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PHOTOELECTRON SPECTRA AND MOLECULAR PROPERTIES

XXIII*. PHOTOELECTRON SPECTRA OF SILICON-SUBSTITUTED YLIDIC SYSTEMS

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Summary

The photoelectron (PE) spectra of the simplest phosphorus ylide $(CH_3)_3P{=}CH_2$ and several C-silyl-substituted derivatives have been measured, and the influence of this substitution on the frontier orbitals is discussed. Experimental values for P=C π-ionization and CNDO/2 calculations on these systems show that "silyl stabilization" is not the consequence of a π-energy lowering but of a decrease of the MO coefficient at the ylidic, quasi-anionic carbon atom.

The PE spectra of the ylides are compared with those of isoelectronic systems, which contain N or O instead of C, and Si instead of P. σ(Si—C) ionizations are shown to be rather dependent on the other groups attached to silicon, and to vary over a remarkable 2 eV range.

Introduction

Schmidbaur et al. were the first to investigate extensively the field of trimethyl *P*-ylides and their organometallic substitution products [1-7]. C-silyl substituted compounds showed extra stability compared to the parent ylide (I). We measured the He(I) photoelectron spectra of several representative silicon substituted ylides (II)-(V), (VIII), and compared them with isoelectronic systems (VI), (VII), (IX)-(XI).

In studies directed towards the question of $(p{-}d)\pi$-bonding, examination of influence of silicon on neighbouring $(p{-}p)\pi$ systems showed for ethylene, butadiene, and acetylene a destabilization of the highest π-level by SiR_3 ($R = H, CH_3$) as compared to hydrogen [8-15]. This substituent effect in the

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* For part XXII see Ref 25

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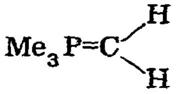
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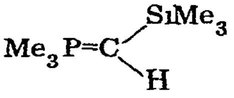
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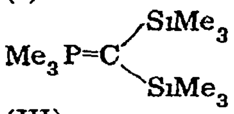
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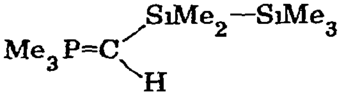
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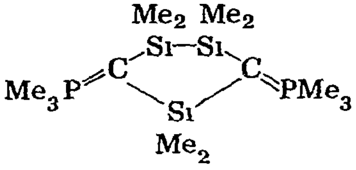
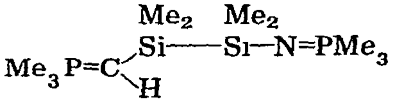

(V)

$Me_3P{=}NH$

(VI)

$Me_3P{=}NSiMe_3$

(VII)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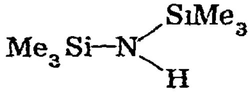
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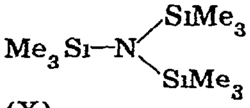
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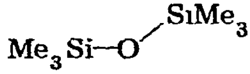
(XI)

ground state* is of the order of one eV, while electronic excited states** are much less affected, probably because of a compensating or even dominating π^*—d back-bonding. With the π-electrons in P=C systems showing extremely low ionization energies, the silicon back-bonding is expected to be much more pronounced than in other molecules having π-systems at higher ionization energies***.

Experimental

Prof. Schmidbaur provided the ylidic phosphorus compounds (I)-(VIII). For preparation see refs. 1-6. Handling and repurification of all substances was

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*The donor effect dominates in the ground state in all "normal" π-systems [8-15]

**The acceptor effect often dominates in the excited state, depending on energy level and coefficient of the substituted centre [8, 9]

***For a simple model, interaction depends on. (1) Energy separation d, $\pi(\pi^*)$, (2) size of coefficient carried out under nitrogen or argon or in a high vacuum line Extreme caution was necessary because trimethyl *P*-ylides are extremely sensitive towards oxygen and water. Even traces of impurities are detectable in the PE spectrum and several decomposition products are more volatile than the parent ylide Ylides of low volatility, (V), (VIII), cannot be measured successfully with the normal gas inlet system of the spectrometer. Even with external heating, either the signal-to-noise ratio is too small or thermal cracking products are recorded. We used the following method of inserting the probe into the heated inlet without decomposition. The substance (if a solid, it is melted under argon) is sucked into an argon-flushed capillary, from which it is transfered into a Schlenk-apparatus containing a sample tube (1 mm Ø, 15 mm long). The first drop is discarded and the tube is then filled to about three quarters. Shortly before measurement the sample inlet tube is "sealed" with a drop of nitrogen-saturated hexane (Uvasol) Such a cover gives sufficient protection against air when used without delay, to transport the sample from the Schlenk tube into the inlet system of the spectrometer, where the hexane is pumped off immediately. After a few minutes the substance can be measured at any reasonable temperature [(V), (VIII) at 60-80°]

Photoelectron spectra were recorded with a Perkin—Elmer PS 16, employing a 127° electrostatic deflection-type analyser (He, I = 21.22 eV excitation). Resolution of at least 0.040 eV was achieved.

Discussions of ionization potentials measured in the low-energy region (6-9 eV) must be carried out with special caution, since we have found varying deviations from the argon calibration, leading to errors in low ionization energies of up to —0.2 eV. For any discussion of effects of this order or less, at least three calibrations at different potentials would be necessary for each spectrum.

Results and discussion

The PE spectra of trimethylmethylenephosphorane* (I) and the three simple Si derivatives (II)-(IV) are presented in Fig. 1. The abscissa gives ionization potentials in electron volts, while the ordinate shows the relative intensity, measured in counts per second.

