Photoelectron Spectra and Molecular Properties. 58.[1,2] Phosphorus Ylides: Gas Phase Ionization Potentials and Charge Distribution

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Abstract: By an elaborate experimental technique, photoelectron spectra have been recorded of 17 salt-free phosphorus ylides, R_3PCXY, with substituents R = CH_3, C_6H_5 and X, Y = H, CH_3, $Si(CH_3)_3$, C_6H_5, $-(CH)_4-$, $CH{=}CH_2$, $CR'{=}CH_2$, $CH{=}CHR'$ (R′ = CH_3, C_6H_5). For the smallest parent system known, $(H_3C)_3PCH_2$, the ionization potentials verify the charge distribution P^+-C^- in full accordance with the results of extensive CNDO calculations. The first PE band at only 6.81 eV, assigned to predominantly carbanion ionization, is shifted to even lower energy in most derivatives. The effect of various substituents, R, X, and Y, are rationalized as follows: (i) exchange R = CH_3 by C_6H_5 delocalizes the P^+ charge, and (ii) substitution of X = H by CH_3 reduces the C^- charge; (iii) no PE band shift is noticed on silylation X = H → $Si(CH_3)_3$ and in analogy to the "perfluoro effect", which leaves π ionizations unaffected, a "silyl effect" towards anion centers can be defined; (iv) the PE splitting pattern of the benzylidene derivative (X = C_6H_5, Y = H) evidences strong inductive as well as conjugative perturbation of the benzene π system; (v) the C^- charge delocalization in the cyclopentadiene ylide (R = C_6H_5, X/Y = $-(CH_2)_4-$) leads to enhanced P^+ charge as manifested by increased phenyl π ionization energies; (vi) largest substituent effects are exhibited if the smallest π system (X: $CH{=}CH_2$) is attached to the C^- carbanion center; the resulting unsymmetrical charge distribution can be demonstrated by additional methyl perturbation (X: $(H_3C)C{=}CH_2$ and $HC{=}C(CH_3)H$). The PE spectroscopic observations on the phosphorus ylides investigated are in accordance with the results of CNDO calculations. In addition the CNDO atomic charges not only yield an empirical linear correlation with ^{13}C NMR chemical shifts but also shed some light on the varying reactivity of differently substituted ylides.

Phosphorus ylides, discovered by Staudinger and Meyer in 1919[3] and used in "Wittig reactions" since 1953,[4] have stimulated numerous investigations on their interesting structure and reactivity.[5] In the meantime, photoelectron spectroscopy has become a most powerful tool to yield—coupled with MO calculations—information on bonding in molecules.[8,9] As a starting point for the following discussion Figure 1 displays combined helium(I),[9] and helium(II),[10] (for ESCA, cf. ref 11) spectra of $(H_3C)_3PCH_2$,[12] the simplest phosphorus ylide known, and an assignment of its ionization energies IE_n based on modified CNDO eigenvalues ϵ_J^{CNDO} assuming validity of Koopmans theorem $IE_n = \epsilon_J^{SCF}$.[13]

The molecule $(H_3C)_3PCH_2$ contains 32 valence electrons giving rise to 16 ionizations, of which 4 are attributed to molecular orbitals with predominant C(2s) character and therefore partly expected[8] outside the helium(I) measurement region >21.21 eV. Eye-catching is the singled out first PE band at only 6.81 eV being indicative for a high negative charge at the ylidic carbon center. The charge distribution P^+-C^- is confirmed by the ESCA ionization energies:[11] P(2p) increased by 1.24 eV relative to $P(CH_3)_3$ and C(1s) lowered by 2.6 eV relative to the internal methyl group standard. The second PE band corresponds to σ_{PC} skeleton ionizations, and mainly due to the P^+ charge, their center of gravity is shifted by 0.5 eV to higher energies relative to $P(CH_3)_3$. The next PE band hill contains several ionizations mainly from the trimethylphosphorus moiety, followed by bands stretching into the helium(II) region and assigned to s-type valence electron ionizations starting with the one of predominant $3s_P$ character (Figure 1).

Additional MO calculations (see Experimental Part) yielded the correlation diagrams dependent on the bond distance $d_{P^+C^-}$ as shown in Figure 2, which provide some clues as to why trimethylphosphorus methylene does not readily decompose to yield a carbene like the arsenic analogue, $R_3AsCH_2 \rightarrow R_3As + CH_2$.[14]

The changes in ϵ_J^{CNDO} and E_{total}^{CNDO} with increasing bond distance $d_{P^+C^-}$ (Figure 2) have been calculated under the assumptions that $(H_3C)_3P + CH_2 \rightleftarrows (H_3C)_3PCH_2$ possibly represents a valley in the hypersurface, and that the transition from the carbene singlet ground state to a higher singlet state can be simulated using the lowest unoccupied orbital. Opening, the angle ∠CPC = 100° to 109.5° yields the minimum of CNDO total energy at $d_{P^+C^-} \sim 1.7$ Å in close correspondence to the experimental value of 1.66 Å found for $(H_5C_6)_3PCH_2$;[15] the stabilization ΔE_{total}^{CNDO} amounts to ~10 eV. CNDO calculations without $3d_P$ orbitals in the basis set lead to only $\Delta E_{total}^{CNDO} \sim 1$ eV at the fictitious bond distance $d_{P^+C^-} \sim 2$ Å, thus indicating the importance of the latter within the model chosen. The simultaneous movement of the CNDO orbital energies (Figure 2) reveals that n_{C^-} is continuously stabilized, whereas σ_{PC} passes through a minimum. Finally, comparison of Figures 1 and 2 illustrates that the difference in ionization potentials $\Delta IE_{1,2}$ is best reproduced at the minimum energy distance $d_{P^+C^-}$.

The detailed description of the parent ylide, trimethylphosphorus methylene, allows discussion of the effects of P^+ and C^- substituents on ionization potentials and charge distribution in derivatives R_3PCXY investigated subsequently.

Experimental Section

General. Preparation, purification, and handling of all ylides except cyclopentadienylidene were carried out in flamed Schlenk-tubes under nitrogen or argon or in a high vacuum line. The solvents were dried using, consecutively, molecular sieves, $LiAlH_4$, and sodium wire and then saturated with nitrogen. Rigorous exclusion of air and moisture is essential because phosphorus ylides and especially the trimethyl derivatives are extremely sensitive to oxidation and hydrolysis.

