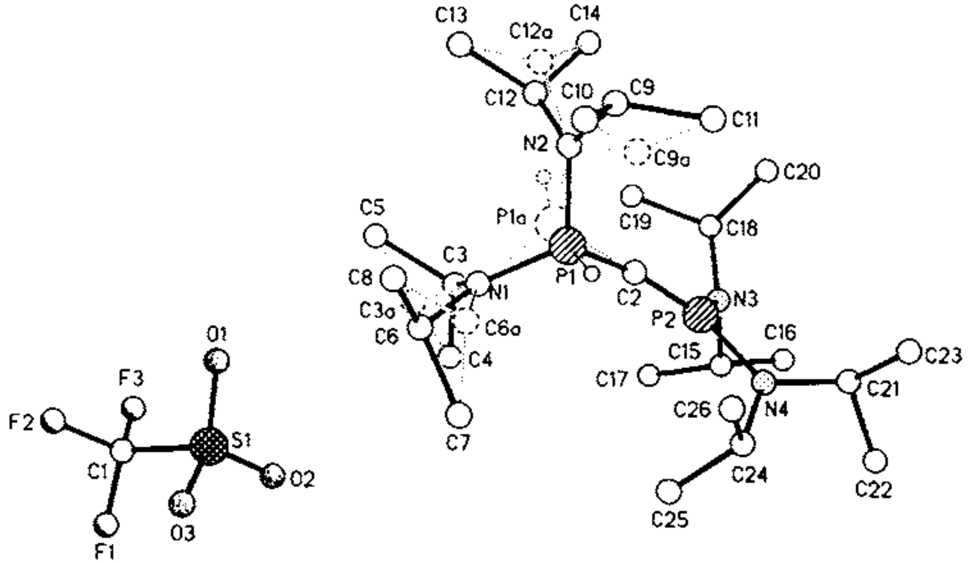
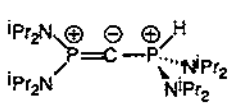


Fig. 2. Stick and ball view of **10**. Selected bond distances (Å) and angles (deg) are as follows: P(1)–N(1) 1.635(4), P(1)–N(2) 1.641(4), P(1A)–N(1) 1.622(5), P(1A)–N(2) 1.638(5), P(1)–C(2) 1.605(5), P(1A)–C(2) 1.616(5), P(2)–C(2) 1.548(4), P(2)–N(3) 1.632(3), P(2)–N(4) 1.635(3); P(1)–C(2)–P(2) 165.1(4), P(1A)–C(2)–P(2) 164.1(4), C(2)–P(2)–N(3) 126.3(2), C(2)–P(2)–N(4) 126.7(2), N(3)–P(2)–N(4) 107.0(2). The minor parts of the disordered cation are shown by dotted atoms.

of phosphinocarbene are very similar, the conclusions of the X-ray analysis of **10** [18] can probably be extended to the silylcarbenes. A ball and stick view of the molecule is shown in Fig. 2, and the pertinent geometric parameters are given in the legend. No interaction with the trifluoromethanesulphonate ion is observed, confirming the ionic character of **10**. The P(2)–C(2) bond length (1.548(4) Å) is in the range expected for a phosphorus–carbon triple bond [20], the P(2) atom is planar, and the value of the P(1)–C(2)–P(2) angle rather large (165.1(4)–164.1(4)°), thus a carbene structure can be ruled out [21]. Because of a disorder of the phosphonio moiety (sof = 0.62(1)), the values of the P(1)–C(2) and P(1a)–C(2) bond lengths (1.605(5) and 1.615(5) may not be accurate. A riding model [22] allowed us to estimate the lower and upper limits of these bond lengths, 1.607 and 1.709 Å respectively. The computed bond distances [10] (Section 2) favour strongly the upper limit of the experimental result. In any case, the P(1)–C(2) bond length is much too short for a phosphorus–carbon single bond, and is more in the range observed for phosphorus ylids [23]. Thus, compound **10** is best described by structure **10a**.



10a

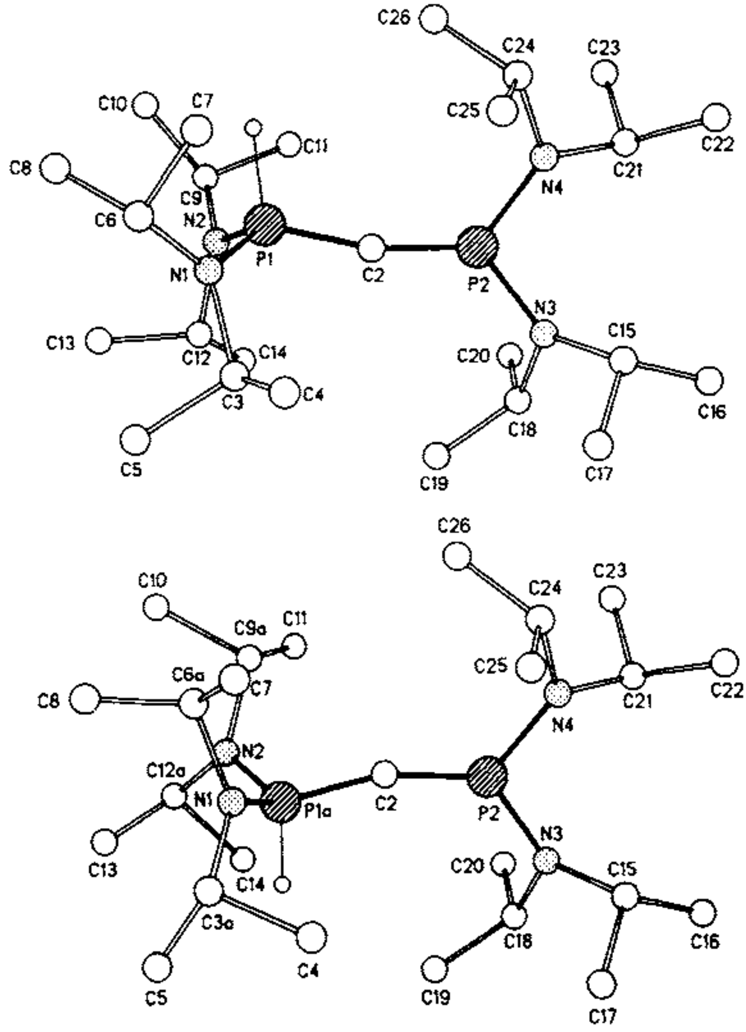


Fig. 3. Stick and ball view of the two units of **10**.

Although it is not clear whether this is a dynamic or static disorder, it is clear from Fig. 3 that the two units result from an inversion at the central carbon, followed by a 180° rotation around the P(1)–C(2) bond. The observation that this carbene has difficulty in maintaining one discrete form in the solid state could well be in line with the low value of the inversion barrier at carbon calculated by Hegarty and co-workers [7] (see Section 2).

5. REACTIVITY

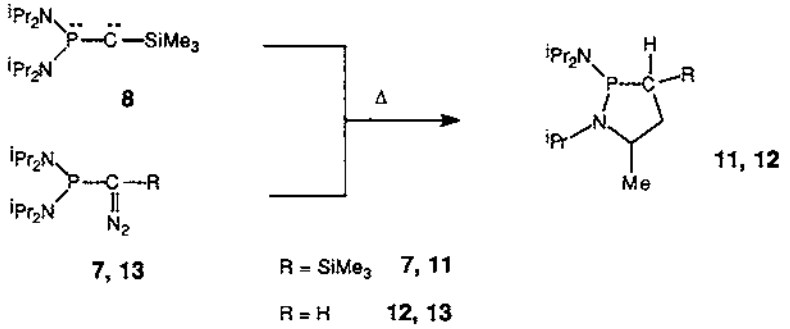
Since the reactivity of (phosphino)(silyl)carbenes is somewhat different from that of the (phosphino)(phosphonio)carbene **10**, they will be presented separately.

5.1. Reactivity of (phosphino)(silyl)carbenes

5.1.1. Intramolecular reactivity

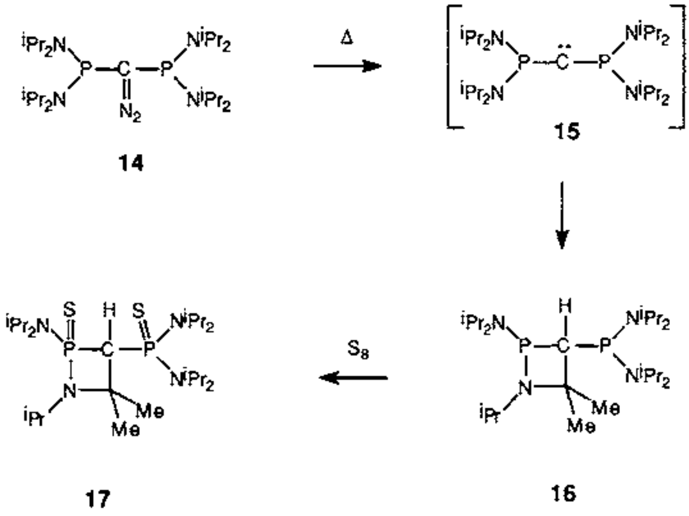
Except for the CH insertion reaction involving the [bis(diisopropylamino)phosphino](trimethylsilyl)carbene **8**, all the reactions presented in this section involved transient carbenes.

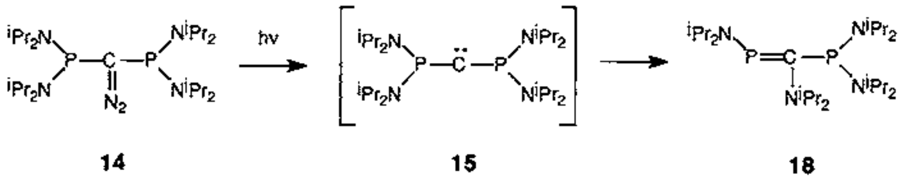
5.1.1.1. CH insertions. The first example of carbon–hydrogen bond insertion of a phosphinocarbene was observed in the thermolysis of P-[bis(diisopropylamino)]-C-(trimethylsilyl)phosphinocarbene **8**, or of its diazo precursor **7**, at 300°C under vacuum [16]. Indeed, the four resulting five-membered ring diastereoisomers **11** (90% total yield) clearly result from the insertion of the carbene into a primary CH bond of an isopropyl substituent. In a similar way, heterocycle **12** was obtained as a 70/30 mixture of two diastereoisomers in 60% yield, from the thermolysis of bis(diisopropylamino)phosphinodiazomethane **13** [16].