Without doubt the initial band of each spectrum must be assigned to the ylide π-electrons, whereas ionizations near 10 eV, 11.5 eV, 12-13 eV, and 13-14 eV may be interpreted by comparison with tetramethylsilane [17] (TMS) and trimethylphosphine [16-18]. These show signals mainly Si—C (t_2), P—C (e), (Si)CH_3, or (P)CH_3 in character, at 10.5 eV, 11.33 eV, 13.7 eV, 14.0 eV respectively. This sequence is in accord with increasing VSIP's (Valence State Ionization Potentials) [19]. For compound (IV), an additional band at 8 63 eV must be assigned to a Si—Si ionization, which is found in hexamethyldisilane at 8.69 eV.

From chemical evidence and from ab initio [20], ETH [21] and CNDO/2 calculations, the dominating characteristic of an ylide is the rather localized and only moderately stabilized electron pair at the ylidic carbon atom. This can

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*The spectrum of (I) was measured by Miss S Elbel and is more fully discussed elsewhere [16] in connection with $(CH_3)_3P{=}X$ (X = NH, O, S, Se, BH_3).

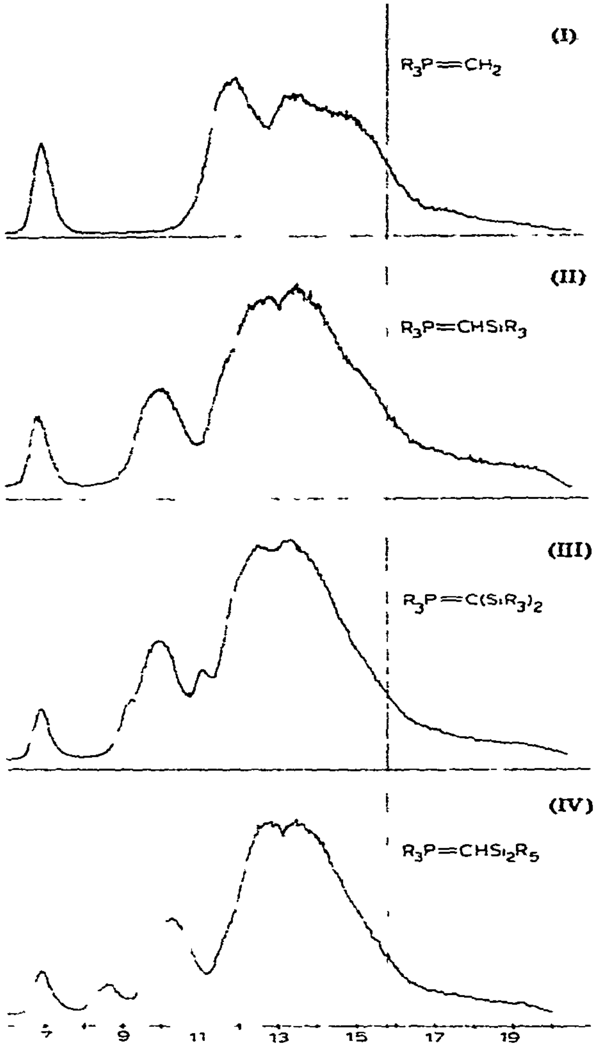

Fig. 1. Photoelectron spectra of ylides (I)-(IV) + argon calibration (15 76 eV)

interact not only with P(d) but also with Si(d) orbitals of proper symmetry, and the amount of stabilization is expected to be larger than $\pi_{CC} \to$ Si(d) in C=C systems. A comparison is given in Fig. 2. In contrast to the nearly unchanged first ionization potentials of compounds (I)-(IV), silicon substituted ylides are known to be stabilized relative to the unsubstituted methylidene, according to the transylidation reaction (1)*.

$$(R_3P{-}CH_2SiR_3)^+\,Cl^- + R_3P{=}CH_2 \rightarrow R_3P{=}CHSiR_3 + (R_3P{-}CH_3)^+\,Cl^- \quad (1)$$

Additional information concerning the electronic properties of ylides can be obtained from the interesting case of two silicon bridged ylidic centers. Fig. 3 gives the PE spectrum of a bis-ylide (V).

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* *Note added in proof* The lattice energies of the two onium salts may also contribute to the overall energetics of reaction (1).

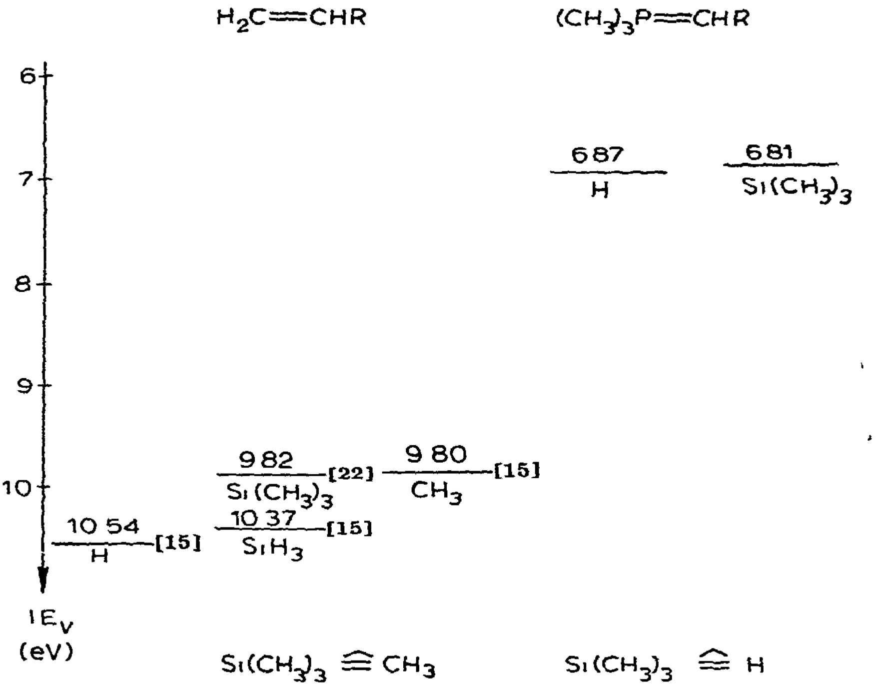


Fig 2 π-Ionization energies of the C=C and P=C π-system for comparison of substituent effects