Synthesis. (i) **Phosphonium Salts.**[16] The phosphonium salts corresponding to the investigated ylides were all accessible in high yields by direct reactions in stoichiometric amounts of phosphines $R^1R^2_2P$ (R^1, R^2 = CH_3, C_6H_5) and the appropriate organic halide. Methyl bromide was bubbled through a solution of the phosphine in benzene. Propenyl and butenyl halides were reacted with trimethylphosphine without solvent at 70 °C in sealed tubes. 1-Chlorobutene (2) as well as 3-chlorobutene (1) yielded mixtures of *cis/trans*-γ-methylallyltrimethylphosphonium salts. The resulting white crystalline precipitates were filtered off, only in the case of methylphosphines under nitrogen. The trimethylphosphonium salts then were simply washed with ether and dried in vacuo. Phenylphosphonium salts where recrystallized twice from methanol after addition of ether and washed thoroughly with benzene and ether before drying. All phosphonium

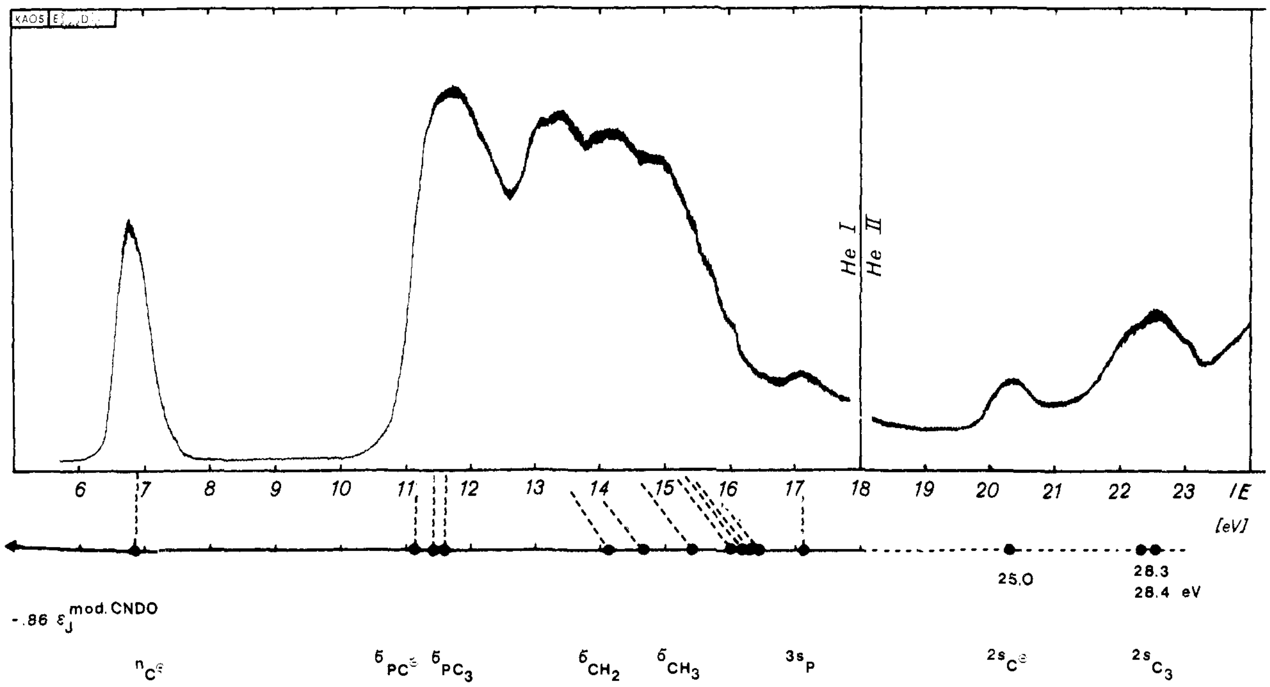


Figure 1. Helium(I)[9] and -(II)[10] photoelectron spectra of trimethylphosphorus methylene as well as CNDO eigenvalues (modified CNDO multiplied by 0.86).

salts were identified by their ^{1}H and ^{13}C NMR spectra in CD_3OD/Me_4Si.

(II) **Phosphorus Ylides.** Phosphoranes can be prepared salt-free by deprotonating the phosphonium salt with sodium amide in boiling THF (A).[16] Precipitating sodium halide was filtered off and the solvent evaporated. The thermally sensitive allylidenetrimethylphosphorane is preferably prepared by low-temperature deprotonation with butyllithium in ether (B)[17] and subsequent short-distance high-vacuum distillation. Trimethylsilylmethylenetriphenylphosphorane was obtained by pyrolysis of the corresponding phosphonium salt (C).[18] Cyclopentodienylidenetriphenylphosphorane was synthesized from pure *cis*-3,5-dibromocyclopentene by deprotonating the biphosphonium salt with aqueous sodium hydroxide (D)[19] and the crude ylide recrystallized from DMF. The phorphorus ylides have been purified as listed in Table I either by recrystallization from benzene or preferentially by distillation in vacuo. Identity and purity were established by ^{1}H NMR, ^{13}C NMR,[20] or PE spectroscopy (see below).

Photoelectron Spectra. Two Perkin-Elmer PS 16 with 127° electrostatic deflection-type analyzers (He(I) excitation = 21.22 eV), and one of them equipped with a heated inlet system, have been used, and a resolution better than 0.04 eV was achieved. For measurement, ylides of high volatility have been sealed off in evacuated NMR tubes, which after checking the NMR spectra were decapitated in the vacuum line of the PE spectrometer and evaporated via the gas inlet system. Allylidenetrimethylphosphorane had to be measured immediately after preparation, because its ready decomposition prevents storage. Ylides of low volatility had to be introduced into the spectrometer using the heated inlet system to provide the necessary vapor pressure. A special procedure was developed to avoid decomposition by contact with air, because only the cyclopentadienylide is stable under aerobic conditions: Liquids are sucked into an argon-flushed capillary, and then transferred into a Schlenk apparatus containing a sample tube of 1 mm diameter and 15 mm long. The first drop is discarded and the tube filled to about three-quarters. Solids may either be melted under argon or the crystals directly filled into the sample tube. Shortly before measurement the sample inlet tube is "sealed" with a drop of nitrogen-saturated hexane (Uvasol), which protects sufficiently against air if the sample is inserted without delay into the spectrometer inlet system. There, the covering hexane layer is pumped off immediately. For several triphenylphosphorus ylides, nevertheless, only the first ionization potentials could be obtained due to thermal decomposition yielding triphenylphosphine. Fortunately, even traces of impurities are detectable in the PE spectrum, especially if decomposition products are more volatile than the parent ylide, e.g., toluene and trimethylphosphine oxide from benzylidene trimethylphosphorane.