In marked contrast, heating bis[bis(diisopropylamino)phosphino]diazomethane **14** [24] in refluxing toluene affords the four-membered ring **16** as a single diastereoisomer in 92% yield. The structure of **16** has been confirmed by an X-ray analysis of the product **17** obtained after treatment with elemental sulphur [25]. The difference in the regioselectivity and stereoselectivity observed in the case of **11**, **12** and **16** has not been explained so far.

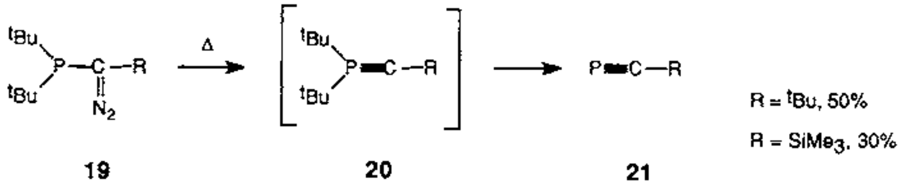
5.1.1.2. 1,2-Migrations of a phosphorus substituent. To date, only two examples of a 1,2 shift possibly involving a phosphinocarbene have been reported. This very usual behaviour for "normal" carbenes has been observed in the thermolysis of P-halogenomethylene phosphorane **1**, as already mentioned (Section 3.1) [12], and in the photolysis of bis(phosphino)diazomethane **14** at 300 nm, affording phosphaalkene **18** [26]. Note, that ab initio calculations predict that the parent phosphinocarbene H_2PCH lies 60 kcal mol^{-1} above the isomeric phosphaalkene, while the energy barrier for the 1,2 shift is only 18 kcal mol^{-1} [7]. In the case of the bis(phosphino)car-





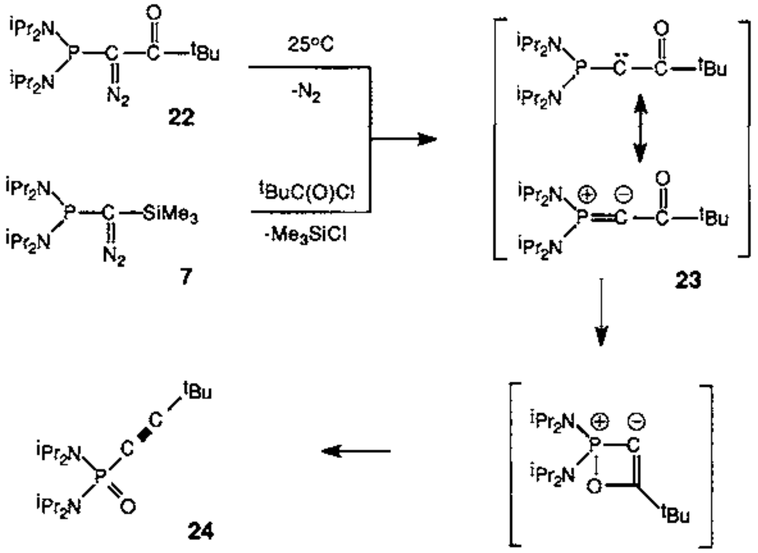
bene substituted by NH_2 groups, the phosphaalkene would be 53 kcal mol^{-1} more stable [10].

5.1.1.3. Fragmentations. Two examples of fragmentation of λ^5-phosphaacetylenes **20** into λ^3-phosphaalkynes **21** have been reported in the flash vacuum pyrolysis (300°C under 10^{-4} mmHg) of (di*tert*-butylphosphino)(*tert*-butyl)- and (trimethylsilyl)-diazomethanes **19**; the two *tert*-butyl groups are eliminated in the form of 2-methylpropene and hydrogen [27].

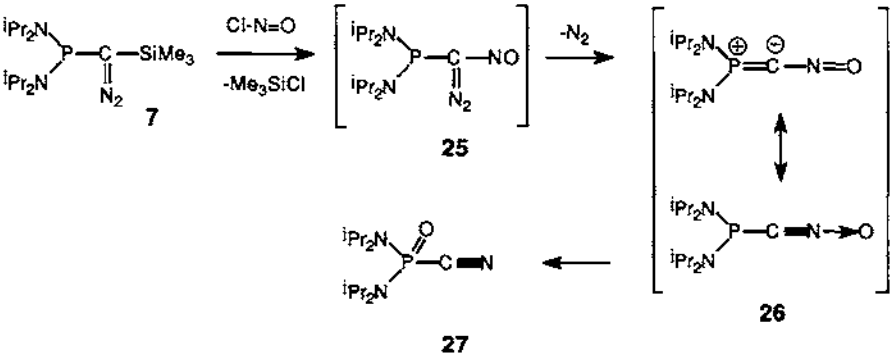


5.1.1.4. Reactions with carbonyl groups. The formation of phosphoranyl alkyne **24**, obtained by spontaneous decomposition at room temperature of phosphinodiazoketone **22**, or by heating [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane **7** with trimethylacetyl chloride, has been explained in terms of an intramolecular

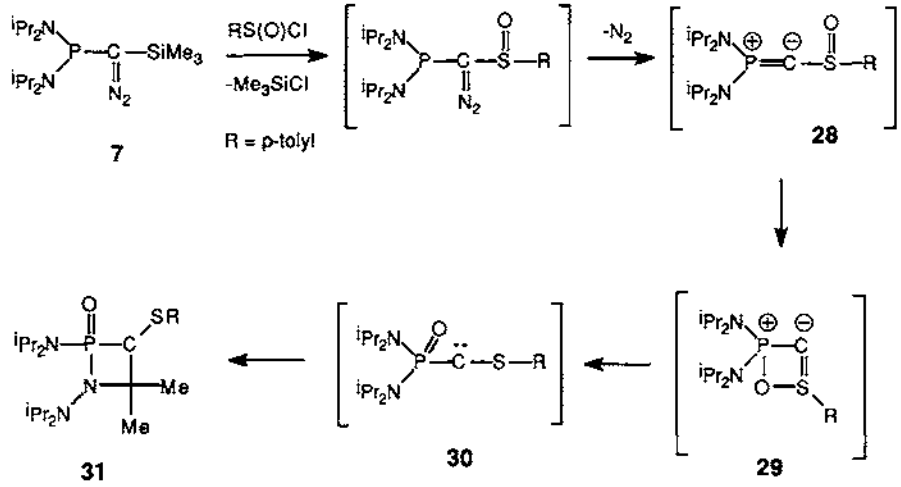
Wittig-type reaction involving the phosphorus-vinyl-ylide form of phosphinocarbene **23** [26].



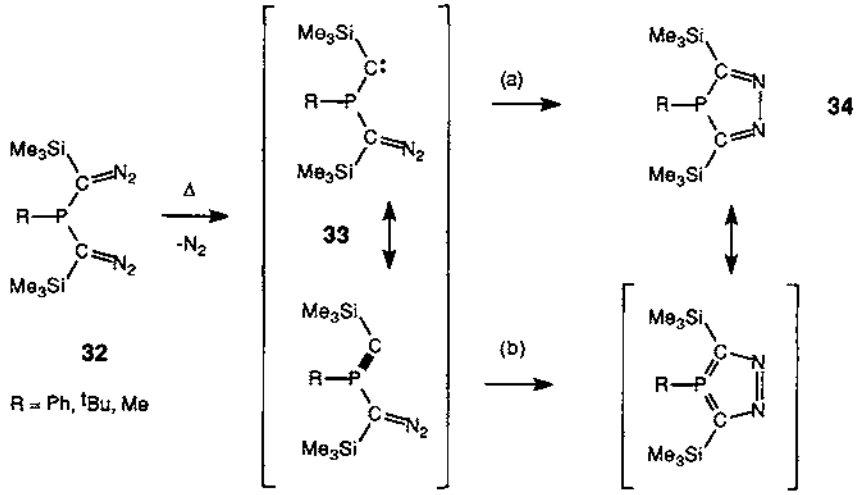
5.1.1.5. Reactions with nitroxides. An exchange reaction occurs when nitrosylchloride is reacted with (phosphino)(trimethylsilyl)diazomethane **7**, giving a transient α-nitroso α-phosphinodiazo derivative **25** and chlorotrimethylsilane. Spontaneous loss of N_2 leads to C-nitroso phosphinocarbene (formulated as a zwitterion), which can also be considered as a λ^3-phosphinonitrile oxide **26**. Rearrangement, via a formal 1–3 oxygen shift, or a Wittig-type reaction, affords the corresponding phosphoranyl nitrile **27** in 75% isolated yield [28].



5.1.1.6. Reactions with sulphoxides. Elimination of trimethylchlorosilane and nitrogen also occurs when [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane **7** is reacted with paratolylsulphinylchloride at low temperature, and the four-membered heterocycle **31** is obtained in 87% yield. A multiple-step mechanism involving a 2+2 cycloaddition of the phosphorus–carbon multiple bond of the (phosphino)(sulphinyl)carbene **28** with the sulphoxide, followed by ring opening of **29**, and insertion of the (phosphoryl)(sulphenyl)carbene **30** into a carbon–hydrogen bond of a diisopropylamino group, well rationalized the formation of **31** [29].



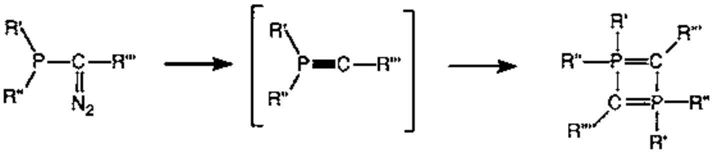
5.1.1.7. Reactions with diazo groups. The formation of diazaphospholes **34**, in the thermolysis of bis(diazomethyl)phosphines **32**, can be explained either by a diazo-carbene coupling reaction (route (a)) or by a 2+3 cycloaddition process involving the PC multiple-bond character of phosphinocarbene **33** (route (b)) [30].