Group-theoretical arguments require two different π-levels, for there is no degeneracy in point group C_{2v}. As would be expected for a strong interaction, two distinct ionizations are observable. The energy separation is 0.32 eV, and the average π-energy is raised by 0.4 eV. Increased electron density lowers the "Si - Si" ionization more than one eV. A future comparison with the 4- and the 6-membered ring compounds is intended.

New questions arise from comparing compound (I) with the isoelectronic imine (VI). Looking at the double bond along the $(CH_3)_3P{=}X$ series ($X = O$, NH, CH_2), the P=X π- and σ-bond energies change according to different VSIP's of X.

The two degenerate π-levels in the oxide (9.8 eV) are split into one π- and one sp^2-electron pair in the imine (8.2/9.2 eV), while there is only one π-orbital left in the related ylide (6.9 eV) [16].

Assignment of the two imine levels can be made through comparison with azomethines, because there is no d-orbital contribution. With the knowledge of

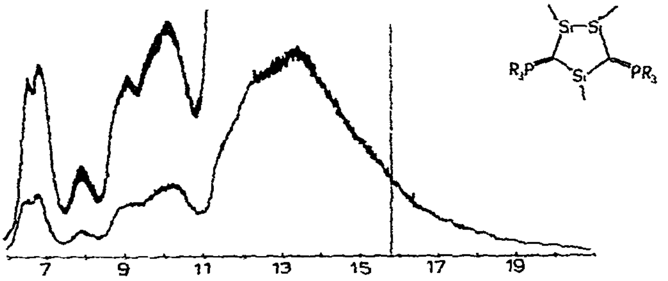


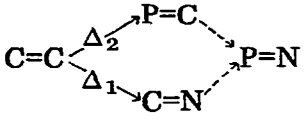
Fig 3 PE spectrum of (V)

the π-energies in ylide (I), *trans*-2-butene and the corresponding azomethine [23] we assign the 8.2 eV band in the phosphine-imine (VI) to the π-ionization and the 9.2 eV band to the lone pair ionization, by the approximation.

$$\begin{aligned}\mathrm{IP}_\pi(\mathrm{P{=}N}) &= \mathrm{IP}_\pi(\mathrm{C{=}C}) + \mathrm{Diff.1} + \mathrm{Diff.2}\\ &= 9.13 \quad + 1.53 \quad - 2.26\\ &= 8.40\ \mathrm{eV}\end{aligned}$$

(closest observed band at 8.2 eV!)

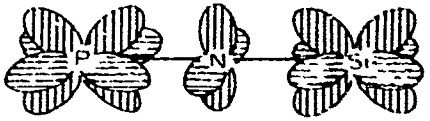
$(CH_3)_3P{=}CH_2$	IP = 6.78 eV
trans-$H_3C{-}CH{=}CH{-}CH_3$	IP = 9.13 eV
trans-$H_3C{-}CH{=}N{-}CH_3$	IP = 10.66 eV



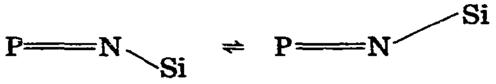
SCHEME 1. π-IONIZATION ENERGIES FOR TWO-CENTER π-SYSTEMS

Next in line, attention is focussed on a comparison of N-lone-pair energies, as a function of the substituent.

Compound (VII) shows only one ionization at 8.3 eV of relative intensity two, compared to the curve integral of the SiC band (Fig. 4). This might suggest two degenerate π-type orbitals, as would be expected for a linear system:



Otherwise, if the two π-levels are accidentally degenerate, the planar inversion probably has a low force constant.



The above discussion now enables us to assign the bands in the more complex system of an ylide imine (VIII) (Fig. 5). Extremely increased π-elec-

TABLE 1
N-LONE-PAIR ENERGIES FOR TWO-CENTER π-SYSTEMS

Compound	IP(eV)	Method	Ref.
trans-$H_3C{-}CH{=}N{-}CH_3$	9.49	PE spectr.	23
trans-$(H_3C)_3C{-}CH{=}N{-}C(CH_3)_3$	8.49	mass spectr	24
trans-$(H_3C)_3C{-}CH{=}N{-}Si(CH_3)_3$	8.16	mass spectr	24
$(CH_3)_3P{=}N{-}H$ (VI)	9.22	PE spectr	16
$(CH_3)_3P{=}N{-}Si(CH_3)_3$ (VII)	8.30	PE spectr	

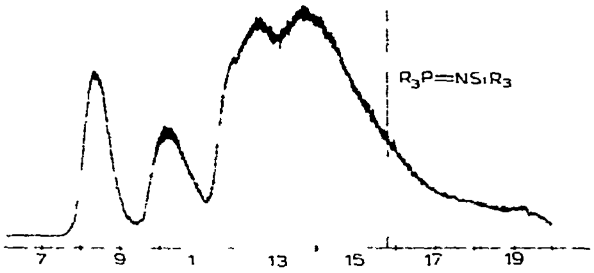


Fig 4. PE spectrum of imine (VII).

tron density results in a further destabilization of the π-levels As in the bis-ylide (V), the accumulation of negative charges so close to one another is very unfavorable because of Coulomb repulsion. The "ylide" ionization is expected to be followed by a "Si—Si" band. Four "π"- and two "n"-electrons, neighbouring the Si—Si bond, lead to a still lower ionization energy (7.44 eV) compared to (V). The electronic environment of the N atom here is probably very similar to that of the silylimine (VII), where n_N and $\pi(N{=}P)$ ionizations are degenerate. The double intensity band following in the spectrum is therefore assigned to the ionization from the P=N part of the system.