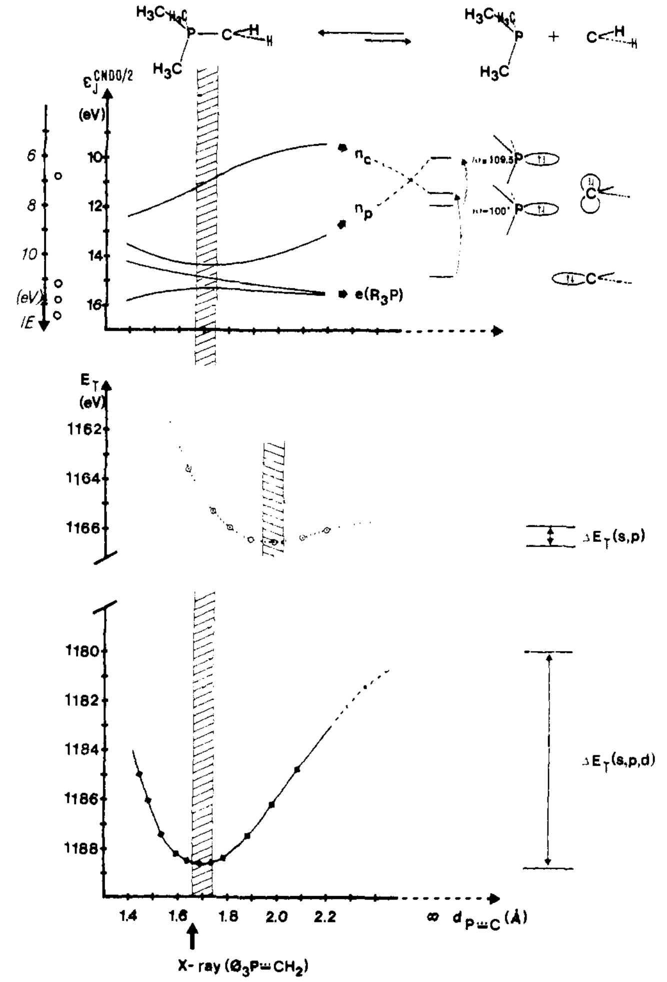


Figure 2. CNDO correlation diagrams: ϵ_J^{CNDO} or E_{total}^{CNDO} vs. bond distance $d_{P=C}$.

Table I. Phosphorus Ylides Investigated and Methods Used for Synthesis, Purification, and Recording of PE Spectrum

Ylide	Synthesis method[a]	Purification method[b]	Color	PE spectra recorded via	
				Gas inlet (°C)	Heated inlet (°C)
$(H_3C)_3PCH_2$	A	Dist.	Colorless	20	
$(H_3C)_3PCHCH{=}CH_2$	B (A)	Dist.	Colorless	20	
$(H_3C)_3PCHC(CH_3){=}CH_2$	A	Dist.	Colorless	20	
$(H_3C)_3PCHCH{=}CH(CH_3)$	A	Dist.	Colorless	20	
$(H_3C)_3PCHCH{=}CH(C_6H_5)$	A	Dist.	Yellow		45
$(H_3C)_3PCHC_6H_5$	A	Dist.	Yellow		50
$(H_3C)_2(C_6H_5)PCH_2$	A	Dist.	Yellow	35	
$(H_3C)(C_6H_5)_2PCH_2$	A	Dist.	Yellow		55
$(C_6H_5)_3PCH_2$	A	Dist.	Yellow		103
$(C_6H_5)_3PCHSi(CH_3)_3$	C	Dist.	Yellow		115
$(C_6H_5)_3PCHCH_3$	A	Cryst.	Red		97–104 dec
$(C_6H_5)_3PC(CH_3)_2$	A	Cryst.	Red		95–105 dec
$(C_6H_5)_3PCHCH{=}CH(CH_3)$	A	Cryst.	Deep purple		115–117 dec
$(C_6H_5)_3PCHC_6H_5$	A	Cryst.	Orange		150
$(C_6H_5)_3PC_5H_4$	D	Cryst.	Light yellow		190

[a] See text for identification of A–D. [b] Key: dist. = distillation, cryst. = crystallization.

Table II. Vertical Ionization Potentials IE_n^V (eV) of Trimethyl- and Triphenylphosphorus Ylides

Compound	Ionization[a,b]					
	n_{C^-}	n_P	π	$\sigma_{\overset{+}{P}-\overset{-}{C}}/\sigma_{PC}$		$\sigma_{CC}/\sigma_{CH}\cdots\cdots$[c]
$(H_3C)_3P$		8.60		11.3		13.7, 14.7 (16.5) (19.5)
$(H_3C)_3PCH_2$	6.81			11.8		(13.1, 13.6, 14.2, 14.9) 17.1
$(H_3C)_3PCHCH{=}CH_2$	6.20		9.20	10.9/11.8		13.6
$(H_3C)_3PCHC(CH_3){=}CH_2$	6.20		8.83	10.8/11.9		13.6
$(H_3C)_3PCHCH{=}CH(CH_3)$	6.02		9.06	10.7/12.0		13.5
$(H_3C)_3PCHCH{=}CH(C_6H_5)$	6.20		8.44 8.90 9.86	10.7/12.3		13.7
$(H_3C)_3PCHC_6H_5$	6.19		8.32 8.90	10.7/11.9	12.9	13.6
$(H_3C)_2(H_5C_6)PCH_2$	6.85		(9.32 9.69)	(11.4)11.8	12.4	13.1, 13.9, 14.6
$(H_3C)(H_5C_6)_2PCH_2$	6.70		(9.13 9.32 9.52)	(10.9/11.3)	12.0	13.0, 14.1, 14.7
$(H_5C_6)_3PCH_2$	6.62		9.27	11.0	11.9	13.9, 14.6, 16.4
$(H_5C_6)_3PCHSi(CH_3)_3$	6.71		————[d]			
$(H_5C_6)_3PCHCH_3$	6.15		————[e]			
$(H_5C_6)PC(CH_3)_2$	6.04		————[e]			
$(H_5C_6)_3PCHCH{=}CH(CH_3)$	5.95		————[e]			
$(H_5C_6)_3PCHC_6H_5$	6.01		8.23 9.25		11.9	13.9, 14.6, 16.6
$(H_5C_6)_3PC_5H_4$	6.66[f] 6.91		9.56	(10.9/11.5)	12.3	14.5, 15.1, 16.9
$(H_5C_6)_3P$		7.80	(8.87 9.16 9.27 9.70)	10.8	11.7	12.4, 13.3, 13.8, 14.5, 16.4

[a] Characterized according to main CNDO calculated contribution. [b] Values in parentheses ( ): overlapping bands. [c] All remaining well-separated peaks with distinct maxima are listed. [d] Compound contaminated with triphenylphosphine due to synthesis method chosen. [e] Thermal decomposition during record of PE spectrum. [f] IE_1 is assigned π by CNDO calculation for the trimethyl derivative.