5.1.2. Intermolecular reactivity

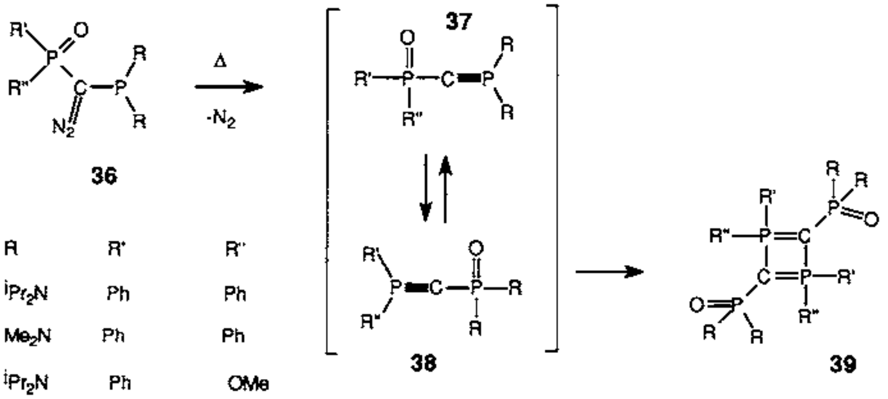
It would be difficult to classify the reactions of phosphinocarbenes into 1,1- and 1,2-additions, or 1+2-, 2+2- and 2+3-cycloadditions, as several mechanisms can be postulated to explain the nature of the products, and also because very similar reagents can give totally different products. Thus, the results are presented systematically.

5.1.2.1. Dimerization. No evidence for the dimerization of stable phosphinocarbenes has yet been reported. However, several examples of head to tail dimerization have been observed involving the multiple bond character of transient phosphinocarbenes, leading to the corresponding $1\lambda^5,3\lambda^5$-diphosphetes **35** [31,32]. $1\lambda^5,3\lambda^5$-diphosphetes **39** have also been obtained in the thermolysis of (phosphino)(phosphoranyl)diazomethanes **36** [32]. However, **39** does not come from the dimerization of the primary generated phosphinocarbenes **37**, but from the isomers **38**, resulting from a 1–3 oxygen shift from phosphorus to phosphorus. These results suggest a possible equilibrium between the two isomeric (phosphino)(phosphoranyl)carbenes **37** and **38**, dimerization occurring for the less sterically hindered isomer. Note that, in contrast



35

R'	R''	R'''
Me_2N	Me_2N	Me_3Si
Ph	Ph	$Ph_2(O)P$
Ph	Ph	$(4\text{-}MeC_6H_4)_2(O)P$

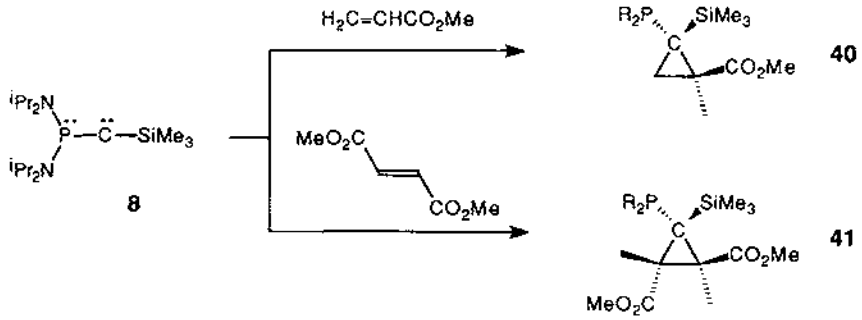


36 **37** **38** **39**

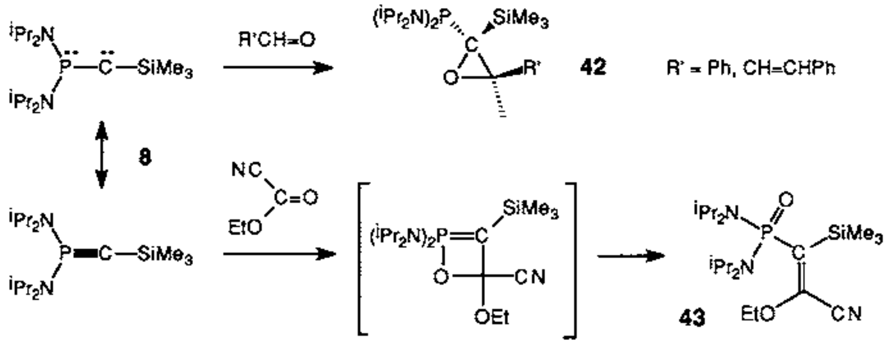
R	R'	R''
$^iPr_2N$	Ph	Ph
Me_2N	Ph	Ph
$^iPr_2N$	Ph	OMe

to the Seppelt compound (F_3S–C–CF_3) [6], no evidence for a carbene–carbene coupling reaction, leading to olefins, has been reported for phosphinocarbenes.

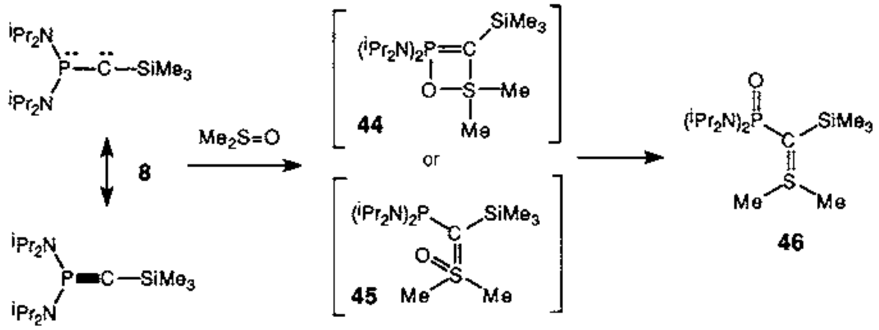
5.1.2.2. Reactions with alkenes. The stable (phosphino)(silyl)carbene **8** is inert towards alkyl-substituted alkenes (nucleophilic carbenes such as dimethoxy carbene do not react with alkyl-substituted olefins) [33] but was found to react, at room temperature, with electron-poor olefins via a 1+2 cycloaddition process clearly involving its nucleophilic carbene character [34]. Cyclopropanes **40** and **41** were obtained in near quantitative yields using methylacrylate and dimethylfumarate respectively. Only one diastereomer was observed in each case. The NMR spectroscopic data for the cyclopropenes suggest a syn attack of the carbene [35] with retention of the stereochemistry of the double bond. However, this could not be proved since no reaction occurred with dimethylmaleate (the difference in reactivity between cis- and trans-olefins towards carbenes has already been noted by Moss et al. [36]).



5.1.2.3. Reactions with carbonyl groups. Electrophilic carbenes are known to react with carbonyl groups through the oxygen lone pair to give carbonyl ylides (R_2C=O–CX_2) [37]. These 1,3-dipolar species are usually characterized by [3+2] cycloaddition or can even be isolated [38]. A small amount of the corresponding oxiranes is sometimes obtained [37a,39]. Although (phosphino)(silyl)carbene **8** does not react with simple ketones, quantitative and stereospecific 2+1 cycloaddition reactions occur at room temperature with benzaldehyde and *trans*-cinnamaldehyde giving rise to the corresponding epoxides **42** [34]. In marked contrast, when a very electron-poor carbonyl group such as in ethylcyanoformate is used, a 2+2 cycloaddition process takes place giving a mixture of *Z* and *E* phosphoranylalkenes **43** and no trace of the corresponding oxirane is detected. These results are in agreement with extended Hückel calculations which show that the HOMO(carbene)–LUMO(CO) separation is decreased by 1 eV on going from aldehyde to cyanoaldehyde, favouring a charge-controlled process rather than a fully concerted mechanism.

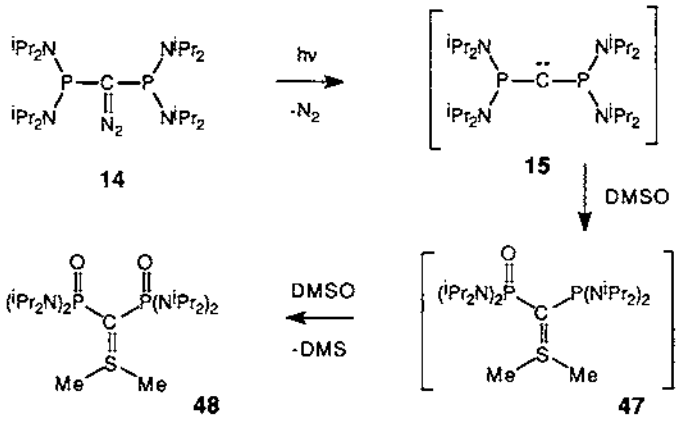


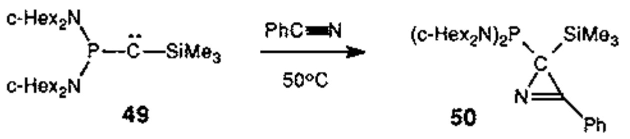
5.1.2.4. Reactions with sulphoxides. Dimethylsulphoxide reacts with phosphinocarbene **8** affording the phosphorylated sulphur ylide **46** in 95% yield. This compound formally results from a 2+2 cycloaddition followed by ring opening of the resulting four-membered cyclic phosphorus ylide **44**. However, a 1+1 addition of the carbene form to the sulphur giving **45**, followed by an oxygen shift from sulphur to phosphorus, cannot be ruled out [16]. In a similar way, transient bis[bis(diisopropylamino)phosphino]carbene **15**, generated by photolysis of the corresponding diazo derivative **14**, reacts with dimethylsulphoxide leading to the (phosphino)(phosphoranyl)sulphur ylide **47**, which is readily oxidized to the corresponding bis(phosphoranyl)sulphur ylide **48** by excess sulphoxide [26].



5.1.2.5. Reactions with nitriles. We have recently found that [bis(dicyclohexylamino)-phosphino](trimethylsilyl)carbene **49** reacts at 50°C via a 1+2 cycloaddition process with benzonitrile, affording the corresponding azirine **50** in high yield [40]. Note that the *tert*-butyl-λ^3-phosphaalkyne ($\mathrm{P{\equiv}C{-}Bu^t}$) [20], although usually much more reactive than nitriles, does not react with carbene **49** under the same experimental conditions.