All the spectra under discussion show an unresolved broad band (half width > 1, 2 eV) near 10 eV It envelops a changing number of ionizations, which are mainly SiC in character, with one or two of the bonds connected to other atoms (C, N, Si) The SiC band location varies over a range of about 2 eV, which makes it valid for a discussion of electronic effects (Table 2)

For comparison, the t_2-SiC ionization energy of tetramethylsilane (10.5 eV) may be used as a standard.

Each substituent, which is a stronger electron donor than the methyl group, leads to a relative increase of electron density at the silicon atom. This, in turn, results in a shift to lower ionization potentials of the remaining Si—C bonds, as revealed by PE spectroscopy. The electronic interactions may be rationalized by means of a hyperconjugation model or through a model with opposing inductive and d-orbital effects

One occupied π-type orbital adjacent to a silicon atom, results in a release of charge density into the vacant d-orbitals [cf. TMS+(II)]. The degree of charge transfer depends on the VSIP of the π-center [cf. (II)+(VII), (III)+(X), (II)+(IX)+(XI)]. Expanding the "d-system" by connecting further silicon atoms to the π-center, reduces this effect because of the distribution of electron charge between several Si centers [cf. (III)+(II), (X)+(IX)]. Of course,

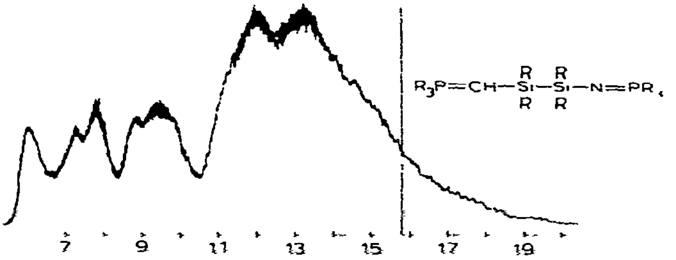


Fig. 5. PE spectrum of ylide imine (VIII).

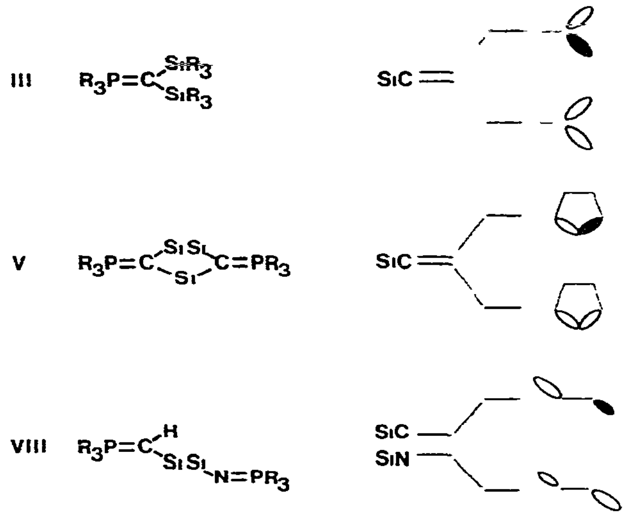


Fig 6. LCBO models for compounds (III), (V) (VIII)

there is not equal distribution in the case of a silicon chain. Increasing distance from the π-centre results in a smaller effect [cf. (IV)+(III)+(II)].

On the other hand, an increasing number of π-centers, neighbouring a silicon atom, will destabilize the further SiC bonds even more [cf. (V)+(II), (III), (IV) and (VIII)+(VII), (IV), (II)]. Furthermore, ylides (III), (V), (VIII) show shoulders at especially low ionization energies, which can be interpreted in terms of an LCBO model (Linear Combination of Bond Orbitals) as interacting SiC bonds (Fig. 6). For compound (VIII) the broadness and asymmetry of the band may be understood in terms of the non-equivalence of C—Si(C) and C—Si(N).

TABLE 2
COMPARATIVE ASSIGNMENT FOR UPPER ENERGY LEVELS OF COMPOUNDS (I)—(X)
Vertical ionization potentials in electron volts

Compd	P=C	Si—Si	P=N	n_N	Si—C	P—C	C—H (Si)	C—H (P)
(I)	6.87					11.8		13.5
(II)	6.81				9.96	11.7	12.6	13.5
(III)	6.92				9.30	11.1		
					10.01	11.9	13.6	14.6
(IV)	6.85	8.63			10.30	11.8	12.7	13.5
(V)	6.11	7.56			8.79			
	6.43				9.83	11.4	12.2	13.1
(VI)			8.19	9.22		12.0		13.4
(VII)			8.30	8.30	10.29	11.8	12.5	13.6
(VIII)	6.18	7.44	7.84	7.84	8.84	11.3	12.0	13.1
					9.62			
				n_N	Si—C	Si—N	C—H(Si)	
(IX)				8.66	10.33	11.29	13.4	
(X)				8.60	10.38	11.65	13.5	