Computational Details. The SCF MO calculations with s,p and s,p,d basis were carried out using either the CNDO/2 QCPE program or a modified version[21] reparametrize to fit PE spectra. Whereas for the parent system $(H_3C)_3PCH_2$ both versions yield nearly the same orbital sequence (Figure 1), CNDO/2 fails for ylides with π substituents placing numerous σ orbitals inbetween the π levels. In addition, Koopmans deviations[13] were approximated[22] for upper π and σ levels of several test compounds. The similar magnitude of the calculated corrections suggests that the CNDO (ground state) orbital sequence may be used for the assignment of the individual radical cation states within the same molecular system as well as for comparison within the series. The successive $\sigma\pi$-coupling of the phsphoranyl unit $[(CH_3)_3P{=}CH\text{-}]$ with methyl, vinyl, and phenyl groups was simulated by setting the appropriate π off-diagonal elements of the Hartree-Fock matrix equal to zero (subroutine SCFCLO). The calculations were based on standard geometries ($d_{P^+C^-} = 1.74$ Å, ∠CPS = 109° ∠PCX = 120°) unless stated otherwise.

Discussion

Representative photoelectron spectra of substituted ylides are displayed in Figure 3; and the vertical ionization potentials are summarized in Table II. The effects of the various substituents R, X, and Y in ylides R_3PCXY are discussed in the following order.

(i) Methyl/Phenyl Exchange at Phosphorus. The P-phenyl substitution of the parent ylide $(H_3C)_3PCH_2$ lowers the first ionization potential assigned to electron removal from the carbanion electron pair n_{C^-} stepwise to 6.62 eV, and simultaneously shifts the center of gravity of the phenyl $\pi_{1,2}$ ionizations closer to that of triphenylphosphine (Table II) for which a tentative deconvolution of the second PE band (Figure 3) favors a 2:2:1:1 split around 9.2 eV in accord with qualitative perturbation arguments based on its C_3-structure.[24] Especially

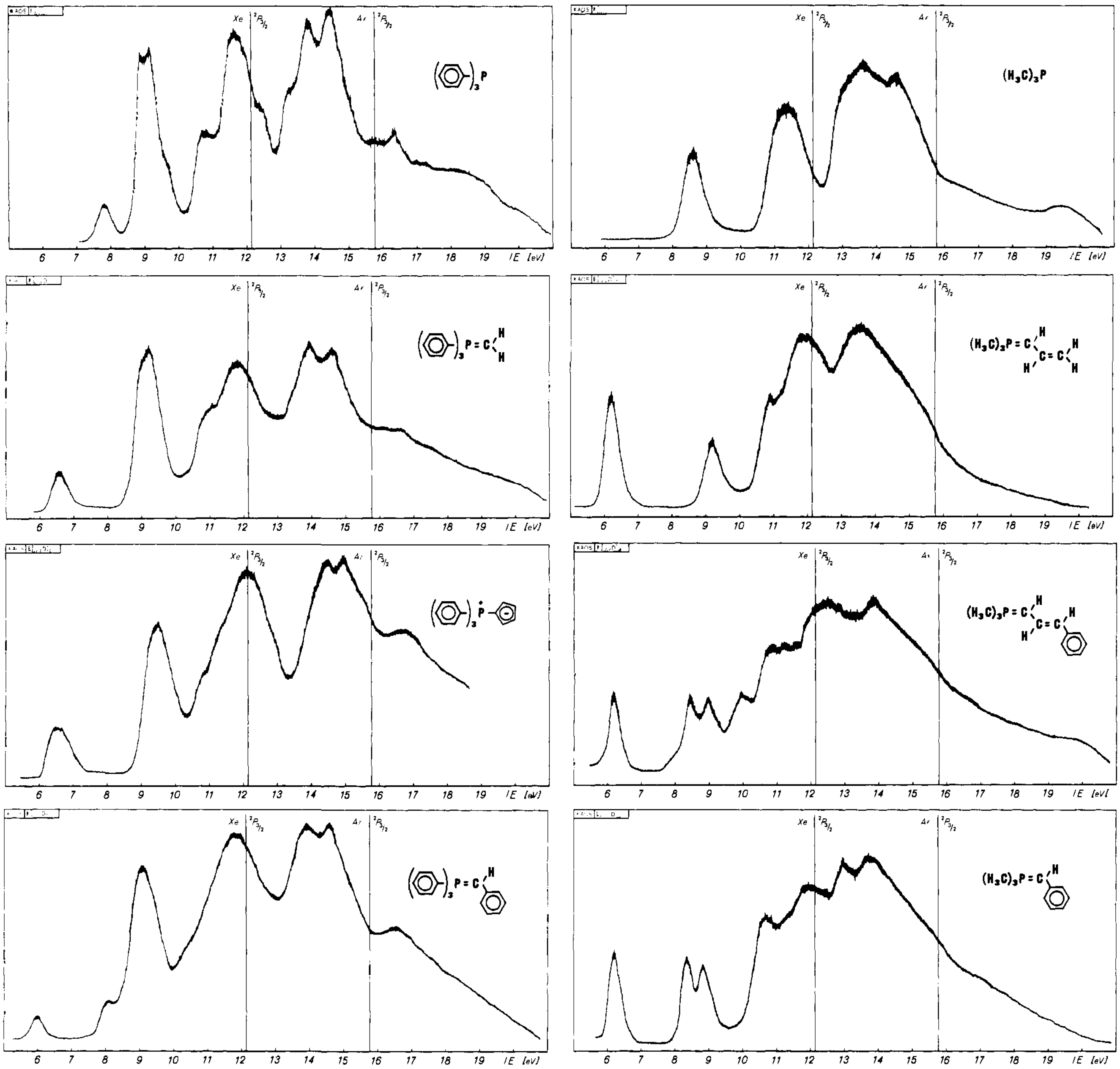


Figure 3. Helium(I) PE spectra of trimethyl- and triphenylphosphorus ylides in comparison to the corresponding phosphines.

in the monophenyl derivative both π_s and π_{as} phenyl ionizations are increased relative to triphenylphosphine due to the P^+ charge. On the other hand, starting from the trimethylphosphorus ylide, successive methyl/phenyl exchange improves the P^+ charge distribution, thereby reduces back-bonding $P^+—C^-$ and leads to the observed decrease of the first ionization potential.

(ii) Effects of Methyl and Trimethylsilyl Substituents at the Carbanion Center. Methyl group effects can be only investigated in ylides prepared from phosphonium salts with three substituents, from which proton abstraction is energetically less favorable, e.g., $[(H_3C)_3P^+CH_2CH_3]$ would yield a methylene ylide. For this reason the triphenyl derivatives have been chosen but because they proved to decompose thermally under measurement conditions yielding triphenylphosphine, only the first ionization potentials are listed in Table II. Methyl- and trimethylsilyl substituents at the carbanion center shift the first ionization potential of phosphorus ylides differently: whereas trimethylsilyl substituents leave the ionization potential unaffected or even—within the measurement limitations for extremely sensitive compounds—seem to slightly increase it, methyl groups cause quite a decrease. Stepwise assemblance simulated by CNDO calculations for separated units, after their formal connection under hydrogen elimination but without π interactions, and for the resulting methyl substituted ylide ($R = CH_3$) clearly emphasize a hyperconjugation model (Figure 4).