5.1.2.6. Reactions with λ^5-phosphonitriles. A multi-step mechanism involving a 2+2 cycloaddition of transient phosphinocarbenes **52** with phosphonitriles **53** [41], both



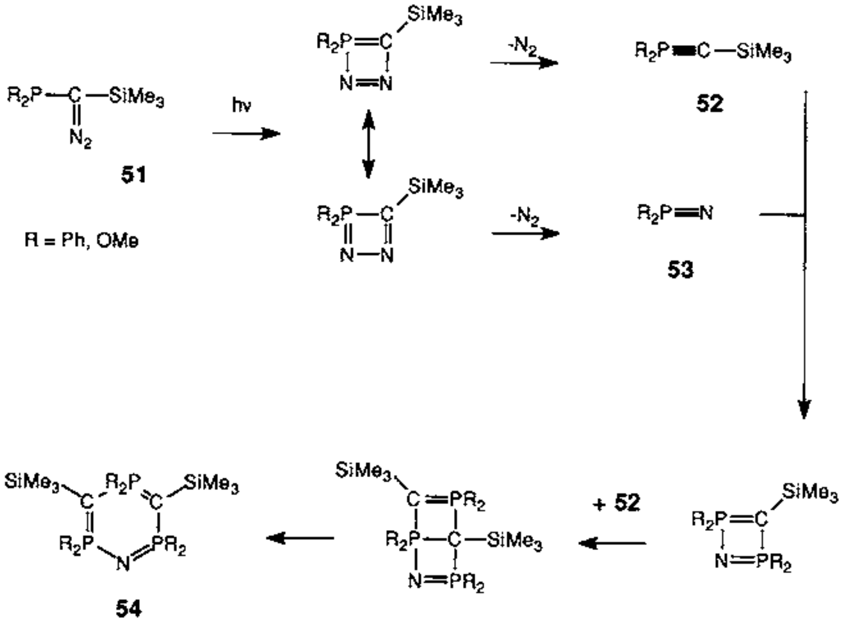


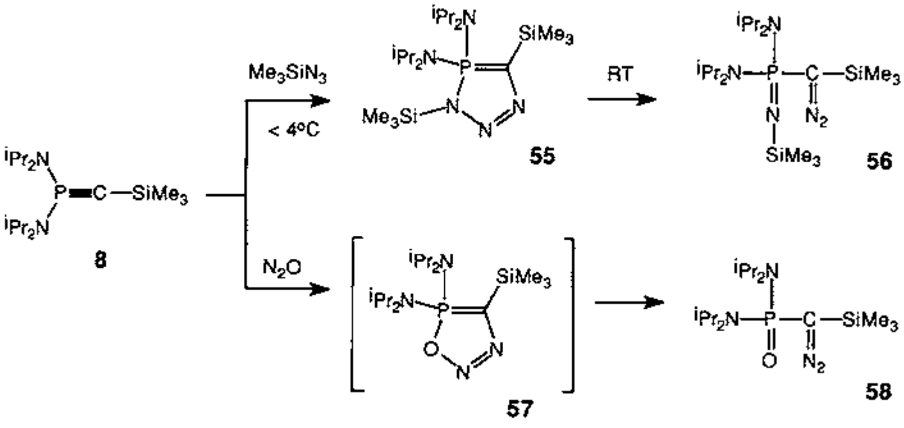
generated by photolysis of (phosphino)(trimethylsilyl)diazomethanes **51**, has been postulated by Regitz [31] to rationalize the formation of $1,2\lambda^5,4\lambda^5,6\lambda^5$-azatriphosphinines **54** (29%–42% yield).

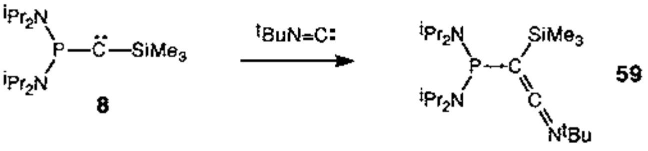
5.1.2.7. Reactions with azides and nitrogen oxide. Trimethylsilylazide and nitrogen oxide react with phosphinocarbene **8** affording diazo derivatives **56** and **58** in 92% and 86% yield respectively. These results have been explained by $2+3$ cycloaddition reactions followed by ring opening of the resulting five-membered rings **55** and **57**. Indeed, the first formed $1,2,3,4\lambda^5$-triazaphosphole **55** was characterized in solution at 4°C [16]. These reactions are strictly analogous to those often reported between azides, or nitrogen oxide, and alkynes [5].

5.1.2.8. Reactions with isocyanides. *Tert*-butyl isocyanide is one of the very rare reagents that react with almost all of the stable phosphinocarbenes reported so far [17]. For example, it reacts with the [bis(diisopropylamino)phosphino](trimethylsilyl)carbene **8**, even at -78°C, affording keteneimine **59** which was isolated after treatment with elemental sulphur as its thioxophosphoranyl analogue in 90% yield. The great reactivity of isonitriles towards phosphinocarbenes can easily be explained in terms of steric factors; the reactive site of RN=C: is not hindered. The reaction giving keteneimine can be considered as an example of carbene–carbene coupling.

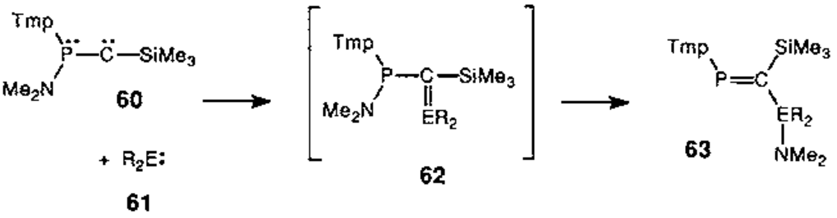
5.1.2.9. Reactions with germanediyls and stannanediyls. [(Dimethylamino)-(2,2,2,6-tetramethylpiperidino)phosphino](trimethylsilyl)carbene **60** reacts with germanium(II) and tin(II) compounds **61** [42], affording C-germylphosphaalkenes







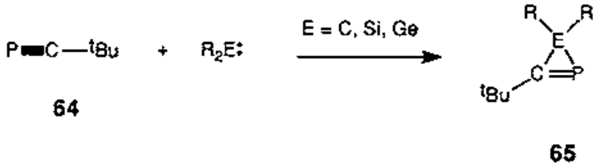
and C-stannylphosphaalkenes **63**, in 42% to 78% yields respectively [43]. By analogy with the reaction between carbenes and isonitriles, it is reasonable to postulate the primary formation of germaethenes and stannaethenes **62**; a subsequent 1,3-shift of the dimethylamino group from phosphorus to germanium or tin producing derivatives **63**. These two reactions are highly chemioselective since we only observe the migration of the smallest phosphorus substituent. The driving force of this rearrangement is probably the reluctance of germanium and tin to be doubly bonded [44].



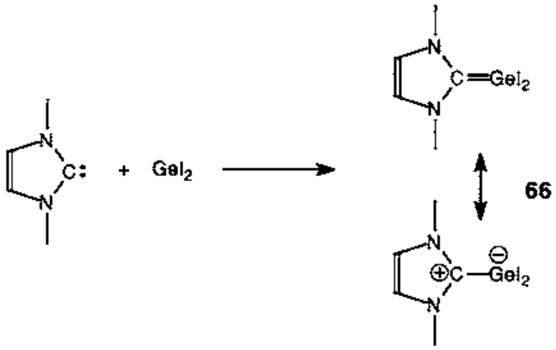
R	E	yield
$(Me_3Si)_2N$	Ge	78%
Mes^*_2N	Ge	46%
$(Me_3Si)_2N$	Sn	42%
$(Me_3Si)_2CH$	Sn	48%

Tmp = 2,2,6,6-tetramethylpiperidino
Mes* = 2,4,6-tri-tert-butylphenyl

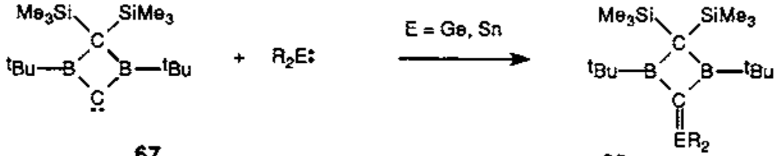
These results are good examples of the striking difference between the reactivity of λ^5-phosphaacetylenes (λ^3-phosphinocarbenes) and λ^3-phosphaacetylenes [20,27]. Indeed, it has been demonstrated that *tert*-butyl-λ^3-phosphaacetylene **64** undergoes 2+1 cycloaddition with carbenes [45], silylenes [46], and germylenes [47], affording three-membered rings **65** containing a phosphorus–carbon double bond. Note that imidazol-2-ylidenes react with germanium diiodide quantitatively affording a stable carbene–germylene adduct **66** [48]. NMR data and X-ray analysis indicate that the newly formed C–Ge bond is not a classical double bond but is highly polarized. In the same way, the cryptocarbene **67** from Berndt and co-workers [49] reacts with germylenes [50a,b] and stannylenes [50b,c] leading to stable germaethenes and stannaethenes **68**.



5.1.2.10. Reactions with iminophosphanes. [(Dimethylamino)(2,2,2,6-tetramethylpiperidino)phosphino](trimethylsilyl)carbene **60** reacts with iminophosphanes **69** leading to phosphaalkenes **71** (23%–87% yield) [51]. By analogy with the results observed in the reaction between carbene **60** and germylenes and stannylenes, it is likely that a carbene–carbenoid coupling type reaction occurs, leading to transient (methylene)(imino)phosphoranes **70**, which would undergo a subsequent migration

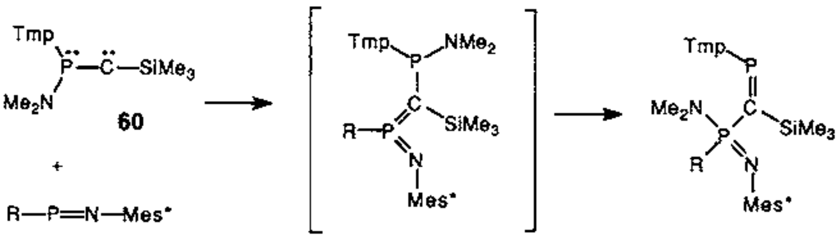


66



67 **68**

of a dimethylamino substituent from the λ^3-phosphorus to the positively charged λ^5-phosphorus atom. Once again, these reactions are highly chemioselective since we only observe the migration of the smallest phosphorus substituent. In the case of chloro- and bromo(imino)phosphanes **69**, a competitive reaction occurred giving rise to another type of phosphaalkene **73**. It seems likely that the first step is an insertion of the carbene into the phosphorus–halogen bond of **69** giving **72**, which undergoes a 1,3-shift of the silyl group from carbon to nitrogen.