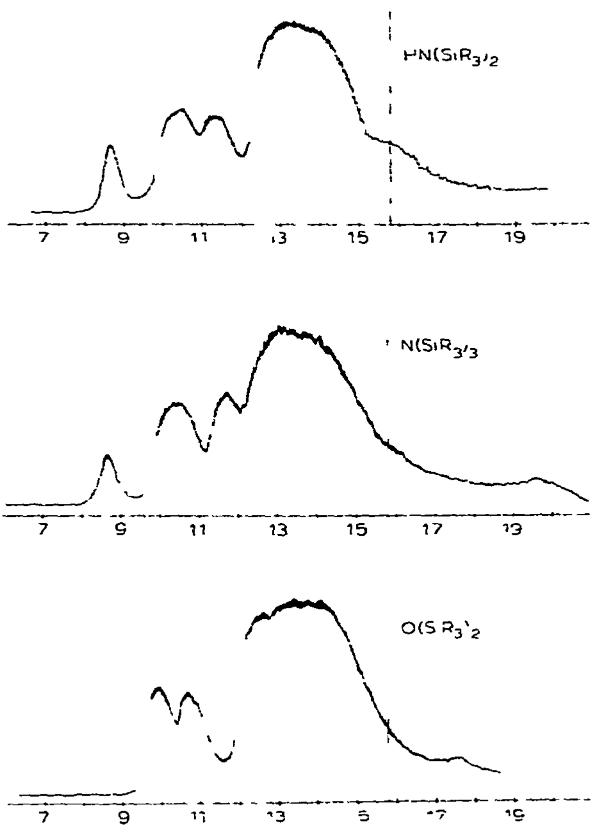


Fig 7 PE spectra of hexamethyldisilazane nonamethyltrisilazane, hexamethyldisiloxane

The PC levels of trimethylmethylenephosphoranes are stabilized relative to trimethylphosphine. Phosphorus basis functions of course should be lowered, depending on the charge distribution of the ylide (P=C) bond Unfortunately, PC ionizations appear usually as a shoulder on the CH-mounds, which prevents accurate measurement, and so we will not discuss them further.

We believe the charge separation in ylides and the effect of different β-atoms [$P(CH_3)_3$ and $Si(CH_3)_3$] to be the reason for two distinct centres of energy in the CH-mounds, being about one eV apart.

Isoelectronic non-ylidic compounds

Photoelectron spectra of compounds (IX), (X), (XI) are shown below (Fig. 7) for comparison with ylides (II), (III), (VII), with which they are isoelectronic and approximately isosteric [23a]. When the relative intensities of the bands are taken into account, PE spectroscopy clearly reveals certain analogies. In particular, the spectra of the amines remind one strongly of those of the corresponding ylides, in which σ(SiN)-type ionizations have taken the place of the σ(PC) bands. Undoubtedly, the lower energy of the N electron pair shows much less tendency for a charge transfer onto the silicon centers than the ylidic one. This in turn results in a more or less unchanged SiC-type ionization, compared to the "TMS-standard". Furthermore, the H—C(Si) levels appear at higher ionization potentials, which would also be expected.

The siloxane (XI), however, cannot simply be taken as an isoelectronic analogue of the ylides (II) and (VII) The dissimilarity of the PE spectrum of hexamethyldisiloxane (IP_1 9 88 eV, IP_2 10.73 eV, IP_3 12.5 eV and IP_4 13.8 eV) with those of (II), (VII), (IX) is a result of the much higher VSIP's of oxygen compared to any other of the central atoms This too, is reproduced by the CNDO results.

In the silazane (IX) the HOMO is preponderantly a nitrogen p_z-orbital with slight bonding interaction with silicon d-orbitals [just as in (II)] followed by several SiC-localized orbitals.

In the siloxane case, however, these same SiC orbitals are the highest occupied ones. The corresponding MO with a large oxygen p_z-coefficient [and no Si(d)-contribution] is even lowered by hyperconjugative SiC interaction.

The CNDO/2 approach

Applying a semi-quantitative MO treatment such as the CNDO/2 method [19], one gets a more delocalized picture of the energy levels in the molecule This may be used for assignment, and is also a valid tool for making further predictions*.

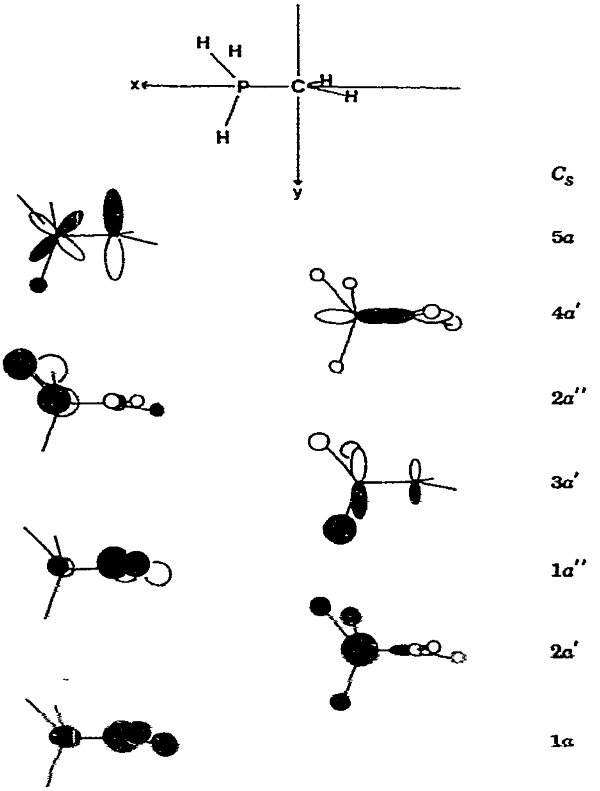


Fig. 8. CNDO/2 molecular orbitals for $H_3P = CH_2$.