The CNDO atomic charges attached to the $>$P-C-C$<$ centers in Figure 4 illusrate that hyperconjugtive destabilization of the highest occupied orbital is not accompanied by an intramolecular $H_3C \rightarrow C^-$ charge transfer. For the orbital mixing in the ethylidenephosphorane model (symmetry C_1) two σ orbitals, ψ_{12} and ψ_{10}, both with predominant $>C^-—CH_2$ contributions have to be considered ($\Delta\epsilon_{19} = 0.51$ eV; $\Delta\epsilon_{12} + \Delta\epsilon_{10} = 0.62$ eV). Whereas the corresponding bands in the PE spectra of the C-methylated ylides are unfortunately hidden under broad ionization humps, they can be observed, e.g., for the π conjugation in benzylidenephosphorane (cf. iii), lending some support also to the CNDO hyperconjugation model (Figure 4).

In general, the smaller effects of trimethylsilyl substituents compared to those of methyl groups can be rationalized either

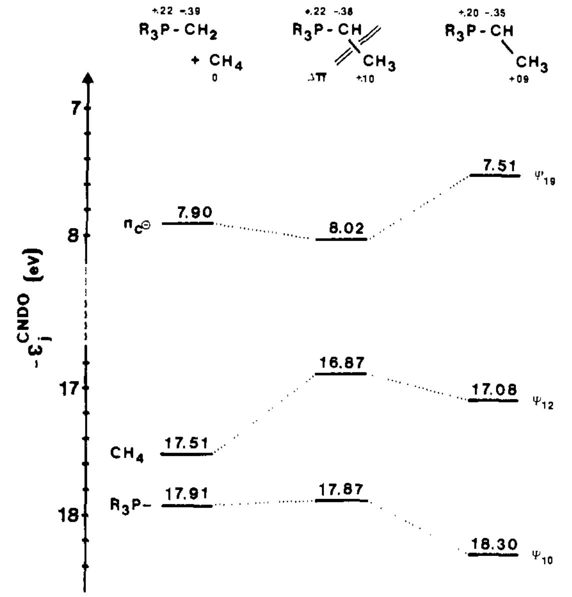
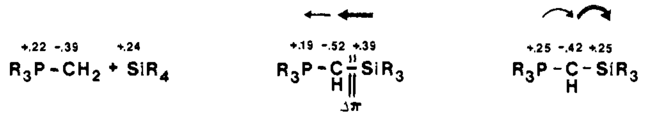


Figure 4. CNDO results for stepwise σπ coupling of the partial systems of ethylidenetrimethylphosphorane.

by reduced hyperconjugation[23] or by additional π → Si back-bonding.[23] The latter model will be preferred to interpret the nearly constant first ionization potential after silylation of the ylide carbanion center[9,14] (Table II) because of the CNDO atomic charges (R = CH$_3$):



$$\overset{+.22\ -.39}{R_3P-CH_2} + \overset{+.24}{SiR_4} \qquad \overset{+.19\ -.52\ +.39}{R_3P-\underset{H}{C}=SiR_3} \qquad \overset{+.25\ -.42\ +.25}{R_3P-\underset{H}{C}-SiR_3}$$

Contrary to the results for methyl substitution (Figure 4), both large σ donation and counteracting π back-bonding are calculated. In close analogy to the "perfluoro effect"[25] towards π systems, i.e., fluorine substituents acting simultaneously as σ acceptors and π donors, therefore a "silyl effect" towards "anion centers" might be defined, i.e., trimethylsilyl groups exerting σ donor plus π acceptor properties to achieve optimum charge distribution.

(iii) **π Interactions in Benzylidenephosphoranes.**[26] The PE spectroscopic differences measured for methylation at the carbanion center (Table II) suggest considerable conjugative interaction also with π substituents, which should be directly observable in case of separated π ionization PE bands. Particularly suited is the phenyl derivative, since in the antisymmetric one of the degenerate benzene e_{1g} orbitals a nodal plane passes through the substitution site, and thus π_{as} as an internal standard permits the splitting Δπ to be read off directly from the PE spectrum (Figure 3). The assignment of the lowest three π ionizations and the orbital movements on stepwise coupling of the partial systems as revealed by modified CNDO calculations analogous to Figure 4 are self-explanatory (Figure 5).

Again (cf. Figure 1) a reasonable numerical correspondence $-0.86\epsilon_J^{CNDO}/IE_n$ is achieved, satisfactorily reproducing the PE spectroscopically determined split $\Delta\pi = IE_3 - IE_2 = 0.56$ eV. Relative to benzene, the π_{as} ionization is lowered by 9.25 eV − 8.34 eV = 0.91 eV and reflects the extreme inductive perturbation by the adjacent carbanion. Comparison of CNDO atomic charges calculated both for benzyl anion and benzylidenephosphorane adds another point of view. The carbon atom charge in the benzyl anion is reduced to about half the amount after coupling to the (H$_3$C)$_3$P$^+$ unit, and the ring carbon charge to about one fifth. Toward the C$^-$ center, the phenyl ring ($\Sigma q_C^{ring} = +0.01$) acts as an acceptor, and it is illustrative to confront the impressive π ionization changes for phenyl substitution at C$^-$ with the almost negligible ones for methyl/phenyl exchange at the P$^+$ center (Table II). Nevertheless, the small effects discussed in section i show up also for trimethyl- and triphenylbenzylidenephosphoranes (Table II): due to better P$^+$ charge delocalization in the phenyl derivative and correspondingly enhanced C$^-$ charge, the ionization potentials decrease further, IE$_1$ from 6.19 to 6.05 eV and IE$_2$ from 8.32 to 8.2 eV, respectively.

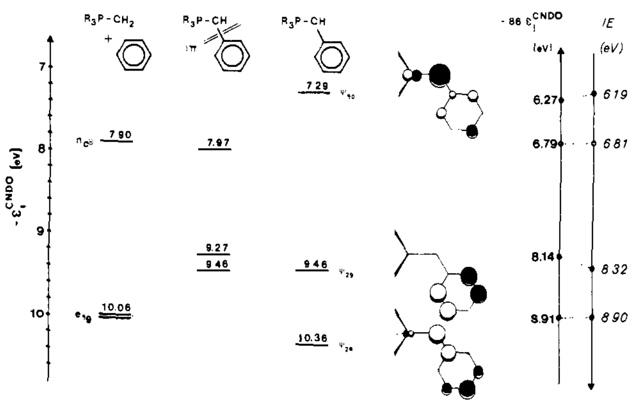
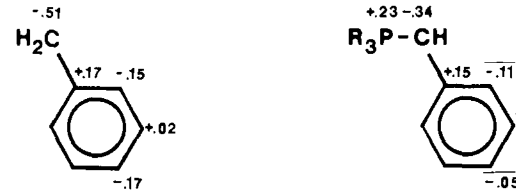
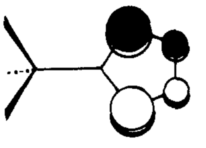


Figure 5. CNDO results for stepwise σπ coupling of the partial systems of benzylidenetrimethylphosphorane.