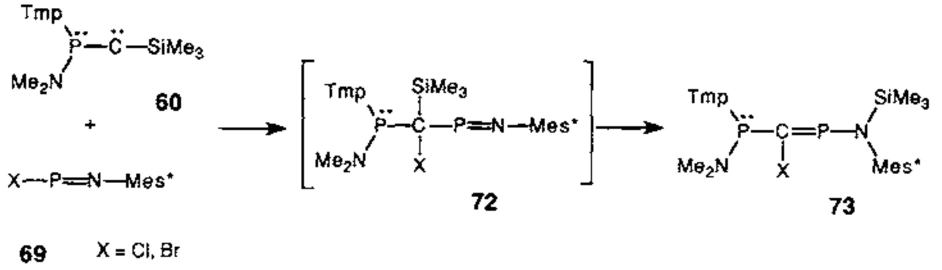
60 **69** **70** **71**

R = ^{t}Bu, MeO, F, Cl, Br

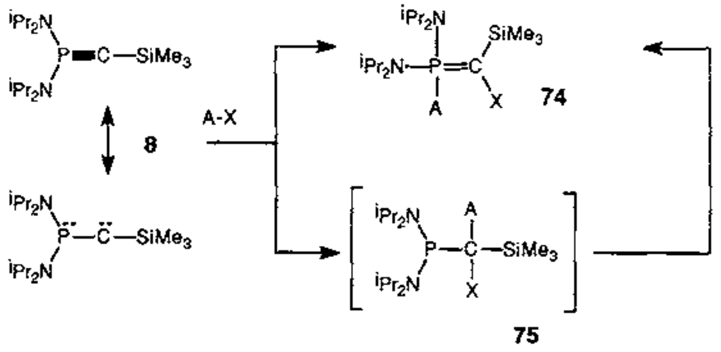
Tmp = 2,2,6,6-tetramethylpiperidino

Mes* = 2,4,6-tri-tert-butylphenyl

5.1.2.11. Reactions with A–X type reagents. Chlorotrimethylsilane [15,16], P-chlorophosphaalkene [52], or dimethylamine [15,16] react with [bis(diisopropylamino)phosphino](trimethylsilyl)carbene **8** (either directly or with **8** prepared in situ by photolysis of the corresponding diazo derivative **7**), giving rise to λ^5-phos-

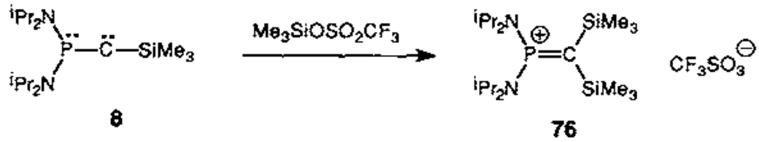


phorus derivatives **74**, in near quantitative yields. To rationalize the formation of these adducts, it is reasonable to postulate a 1-2 addition of the trapping agent to the phosphorus–carbon multiple bond of **8**. However, one can argue that a 1-1 addition of the trapping agents on the carbene form (in other words a carbene insertion into the AX bond) giving **75**, followed by a subsequent rearrangement, might also explain the nature of the observed products; chloromethylenephosphine-methylenechlorophosphorane rearrangements have already been exemplified [53]. Formal 1-2 addition of methanol to bis[bis(diisopropylamino)phosphino]carbene **15** has also been reported [26].



A-X: Cl-$SiMe_3$, Cl-P=C$(SiMe_3)_2$, Me_2N-H

5.1.2.12. Reactions with alkylating agents. The addition of trimethylsilyl trifluoromethanesulphonate to phosphinocarbene **8** proceeds cleanly to give a new type of phosphorus cation, namely the methylenephosphonium salt **76** [54]. This extremely air-sensitive compound, which is valence isoelectronic to olefins, has a ^{31}P chemical shift of +130 ppm, and the signal corresponding to the quaternary carbon appears



at +76.5 ppm with a phosphorus–carbon coupling constant of 87.6 Hz. This unusual compound, characterized structurally by X-ray diffraction (Fig. 4), has a short carbon–phosphorus double bond (1.62 Å), and trigonal planar phosphorus centre and carbon atoms with a dihedral angle of 60°. This value is significantly larger than that reported for the most crowded olefin [55].

Formally, this compound can be viewed as the product of a carbene–carbenoid coupling between bis(trimethylsilyl)carbene and bis(diisopropylamino)phosphenium triflate. Theoretical calculations [56] also reveal a short polar P–C bond. The electronegative amino groups at phosphorus and the electropositive silyl groups at carbon maintain the ionic character of the P–C double bond, thus avoiding a biradical as the π-bond is broken through rotation. This characteristic and the availability of an empty d-orbital orthogonal to the 3p orbital at phosphorus leads to facile rotation of the double bond (20 kcal mol^{-1}), shortening of the bond through Coulomb bond stabilization, and a large dihedral angle due to the bulky substituents. Note, that another route to methylenephosphonium salt has been reported by Grützmacher and Pritzkow [57].

5.1.2.13. Reactions with Lewis acids. The formation of transient adducts of electrophilic carbenes with Lewis bases is well documented [58], but there is only one report of a stable Lewis acid–carbene complex [59]. Owing to its nucleophilic character, [bis(dicyclohexylamino)phosphino](trimethylsilyl)carbene **49** reacts with a variety of Lewis acids [19,60,61]. The fate of the reaction appears to be strongly dependent on the nature of the acids, but it seems likely that in all cases the first step is the formation of a carbene–Lewis acid adduct **77**. In fact such compounds **77a–c** have been isolated using aluminium, gallium, and indium trichloride [61]. The deshielded ^{31}P and ^{13}C NMR chemical shifts observed for **77a–c** ($\delta^{31}\text{P} \approx +130$, $\delta^{13}\text{C} \approx +76$, $J_{\text{PC}} \approx 85$ Hz) are consistent with the presence of a double bond and positive charge development at phosphorus, and these spectroscopic data are in fact very similar to those observed for the methylenephosphonium salt **76**. This similarity is confirmed by X-ray analysis of the gallium adduct **77b** (Fig. 5): (i) the phosphorus and carbon atoms adopt a trigonal planar geometry; (ii) there is a twist angle between the two plans of 34.1°; (iii) the phosphorus–carbon bond distance is rather short (1.61 Å).

When triethylborane is used, the borane–carbene adduct **77d** is stable in solution for several weeks at −20°C, but only for a day at room temperature [19]. Elimination of diethyl(dicyclohexylamino)borane occurs, leading to phosphaalkene **79** which was isolated in near quantitative yield. This fragmentation can be rationalized by a classical migration of an ethyl group from the four-coordinated boron atom to the electron-deficient α-carbon [62] giving **78**, followed by a 1,2-elimination of diethyl(dicyclohexylamino)borane.

Lastly, when dimesitylfluoroborane [60], trimethoxyborane [60], trimethylaluminium, trimethylgallium or trimethylindium [61] were used, phosphorus ylides

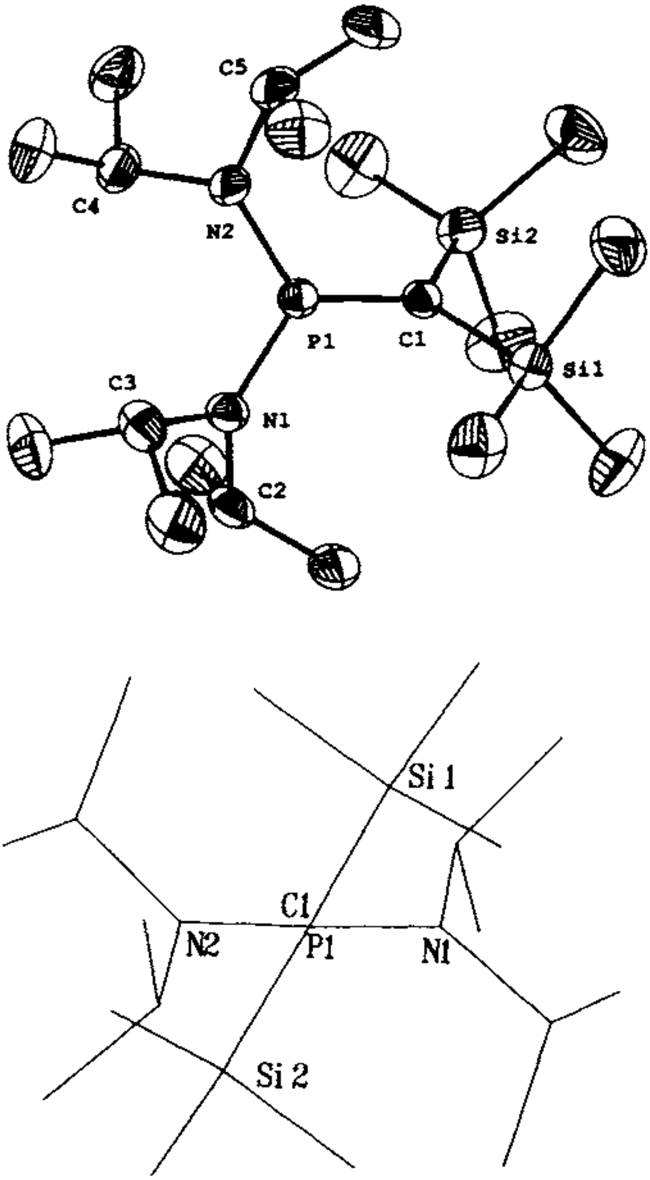


Fig. 4. Thermal ellipsoid diagram (30% probability) of methylenephosphonium **76** showing the atom numbering scheme, and simplified view of the molecule showing the twist angle. Pertinent bond lengths (Å) and bond angles (deg) are as follows: P(1)–C(1) 1.620(3), C(1)–Si(1) 1.875(3), P(1)–N(1) 1.615(3), C(1)–Si(2) 1.913(3), P(1)–N(2) 1.610(3); N(1)–P(1)–C(1) 123.4(1), C(2)–N(1)–P(1) 121.0(2), N(2)–P(1)–C(1) 124.4(1), C(3)–N(1)–P(1) 123.1(2), N(2)–P(1)–N(1) 112.2(1), C(2)–N(1)–C(3) 115.6(2), Si(1)–C(1)–P(1) 121.7(1), C(4)–N(2)–P(1) 120.2(2), Si(2)–C(1)–P(1) 119.3(1), C(5)–N(2)–P(1) 124.4(2), Si(2)–C(1)–Si(1) 119.1(1), C(4)–N(2)–C(5) 115.1(2).