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* SFC - MO calculations were done with QCPE program 141 on a UNIVAC 1108/Zentrales Rechen-institut, Universität Frankfurt.

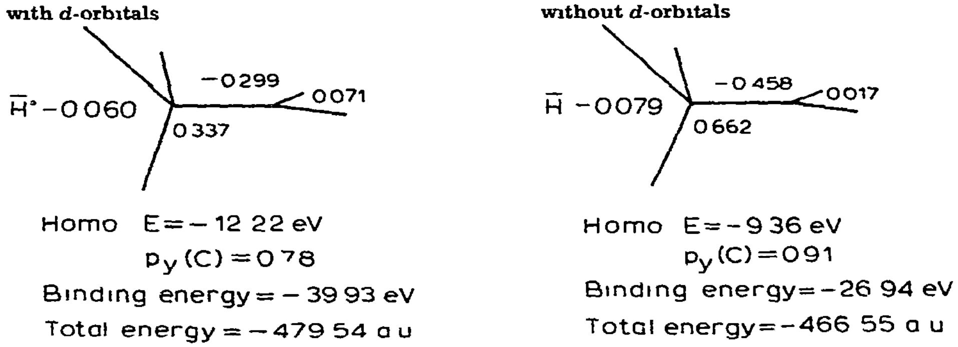

Fig 9 CNDO/2-atomic charges and representative energies for $H_3P=CH_2$

Theoretical studies on the ab initio and ETH level have already been concerned with the question of bonding in the simplest hypothetical phosphorus ylide $H_3P=CH_2$ [20,21]

Fig. 8 shows the LCAO - MO representation for the seven occupied valence shell molecular orbitals, constructed with the dominating CNDO/2 coefficients. The resulting orbital sequence (1*a*′ 2*a*′ 1*a*″ 3*a*′ 2*a*″ 4*a*′ 5*a*′) is satisfactorily in accord with the ab initio results. Only the neighbouring 4*a*′ and 2*a*″

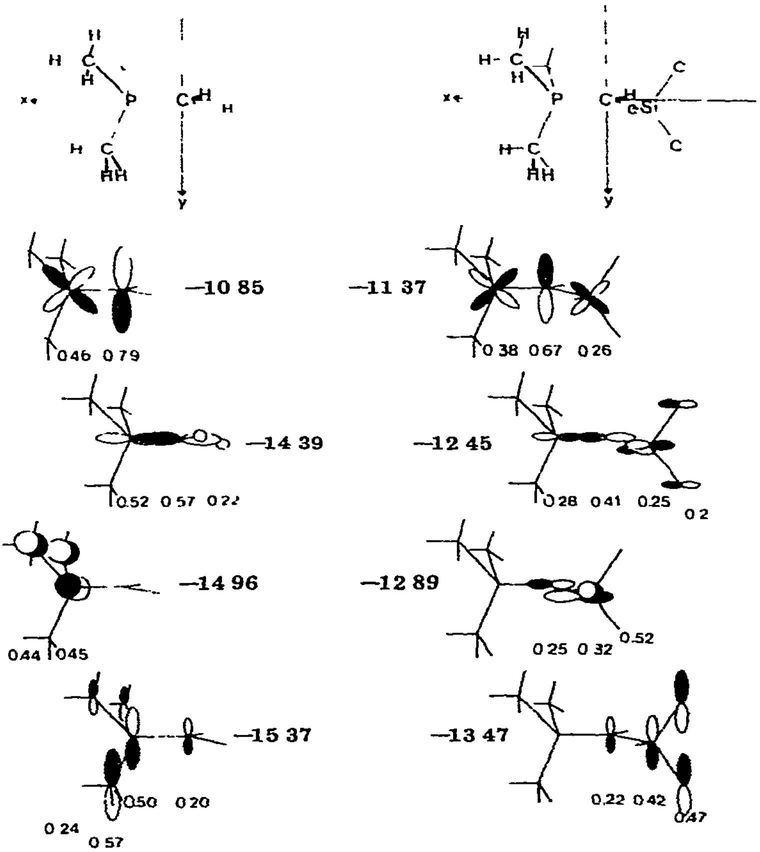

Fig. 10 The four highest occupied MO's for $Me_3P=CH_2$ and $Me_3P=CH—SiMe_3$ including MO energies and coefficients