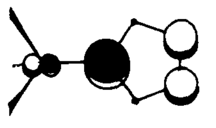


Σq_C	-.77	-.40
Σq_C^{ring}	-.26	-.06

(iv) **Charge Delocalization in Cyclopentadienylidenephosphorane.** Incorporating the carbanion center into a $(4n + 2)\pi$ electron system like cyclopentadiene anion leads to the known drastic changes in molecular properties: the resulting phosphorus ylide is no longer sensitive to moisture or air and becomes a non-Wittig ylide with respect to its reactions.[5a] Nevertheless, the first PE band is centered at ~6,7 eV. The tentative deconvolution using an expanded record suggests that it hides two ionizations separated by ~0.3 eV, which according to CNDO calculations for the methyl derivative[27] are assigned to predominantly cyclopentadiene π orbitals:



$\varepsilon_{25} = -7.59$ (eV)



$\varepsilon_{24} = -7.93$ (eV)

Relative to cyclopentadiene anion with its highest occupied orbitals at $\epsilon_{12,13}^{CNDO} = -2.3$ eV, a considerable inductive lowering is calculated, whereas the conjugative split of their degeneracy $\Delta\epsilon_J^{CNDO} = 0.34$ eV seems moderate and correlates with the estimated difference of the ionization potentials IP$_2$ − IP$_1$ ~ 0.3 eV. The third occupied π orbital of the ylide is

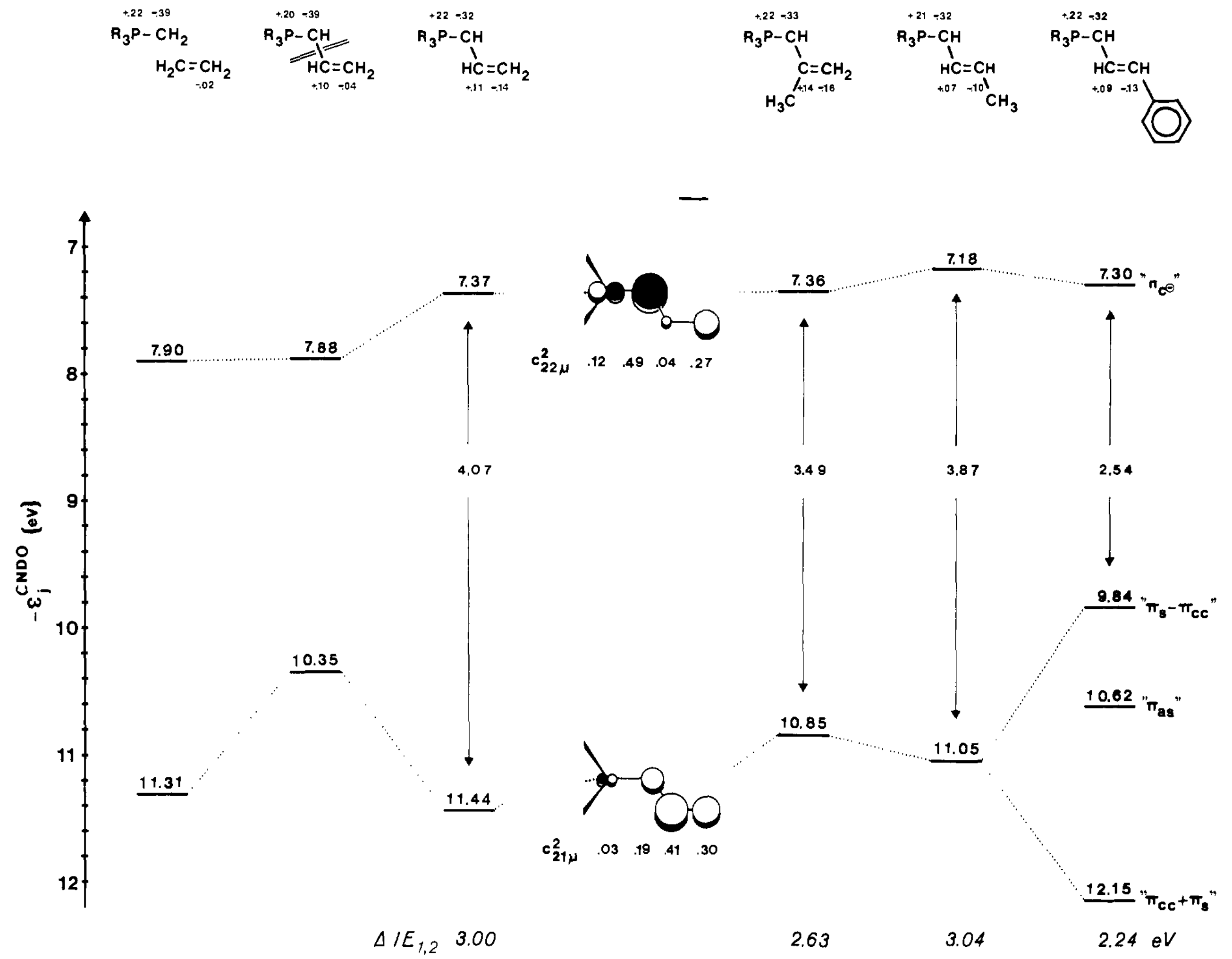
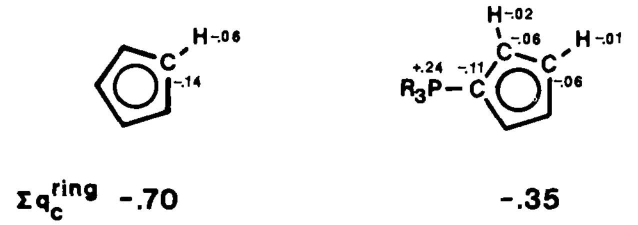


Figure 6. CNDO eigenvalues, π orbital diagrams, and atomic charges for allylidenetrimethylphosphoranes.

calculated $\Delta\epsilon_\pi^{CNDO} \sim 5$ eV below. The CNDO atom charges

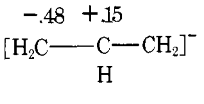


emphasize an extensive C$^-$ charge delocalization over the ring carbons, and analogous to the benzylidene derivative about half the cyclopentadiene anion charge is transferred on formal coupling with the $(H_3C)_3P^+$ moiety. Consequently, the P$^+$ charge remains quite high, a CNDO prediction, which is nicely supported by the largest increase of the phenyl π ionization center of gravity observed PE spectroscopically for triphenylphosphorus ylides: up to 9.6 eV (Table II). Summarizing in comparison to the benzylidene derivative discussed in section iii, the cyclopentadienylidene phosphorane shows due to incorporation of the C$^-$ center into a $(4n + 2)$ π system a smaller $\pi_{P^+C^-}$ interaction, a stronger C$^-$ delocalization, and correspondingly a larger P$^+$ charge.