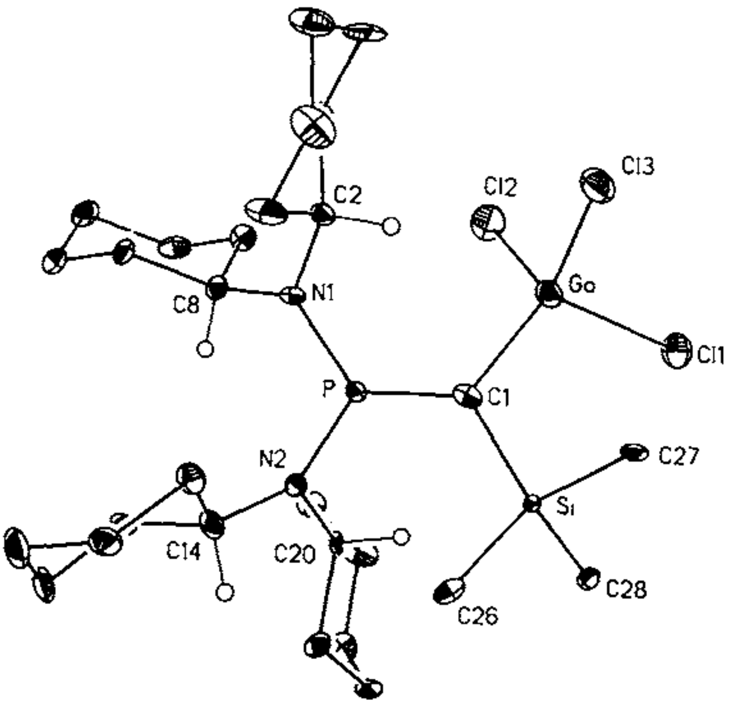
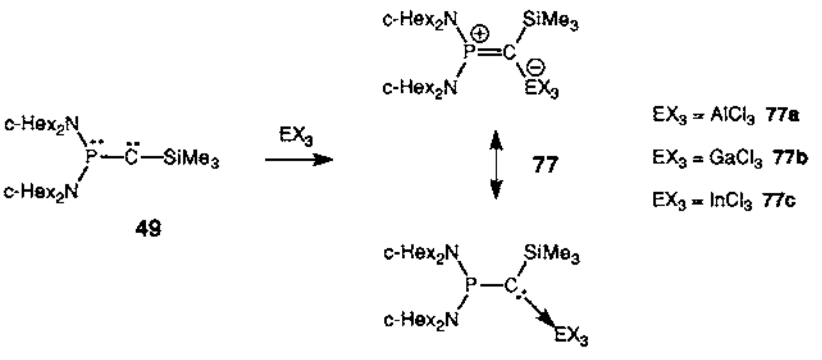
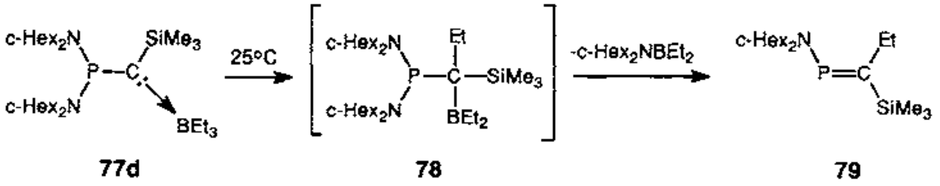
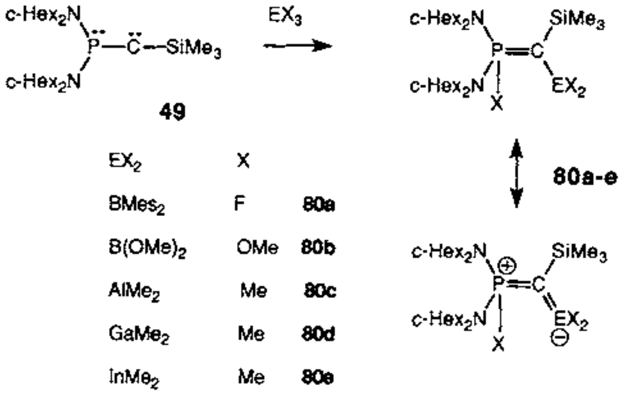


Fig. 5. ORTEP view of **77b** showing the atom labelling scheme. Important bond distances (Å) and angles (deg) are as follows: P–C(1) 1.601(9), P–N(1) 1.622(7), P–N(2) 1.619(8), C(1)–Si 1.886(8), C(1)–Ga 1.978(10), Ga–C(11) 2.210(3), Ga–C(12) 2.179(3), Ga–C(13) 2.2.198(3); N(1)–P–N(2) 113.4(4), N(1)–P–C(1) 125.1(5), N(2)–P–C(1) 121.4(4), P–C(1)–Si 121.8(6), P–C(1)–Ga 122.6(5), Si–C(1)–Ga 115.7(5), C(1)–Ga–C(11) 111.4(3), C(1)–Ga–C(12) 113.9(3), C(1)–Ga–C(13) 112.8(3), C(11)–Ga–C(12) 105.49(11), C(11)–Ga–C(13) 104.35(12), C(12)–Ga–C(13) 108.19(12).



80a–e were obtained in good yield, and no intermediates were detected spectroscopically. Once again, it is reasonable to postulate the formation of a carbene adduct of type **77**, followed by a 1,2-migration leading to a phosphine of type **78**. Finally, instead of undergoing a 1,2-elimination, a classical methylenephosphane–phosphorus ylide conversion [53] would lead to **80**.





EX₂	X	
BMes₂	F	80a
B(OMe)₂	OMe	80b
AlMe₂	Me	80c
GaMe₂	Me	80d
InMe₂	Me	80e

Although numerous so-called stabilized phosphorus ylides have been studied, in which the negative charge is delocalized into an organic [63] or organometallic [64] framework, compounds **80a** [60] and **80d** [61] were the first examples studied by X-ray diffraction (Figs. 6 and 7) which involve C substituted by a group 13 element. These compounds are of interest since they can also be considered as boron–carbon and gallium–carbon double-bonded compounds C-substituted by a phosphonio group. Indeed, the boron–carbon bond length in **80a** (1.52 Å) is shorter than a usual boron–carbon single bond (1.58–1.62 Å), but a little longer than a boron–carbon double bond of, for example, $Mes_2B{=}CH_2^-$ (1.44 Å) [65]. This boron–carbon π-type interaction was confirmed by NMR in solution. In the same way, the gallium–carbon bond length in **80d** (1.93 Å) is the shortest of such distances reported so far.

5.2. *Reactivity of the (phosphino)(phosphonio)carbene 10*

Compared with (phosphino)(silyl)carbenes, very little is known concerning the reactivity of the only known (phosphonio)carbene **10** [18,66]. In fact, no reaction typical of carbene behaviour has been reported. However, compound **10** appeared to be a powerful building block for new interesting species. First, it should be noted that (phosphino)(phosphonio)carbene **10** is stable with respect to possible migration of the hydrogen atom from phosphorus to the carbene centre, although calculations on the amino analogue (H_2N instead of (Pr^i_2N)) predict **81** to be more stable than **10** by 17 kcal mol^{-1} at the MP2 level [10]. The energy barrier for the 1,2-shift is probably too high.

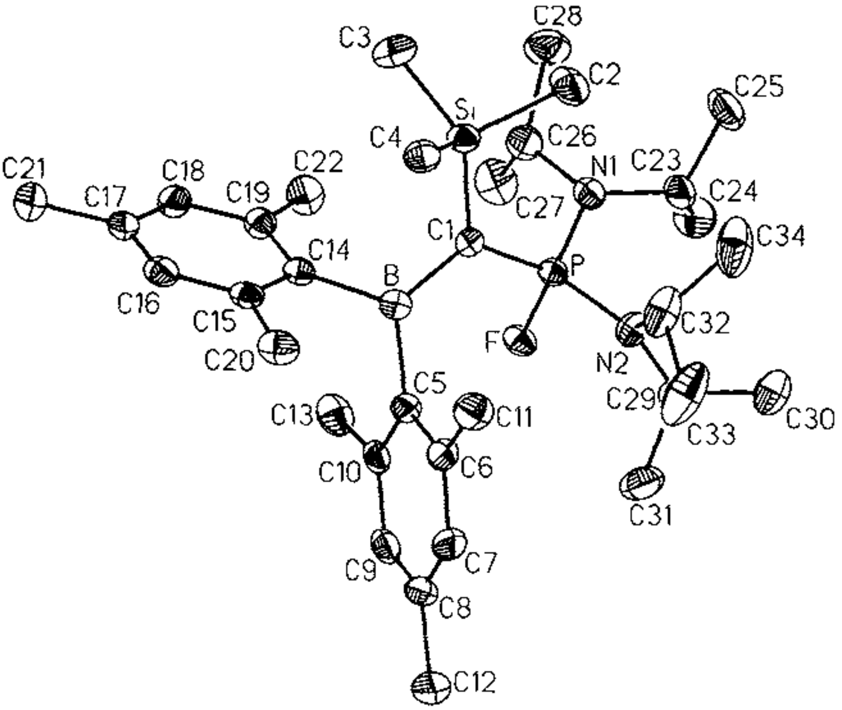


Fig. 6. Molecular structure of **80a** showing the atom-numbering scheme. Pertinent bond lengths (pm), bond angles (deg), and dihedral angles (deg) are as follows: B–C(1) 152.5(4), P–C(1) 169.6(2), Si–C(1) 187.2(3), B–C(14) 162.9(3), B–C(5) 161.5(4), P–F 158.5(1), P–N(1) 166.3(2), P–N(2) 165.5(2); P–C(1)–Si 123.3(1), P–C(1)–B 117.9(2), Si–C(1)–B 118.8(2), C(1)–B–C(5) 123.4(2), C(5)–B–C(14) 114.6(2), C(1)–B–C(14) 122.0(2); C(14)–B–C(1)–P 147.9, C(14)–B–C(1)–Si 32.3, C(5)–B–C(1)–P 30.6, C(5)–B–C(1)–Si 149.1, C(1)–B–C(5)–C(6) 72.4, C(1)–B–C(5)–C(10) 110.0, C(1)–B–C(14)–C(19) 63.7, C(1)–B–C(14)–C(15) 122.8.