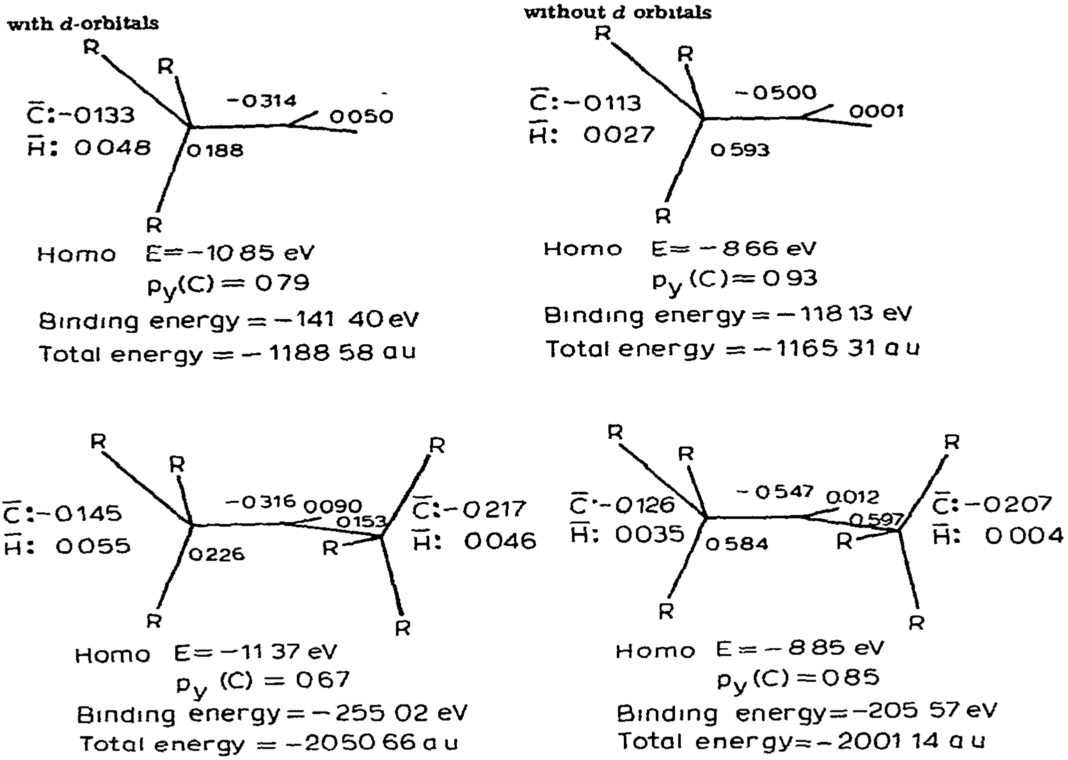

Fig 11 HOMO properties, binding-, total energy and atomic charges depending on the basis set Top $Me_3P{=}CH_2$ bottom $Me_3P{=}CH{-}SiMe_3$

orbitals have changed places. The orbitals $3a'$ and $2a''$ originate from the corresponding degenerate pair of P—H-bonds in the C_{3v}-symmetric phosphine. A similar picture, of course, is typical for the $P(CH_3)_3$ group in ylides of almost C_{3v} local symmetry.

For a more complete comparison with the other two calculational methods, the molecular distribution of atomic charges is given below (Fig. 9).

Pictures for the four highest occupied molecular orbitals of the simplest existing methylidene (I) and its silicon derivative (II) are presented in Fig. 10. The numbers given are the calculated MO coefficients and energies* of the CNDO/2 approximation. The analogous values to Fig. 9, as are relevant for a comparison of calculations, where *d*-type Slater functions are included or not, are given in Fig. 11.

Reactivity differences of ylides induced by silicon ("silicon stabilization") such as those observed by Schmidbaur et al., may be well understood as a withdrawal of electron density from the p_y-orbital of the ylidic carbon atom. Such a problem is preferably approached through comparison of the charge distribution in the HOMO's of the different species.

As revealed by photoelectron spectroscopy, the energetic availability of the HOMO electrons proves to be quite unchanged. As should be expected, one does find characteristically differing MO coefficients (Table 3).

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* Use of *s*-functions in the CNDO/2 version, when calculating the two-electron-integrals, may be the reason for a too small calculated inductive effect. This leads to a slight artificial HOMO stabilization on silicon substitution

TABLE 3
HOMO COEFFICIENTS AND NET ATOMIC CHARGES OF YLIDIC SYSTEMS

Highest occupied π-level			
P (d_{xy})	C(p_y)	Si(d_{xy})	Calculated system
0 50	0 78		$H_3P{=}CH_2$
0 41	0 63	0 28	$H_3P{=}CH{-}Si(CH_3)_3$
0 34	0 51	0 24/0 24	$H_3P{=}C(Si(CH_3)_3)_2$
0 39	0 63	0 31/0 02	$H_3P{=}CH{-}Si_2(CH_3)_5$
0 46	0 79		$Me_3P{=}CH_2$
0 38	0 67	0 26	$Me_3{=}CH{-}Si(CH_3)_3$
Charge on the atom			
q(P)	q(C)	q(Si)	
+	—	+	
0 337	0 299		$H_3P{=}CH_2$
0 365	0 304	0 169	$H_3P{=}CH{-}Si(CH_3)_3$
0 381	0 237	0 171	$H_3P{=}C(Si(CH_3)_3)_2$
0 378	0 290	0 043/0 059	$H_3P{=}CH{-}Si_2(CH_3)_5$
0 188	0 314		$Me_3P{=}CH_2$
0 226	0 316	0 153	$Me_3P{=}CH{-}Si(CH_3)_3$

The limiting size of the matrices of the QCPE program No 141 did not allow calculations for bigger systems such as compound (III) etc. For this reason we approximated those molecules by the before used method of replacing the methyl groups at the phosphorus by hydrogen atoms. The σ-system is relatively unaffected by this, and shows up more clearly.

A model calculation for the exocyclic bis-ylide (V) has been done, where all methyl groups have been substituted by hydrogen atoms. The seven highest MO's are given in Fig. 12. The orbital sequence has been changed in order to account for the known differences in SiC-vs-SiH-containing molecules. It should be noted that even this poor approximation nicely shows the π_+/π_- levels, a strongly localized and destabilized Si—Si bond, as well as split C—Si—C-bonds, as expected from LCBO arguments (Fig 6)

Conclusions

More detailed studies directed towards complete understanding of ylidic systems are already in preparation So far "silicon stabilization" has proved not to be a stabilization of the HOMO, which means the ylide π-level. In the CNDO/2 approximation the basis for Schmidbaur's transylidation reactions appears to be a change in MO coefficients.