(v) **Allylidenephosphoranes: Allylanion Perturbations.** In conclusion, PE spectroscopic findings are reported on the attchment of the smallest π system ethylene to the carbanion center forming a phosphonium substituted allyl anion. Besides large and translucent effects observed, additional information can be gathered by further methyl and phenyl perturbations.

The PE spectrum of allylidene trimethylphosphorane (Figure 3) displays two bands at lower ionization potentials (Table II: 6.20 and 9.20 eV) which are straightforwardly assigned either by CNDO calculations or by the additional substituent perturbations to predominantly n_{C^-} and π_{CC} orbitals (Figure 6).

Figure 6 shows that the differences in CNDO eigenvalues, $\Delta\epsilon_J^{CNDO}$, reasonably resemble those in ionization potentials $\Delta IP_{1,2}$. The calculated atomic charges display the following characteristics: P$^+$ remains constant both on coupling on the subunits and in all four derivatives, C$^-$ is reduced relative to allyl anion



$$\overset{-.48}{[H_2C}\text{——}\overset{+.15}{\underset{H}{C}}\text{——}CH_2]^-$$

by π coupling, and the substituent dependent effects at β and γ carbons can be rationalized by methyl groups pushing charge to the adjacent unsubstituted vinyl carbon center—in close analogy to the β-effect discussed for ^{13}C NMR shifts.[28] The changes in the π ionization potentials IE$_1$ and IE$_2$ are best interpreted starting from the $(CH_3C)_3P^+$ perturbed allyl anion π orbitals (Figure 6). According to the squared orbital coefficients $c_{J\mu}{}^2$, the highest occupied orbital ψ_{22} still almost possesses a node through the central carbon, and correspondingly IE$_1$ is not lowered on β methyl substitution (Figure 6). The shifts ΔIE_1 and ΔIE_2 on γ methyl substitution can be comprehended by first-order perturbation $\Delta IP \sim \delta\epsilon_J \sim c_{J\mu}{}^2\delta\alpha_{CH_3}$ with $\delta\alpha_{CH_3} \sim 0.6$ eV. The relatively large decrease ΔIE_2 =

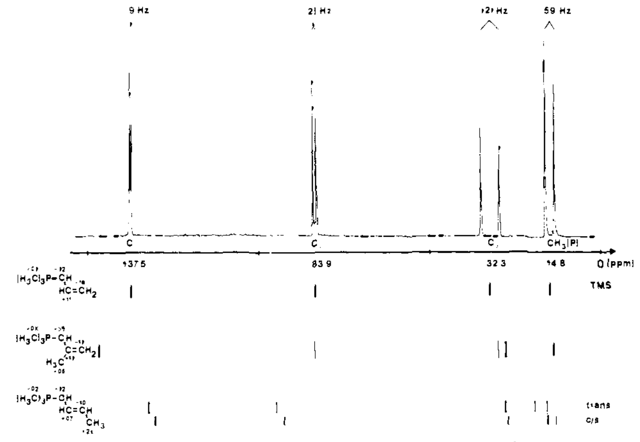
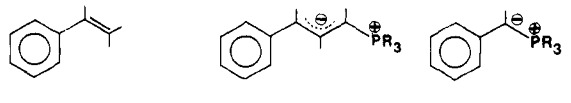


Figure 7. ^{13}C NMR spectrum of allylidenephosphorane[32] and changes in chemical shifts[20] and in CNDO atomic charges due to methyl substitution.

−0.38 eV on β-methyl substitution (ΔIE_1 being too small to detect any deviation) requires an additional explanation: For analogous observations concerning methyl substituted butadines[29] and hexatrienes[30] a "through space" π interaction with the double bond opposite has been proposed.[29] Finally, the phenyl substituent effect in cinnamylidene phosphorane (Figure 6) becomes transparent looking at benzene π_{as} ionization potential shifts along the series



$IE(\pi_{as})$ 9.25 eV 8.90 eV 8.32 eV

which is evidence for the perturbation of the benzene ring by an adjacent allylic anion center: therefore cinnamylidene phosphorane also might be considered an 1-phenyl-3-trimethylphosphonium substituted allylanion.

Summarizing the PE investigations and the CNDO results, the allylidenephosphorane π system can be fully rationalized on the basis of an allyl anion model with its orbitals "visualized" by substituent perturbations.

(vi) **^{13}C NMR Chemical Shifts.** Throughout the preceding discussions CNDO atomic charges have been used to further rationalize ionization energy changes cf. Figures 4 and 6). n order to support these arguments, an empirical correlation with ^{13}C NMR chemical shifts has been attempted in spite of reservations justified in other cases[31] with presumably less pronounced charge domination as to be expected for ylides. To begin with, Figure 7 shows the ^{13}C NMR spectrum of allylidenephosphorane and the changes in chemical shifts due to methyl substitution.[20]

Obviously, the ^{13}C chemical shifts of allylidenephosphorane and methyl derivatives are reflected even in some detail by the calculated CNDO atomic charges (cf. also Figure 6). Within the "sp^2-hybridized" carbons, the C_α signals display the largest high-field shift, followed by C_γ and the almost normal C_β (cf. ethylene $\delta^{13}C = +122$ ppm[28]). Methyl substitution in β position increases and in γ position reduces the charge differences in the allyl system. Even some of the calculated smaller changes, e.g., for C_β or the near-constancy for C_α are in accord with the observed ^{13}C NMR signals.[20] The correlation $\delta^{13}C/q_C^{CNDO}$ can be generalized to comprise also the other trimethylphosphorus ylides; for the conjugated derivatives listed in Table III an optimum regression results if CNDO π partial charges, q_C^π, are employed (Figure 8).

As evident from Figure 8, the $\delta^{13}C$ shifts group themselves according to α, β, and γ positions around a regression line with a slope of 240 ppm/unit charge, which incorporates in addition to benzene also ethylene[28] as well as other π hydrocarbons. The satisfactory heuristic correspondence suggests that it is predominantly the carbon charge and the related $1/r^3$ dependence of the paramagnetic term,[31] i.e., the radius of the carbon p_π orbital, which are responsible for the direction and magnitude of the observed shifts. Accordingly, CNDO partial π and/or net atomic charges reliably approximate the actual electon distribution in ylides, and therefore contribute another aspect to the interpretation of PE spectra.