The addition of sodium tetrafluoroborate to **10** led to carbodiphosphorane **82** possessing a P–H bond, which was isolated in 70% yield. Although **82** is thermally quite stable as a solid (mp 116°C), it slowly rearranges in solution at room temperature (1 week) into its isomeric phosphorus ylide **83**. This result was not surprising since calculations predicted **83** to be 70 kJ mol^{-1} more stable than **82**. Carbodiphosphoranes ($R_3P{=}C{=}PR_3$) are known [67], but ylides with a P–H bond are rare [68]. Therefore, the spectroscopic characterization of **82** was unexpected. Even more surprising was the characterization of carbodiphosphorane **84** featuring two P–H bonds. This compound prepared by treatment of **10** with *tert*-butyllithium rearranged in solution at room temperature in the course of 16 h to give the phosphorus ylide with one remaining P–H bond **85** which is also unstable and completely transforms overnight into the diphosphinomethane **86**. Note that calculations for model compounds ($R{=}NH_2$) predicted **84** to be 28 kcal mol^{-1} less stable than **85**, which is also 34 kcal mol^{-1} above **86**. The surprising stabilities of **84** and

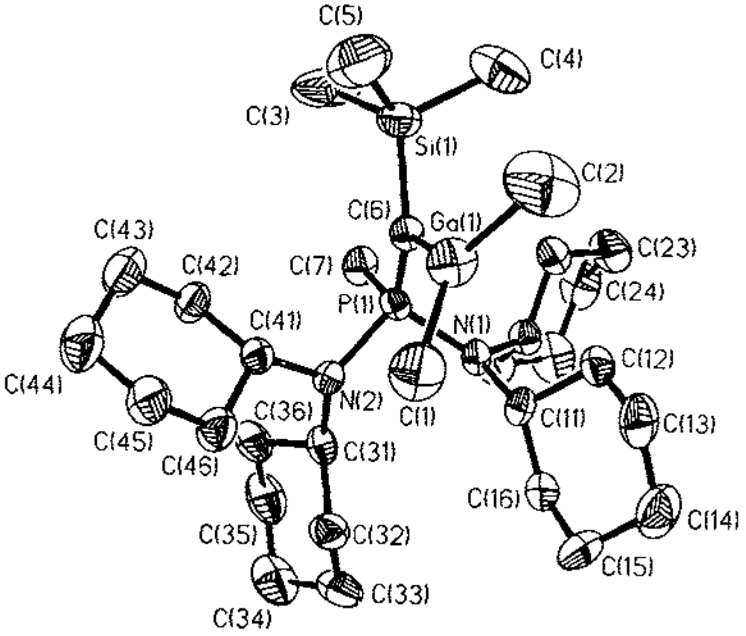
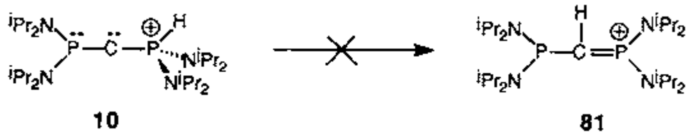
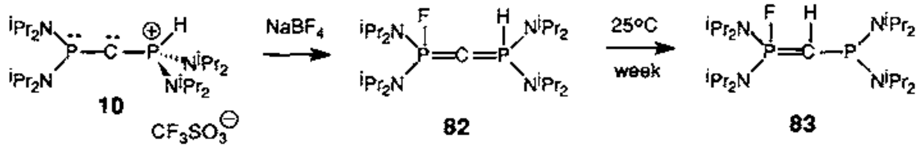


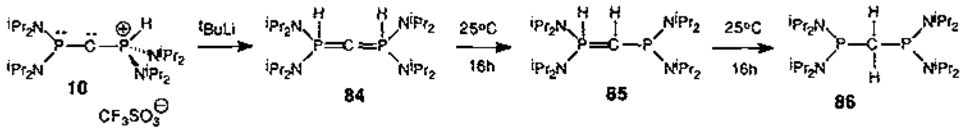
Fig. 7. ORTEP view of **80d** showing the atom labelling scheme. Important bond distances (Å) and angles (deg) are as follows: P–C(6) 1.658(7), P–C(7) 1.808(6), P–N(1) 1.693(5), P–N(2) 1.690(5), C(6)–Si(1) 1.829(7), C(6)–Ga(1) 1.935(6), Ga(1)–C(1) 1.994(8), Ga(1)–C(2) 1.988(10), C(6)–P(1)–C(7) 113.4(3), C(6)–P(1)–N(1) 118.1(3), C(6)–P(1)–N(2) 112.6(3), C(7)–P(1)–N(1) 103.8(3), C(7)–P(1)–N(2) 105.3(3), N(1)–P(1)–N(2) 102.2(3), Ga(1)–C(6)–P(1) 120.0(4), Ga(1)–C(6)–Si(1) 110.3(3), Si(1)–C(6)–P(1) 129.1(4), C(1)–Ga(1)–C(2) 112.1(4), C(1)–Ga(1)–C(6) 125.4(3), C(2)–Ga(1)–C(6) 122.5(3).



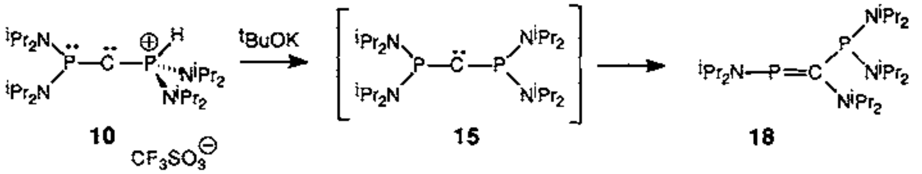


85 are probably due to the presence of bulky substituents, since tetracoordinate phosphorus atoms accommodate better the steric hindrance than do the tricoordinate centres.

The addition of fluoride to **10**, giving **82**, demonstrates the strong Lewis acid character of the three-coordinate phosphorus centre, while the reaction with *tert*-butyllithium, leading to **84**, showed that **10** can be easily reduced. It is also possible



to abstract the proton using a strong base such as potassium *tert*-butoxide. In this case, phosphaalkene **18**, obtained in 45% yield, clearly arises from the transient formation of bis(phosphino)carbene **15** which undergoes a 1,2-shift of an amino substituent from phosphorus to the carbene centre (we have already shown that phosphaalkene **18** can be obtained by photolysis of the corresponding diazo compound **14** [26]). Once again, the isomerization of **15** to **18** is in agreement with the calculations which found **18** to be 53 kcal mol^{-1} below **15**.



6. CONCLUSIONS

From the reactivity patterns, we see the dual nature of the phosphinocarbenes. Products expected from classical carbene reactivity as well as adducts of phosphorus–carbon multiply bonded species are obtained, demonstrating the vast synthetic potential of these compounds in organic and inorganic chemistry. A simple description of the bonding situation based on the observed reactivity leads quickly to non-classical valence bond structures. Spectroscopic studies suggest a multiply bonded formulation, which is confirmed by ab initio calculations. The triplet being close to the singlet state, it may well be involved in the reactivity patterns of this unique compound. Perhaps most important is the demonstration of the utility of heteroatoms in stabilizing highly reactive compounds. Using substituents with third and fourth row elements, several species, hitherto believed to be only transient intermediates, will probably be isolated at room temperature in the future.

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REFERENCES

1 M. Regitz, Angew. Chem., Int. Ed. Engl., 30 (1991) 674.

2 A.J. Arduengo III, H.V.R. Dias, R.L. Harlow and M. Kline, J. Am. Chem. Soc., 114 (1992) 5530.

3 A.J. Arduengo III, R.L. Harlow and M. Kline, J. Am. Chem. Soc., 113 (1991) 361.

4 W. Kirmse (Ed.), Carbene Chemistry, Academic Press, New York, 1971.

5 P. Caramella, P. Grünanger, in A. Padwa (Ed.), 1,3-Dipolar Cycloaddition Chemistry, Wiley, New York, 1984.

6 (a) B. Potter, K. Seppelt, A. Simon, E.M. Peters and B. Hettich, J. Am. Chem. Soc., 105 (1985) 980.
(b) D. Christen, H.-G. Mark, C.J. Marsden, H. Oberhammer, G. Schatte, K. Seppelt and H. Willner, J. Am. Chem. Soc., 109 (1987) 4009.
(c) D.A. Dixon and B.E. Smart, J. Am. Chem. Soc., 108 (1986) 2688.
(d) R. Gerhardt, T. Greibig, J. Buschmann, P. Luger and K. Seppelt, Angew. Chem., Int. Ed. Engl., 27 (1988) 1534.

7 M.T. Nguyen, M.A. McGinn and A.F. Hegarty, Inorg. Chem., 25 (1986) 2185.

8 M.R. Hoffmann and K. Kuhler, J. Chem. Phys., 94 (1991) 8029.

9 D.A. Dixon, K.D. Dobbs, A.J. Arduengo III and G. Bertrand, J. Am. Chem. Soc., 113 (1991) 8782.

10 O. Treutler, R. Ahlrichs and M. Soleilhavoup, J. Am. Chem. Soc., 115 (1993) 8788.

11 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, Chem. Phys. Lett., 162 (1989) 165.