Proton resonance shifts show a similar variation as do ionization potentials. Although exact mathematical correlation is impossible because of anisotropy effects, one common feature should be pointed out. This is, that increased

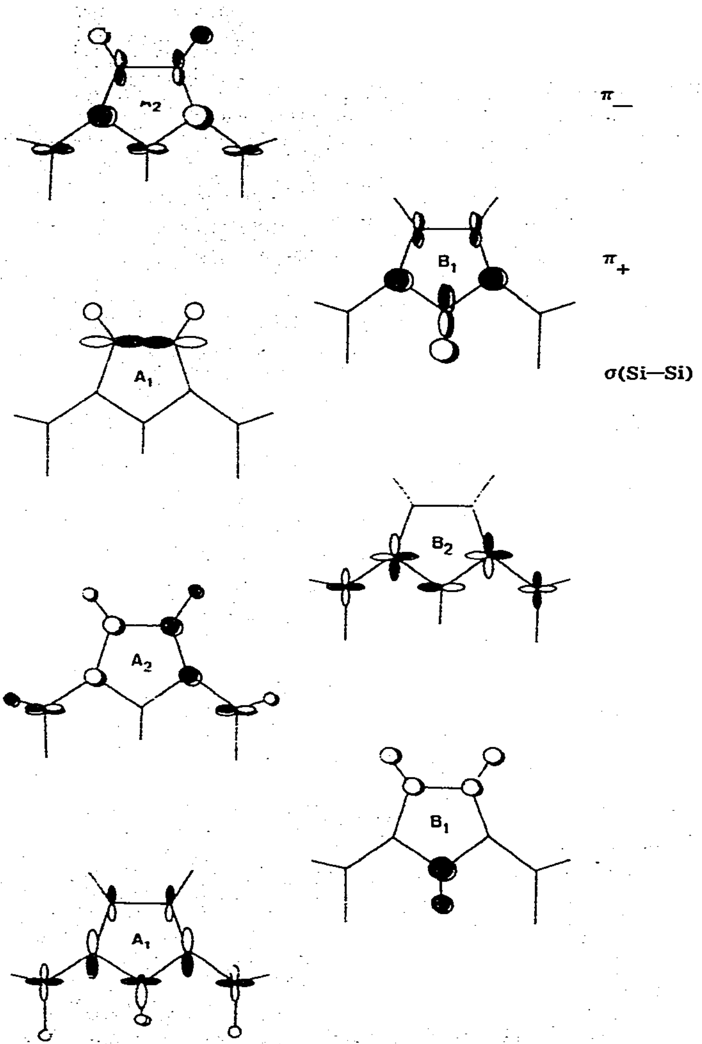

Fig. 12. The seven highest occupied MOs for the bis-ylide (V).

negative charge at the carbon atom results in a better shielding of the attached hydrogen atom. At the same time it raises carbon basis functions, resulting in a lower ionization potential, when ionization is from a carbon localized molecular orbital. This is reflected in the CNDO/2-atomic charges.

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References

1 H Schmidbaur and W Wolfsberger Chem Ber 100 (1967) 1000

2 H Schmidbaur and W Tronich, Chem Ber 100 (1967) 1032

3 H Schmidbaur and W. Malisch, Chem Ber 103 (1970) 97

4 H Schmidbaur and W Malisch, Chem Ber 103 (1970) 3007.

5 H Schmidbaur and W Vornberger, Chem Ber 105 (1972) 3173

6 H Schmidbaur and W. Vornberger, Chem. Ber 105 (1972) 3187

7 H Schmidbaur, W Buchner and D Scheutzow, Chem Ber 106 (1973) 1251

8 H Alt H Bock F Gerson and J Heinzer, Angew Chem 79 (1967) 933

9 H Bock and H. Seidl, J Organometal Chem 13 (1968) 87

10 H Bock, H. Seidl and M. Fochler, Chem Ber 101 (1968) 2815

11 H Bock and H Seidl, J Amer Chem Soc 90 (1968) 5694

12 H Bock and H Seidl, J Chem Soc B (1968) 1158

13 J Kroner and H Bock, Theor Chim Acta 12 (1968) 214

14 C G Pitt and H Bock, J Chem. Soc Chem. Commun (1972) 28

15 P Mollere, H Bock, G Becker and G Fritz, J Organometal Chem , 46 (1972) 89

16 H Bock and S Elbel, to be published

17 H. Bock and W Ensslin, Angew. Chem 83 (1971) 435

18 J H Hillier and V.R Saunders, Trans Faraday Soc 66 (1970) 2401

19 J Pople and D Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill New York 1970,
H Hinze and H H Jaffe, J Amer Chem Soc 82 (1962) 545

20 I Absar and J R Van Wazer, J Amer Chem Soc 94 (1972) 2382

21 R Hoffmann, D B Boyd and S Z Goldberg, J Amer Chem Soc 92 (1970) 3929

22 U Weidner and A Schweig, Angew Chem 84 (1972) 167

23 E Haselbach J A Hashmall E Heilbronner and V Hornung, Angew Chem , Int Ed Engl 8 (1969) 878

23a H. Schmidbaur Fortschr. Chem Forsch , 13 (1969) 167, Advan Organometal Chem , 9 (1970) 260

24 U Krynitz Ph D Thesis, Univ of Munich, 1969

25 H. Bock and B G Ramsay, Angew Chem., 85 (1973) 773 Angew Chem , Intern. Ed. Engl. 12 (1973) in press