12 R. Appel, J. Peters and R. Schmitz, Z. Anorg. Allg. Chem., 475 (1981) 18; 475 (1981) 6204.

13 J. Svara, E. Fluck and H. Riffel, Z. Naturforsch., Teil B, 40 (1985) 1258.
B. Neumüller and E. Fluck, Phosphorus Sulfur, 29 (1986) 23.

14 M. Regitz, Diazoalkanes, Thieme, Stuttgart, 1977.
M. Regitz and G. Mass, Top. Curr. Chem., 97 (1981) 71.

15 A. Baceiredo, G. Bertrand and G. Sicard, J. Am. Chem. Soc., 107 (1985) 4781.
A. Baceiredo and G. Bertrand, Phosphorus Sulfur, 26 (1986) 57.

16 A. Igau, H. Grützmacher, A. Baceiredo and G. Bertrand, J. Am. Chem. Soc., 110 (1988) 6463.

17 G. Gillette, A. Baceiredo and G. Bertrand, Angew. Chem., Int. Ed. Engl., 29 (1990) 1123.
G. Gillette, A. Igau, A. Baceiredo and G. Bertrand, New J. Chem., 15 (1991) 393.
G. Bertrand, Heteroatom, 2 (1991) 29.

18 M. Soleilhavoup, A. Baceiredo, O. Treutler, R. Ahlrichs, M. Nieger and G. Bertrand, J. Am. Chem. Soc., 114 (1992) 10959.
M. Soleilhavoup, G. Alcaraz, R. Reau, A. Baceiredo and G. Bertrand, Phosphorus Sulfur, 76 (1993) 49.

19 G. Alcaraz, R. Reed, A. Baceiredo and G. Bertrand, J. Chem. Soc., Chem. Commun., (1993) 1354.

20 M. Regitz and O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990.

21 C.W. Bauschlicher, Jr., H.F. Schaefer III and P.S. Bagus, J. Am. Chem. Soc., 99 (1977) 7106.

22 C.R. Johnson, Crystallographic Computing, Munksgoord, (1970) 220.
J.D. Dunitz, E.F. Maverick and K.N. Trueblood, Angew. Chem., Int. Ed. Engl., 27 (1988) 880.

23 E. Fluck, B. Neumüller, R. Braun, G. Heckmann, A. Simon and H. Borrmann, Z. Anorg. Allg. Chem., 567 (1988) 23.

24 M.J. Menu, Y. Dartiguenave, M. Dartiguenave, J.J. Bonnet, G. Bertrand and A. Baceiredo, J. Organomet. Chem., 372 (1989) 201.

25 M.J. Menu, Y. Dartiguenave, M. Dartiguenave, A. Baceiredo and G. Bertrand, Phosphorus Sulfur, 47 (1990) 327.

26 A. Baceiredo, A. Igau, G. Bertrand, M.J. Menu, Y. Dartiguenave and J.J. Bonnet, J. Am. Chem. Soc., 108 (1986) 7868.

27 M. Regitz and P. Binger, Angew. Chem., Int. Ed. Engl., 27 (1988) 1484.

28 G. Sicard, A. Baceiredo, G. Crocco and G. Bertrand, Angew. Chem., Int. Ed. Engl., 27 (1988) 301.

29 G. Sicard, H. Grützmacher, A. Baceiredo, J. Fischer and G. Bertrand, J. Org. Chem., 54 (1989) 4426.

30 H. Keller and M. Regitz, Tetrahedron Lett., 29 (1988) 925.

31 M. Regitz, personal communication (1986).

32 H. Keller, G. Maas and M. Regitz, Tetrahedron Lett., 27 (1986) 1903.

33 R.A. Moss, M. Wlostowski, S. Shen, K. Krogh-Jespersen and A. Matro, J. Am. Chem. Soc., 110 (1988) 4443.

34 A. Igau, A. Baceiredo, G. Trinquier and G. Bertrand, Angew. Chem., Int. Ed. Engl., 28 (1989) 621.

35 M. Brookhart and W.B. Studabaker, Chem. Rev., 87 (1987) 411.

36 R.A. Moss, S. Shen, L.M. Hadel, G. Kmiecik-Lawrynowicz, J. Wlostowska and K. Krogh-Jespersen, J. Am. Chem. Soc., 109 (1987) 4341.

37 (a) P. De March and R. Huisgen, J. Am. Chem. Soc., 104 (1982) 4952.
(b) P. De March and R. Huisgen, J. Am. Chem. Soc., 104 (1982) 4953.

38 D.S. Wulfman and B. Poling, in R.A. Abramovitch (Ed.), Reactive Intermediates, Vol. 1, Plenum, New York, 1980, p. 321.

39 M. Regitz, Synthesis, (1972) 351.

40 G. Alcaraz, U. Wecker, A. Baceiredo and G. Bertrand, unpublished results (1994).

41 G. Sicard, A. Baceiredo, G. Bertrand and J.P. Majoral, Angew. Chem., Int. Ed. Engl., 23 (1984) 459.
A. Baceiredo, G. Bertrand, J.P. Majoral, G. Sicard, J. Jaud and J. Galy, J. Am. Chem. Soc., 106 (1984) 6088.
A. Baceiredo, G. Bertrand, J.P. Majoral, F. El Anba and G. Manuel, J. Am. Chem. Soc., 107 (1985) 3945.
M. Granier, A. Baceiredo, Y. Dartiguenave, M.J. Menu and G. Bertrand, J. Am. Chem. Soc., 112 (1990) 6277.
G. Bertrand, J.P. Majoral and A. Baceiredo, Acc. Chem. Res., 19 (1986) 17.

42 J. Satgé, J. Organomet. Chem., 400 (1990) 121.

43 V.D. Romanenko, A.O. Gudima, A.N. Chernega and G. Bertrand, Inorg. Chem., 31 (1992) 3493.

44 J. Barrau, J. Escudié and J. Satgé, Chem. Rev., 90 (1990) 283.

45 O. Wagner, M. Ehle and M. Regitz, Angew. Chem., Int. Ed. Engl., 28 (1989) 225.
H. Memmesheimer, J.R. Al-Dulayymi, M.S. Baird, T. Wettling and M. Regitz, Synlett., (1991) 443.

46 A. Schäfer, M. Weidenbruch, W. Saak and S. Pohl, Angew. Chem., Int. Ed. Engl., 26 (1987) 776.

47 A.H. Cowley, S.W. Hall, C.M. Nunn and J.M. Power, J. Chem. Soc., Chem. Commun., (1988) 753.

48 A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese and F. Davidson, Inorg. Chem., 32 (1993) 1541.

49 R. Wehrmann, H. Klusik and A. Berndt, Angew. Chem., Int. Ed. Engl., 23 (1984) 826.

50 (a) H. Meyer, G. Baum, W. Massa, S. Berger and A. Berndt, Angew. Chem., Int. Ed. Engl., 26 (1987) 798.

(b) A. Berndt, H. Meyer, G. Baum, W. Massa and S. Berger, Pure Appl. Chem., 57 (1987) 1011.
(c) H. Meyer, G. Baum, W. Massa, S. Berger and A. Berndt, Angew. Chem., Int. Ed. Engl., 26 (1987) 546.
51 V.D. Romanenko, A.O. Gudima, A.N. Chernega and G. Bertrand, unpublished results (1994).
52 A. Igau, A. Baceiredo, G. Bertrand, K. Kuhnel Lysek and E. Niecke, New J. Chem., 13 (1989) 359.
53 R. Appel, M. Huppertz and A. Westerhaus, Chem. Ber., 116 (1983) 114.
54 A. Igau, A. Baceiredo, H. Grützmacher, H. Pritzkow and G. Bertrand, J. Am. Chem. Soc., 111 (1989) 6853.
55 H. Sakurai, K. Ebata, C. Kabuto and Y. Nakadaira, Chem. Lett., (1987) 301.
56 L.L. Lohr, H.B. Schlegel and K. Morokuma, J. Phys. Chem., 88 (1984) 1981.
G. Trinquier and J.P. Malrieu, J. Am. Chem. Soc., 109 (1987) 5303.
M. Ehrig, H. Horn, C. Kölmel and R. Ahlrichs, J. Am. Chem. Soc., 113 (1991) 3701.
57 H. Grützmacher and H. Pritzkow, Angew. Chem., Int. Ed. Engl., 30 (1991) 709.
58 M. Regitz (Ed.), Carbene (carbenoide). In Methoden der Organischen Chemie (Houben-Weyl), Vol. E19b, Parts 1 and 2, Thieme, Stuttgart, 1989.
59 A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese and F. Davidson, J. Am. Chem. Soc., 114 (1992) 9724.
60 K. Horchler v. Locquenghien, A. Baceiredo, R. Boese and G. Bertrand, J. Am. Chem. Soc., 113 (1991) 5062.
61 A.H. Cowley, F.P. Gabbaï, C.J. Carrano, M.R. Bond and G. Bertrand, Angew. Chem., Int. Ed. Engl., 33 (1994) 578.
62 H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Syntheses via Boranes, Wiley-Interscience, New York, 1975.
63 A.J. Speziale and K.W. Ratts, J. Am. Chem. Soc., 87 (1965) 5603.
K.A. Ostoja Starzewski and H. Bock, J. Am. Chem. Soc., 98 (1976) 8486.
64 D. Lappas, D.M. Hoffman, K. Folting and J.C. Huffman, Angew. Chem., Int. Ed. Engl., 27 (1988) 587.
65 M.M. Olmstead, P.P. Power, K.J. Weese and R.J. Doedens, J. Am. Chem. Soc., 109 (1987) 2541.
66 M. Soleilhavoup, A. Baceiredo and G. Bertrand, Angew. Chem., Int. Ed. Engl., 32 (1993) 1167.
67 H.J. Bestmann and R. Zimmermann, Methoden der Organischen Chemie (Houben-Weyl), Vol. E1, Thieme, Stuttgart, 1982, p. 616.
H.J. Bestmann and R. Zimmermann, in B.M. Trost, I. Fleming and E. Winterfeldt (Eds.), Comprehensive Organic Synthesis, Vol. 6, Pergamon, Oxford, 1991, p. 171.
68 O.I. Kolodyazhnyi and V.P. Kukhar, Russ. Chem. Rev., 52 (1983) 1096.