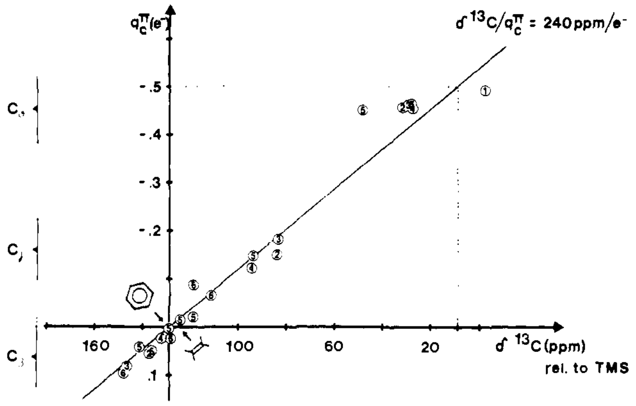
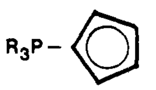


Figure 8. Correlation of chemical shifts ^{13}C (ppm relative to $Si(CH_3)_4$) vs. CNDO π charges q_C^π (cf. Table III).

A critical test of the CNDO predictions (Figure 8) is the ^{13}C NMR chemical shifts of cyclopentadienylidenephosphorane, the ylide with the most peculiar molecular properties (iv):



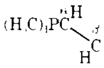
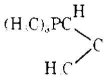
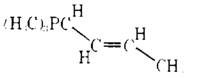
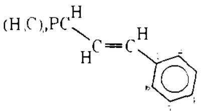
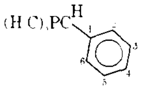
	C_α	C_β	C_γ
q_C^π (R= CH_3)	−.28	−.12$_5$	−.10
$\delta^{13}C$ (R= C_6H_5)	78.3	114.6	117.2

Although ^{13}C chemical shifts for the trimethylphosphorane are not yet available,[27] the literature values for the phenyl derivative[33] already fit the trend (Figure 8). Relative to "normal" ylides, the ^{13}C NMR signal is shifted ca. −80 ppm relative to the parent compound into the C_γ region, in full agreement with the diminished charge. In addition, C_β and C_γ charges are reduced relative to the cyclopentadienide system (iv). Both P charge and π delocalization add to a most effective stabilization of the π anion.

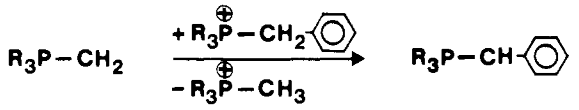
(vii) Concluding Remarks: Ylide-Stabilzed Carbanions. Thrughout the preceding chapters, several independent models have been emphasized: the coupling of carbene and phosphine to yield phosphorane, the stepwise assemblance of substituted ylides introducing σ and π interactions consecutively, and the stabilization of carbanions due to adjacent R_3P^+ centers. For the latter approach, the orbital energy changes, which accompany the charge redistribution in the typical systems discussed (cf. ii through v) have been calculated. The resulting CNDO orbital movements do have in common: a large stabilization due to the $(H_3C)_3P^+$ substitution, a small lowering on inclusion of 3d orbitals into the basis set, and shifts of comparable magnitude within the same system, i.e., no orbital crossings. Eventually, a satisfactory correlation with the corresponding PE ionization energies results. In this connection, the convincing empirical relation between ^{13}C NMR chemical shifts and CNDO charges (Figure 8) has to be mentioned again, because it further supports the above stressed rationalization of ylides as polarized carbanions.

The chemical reactivity of zwitterions like ylides presumably is governed by their charge distribution. Assuming further that the CNDO charges adequately approximate the electronic

Table III. CNDO π Partial Charges $q_C{}^{\pi}$ and ^{13}C Chemical Shifts $\delta\,^{13}$C (ppm relative to $Si(CH_3)_4$) for the sp^2 Carbons of Trimethylphosphoranes

No.	Ylide		C_α	C_β	C_γ	C_1	$C_{2/6}$	$C_{3/5}$	C_4
1	$(H_3C)_3PCH_2$	$q_C{}^{\pi}$ $\delta\,^{13}C$	−0.491 −2.4						
2		$q_C{}^{\pi}$ $\delta\,^{13}C$	−0.457 −32.3	+0.057 +137.5	−0.150 +83.9				
3		$q_C{}^{\pi}$ $\delta\,^{13}C$	−0.462 +29.8	+0.081 +146.2	−0.183 +83.5				
4		$q_C{}^{\pi}$ $\delta\,^{13}C$	−0.453 +27.7	+0.024 +131.9	−0.123 +94.5				
5		$q_C{}^{\pi}$ $\delta\,^{13}C$	−0.452 −49.0	+0.050 +136.7	−0.148 +94.0	+0.041 +142.4	−0.020 +119.0	+0.003 +129.2	−0.013 +125.1
6		$q_C{}^{\pi}$ $\delta\,^{13}C$	−0.463 +27.9			+0.096 +147.3	−0.089 +121.5	+0.023 +128.3	−0.067 +115.2

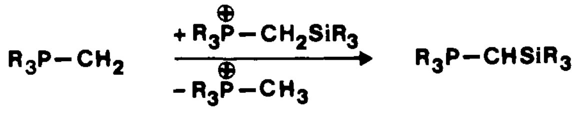
structure of ylides, they will be tentatively taken as a basis, to derive some systematic aspects on ylide reactivity. To avoid stereochemical complications, a simple proton transfer reaction will be considered, i.e., one of the so-called "transylidations" first reported by Bestmann and co-workers[5b], e.g.



q_C: −.39 −.34

q_C^{π}: −.49 −.46

Obviously, both CNDO net and π charge (cf. Figure 4 and Table III) are reduced in the product. For the analogous generation of a trimethylsilylphosphorane[5d]



$$R_3P{-}CH_2 \xrightarrow[-\,R_3\overset{\oplus}{P}-CH_3]{+\,R_3\overset{\oplus}{P}-CH_2SiR_3} R_3P{-}CHSiR_3$$

q_C: −.39 −.42

q_C^{π}: −.49 −.44

only a reduced π charge, is calculated while the net charge of the ylidic carbon even slightly increases due to the σ donor property of R_3Si substituents (cf. ii). Furthermore, in certain ylide reactions an increase of the P^+ charge, which stabilizes the carbanion, may play an important role.

Summarizing, ylides are the more stable and the more favored, the better the C^- charge is delocalized in the carbanion part and the larger the P^+ charge. The most striking example represents the air-stable non-Wittig triphenylcyclopentadienylidenephosphorane, which exhibits the highest P^+ charge observed so far, i.e., the largest increase in phenyl ionizations (Table II), as well as the most effective C^- delocalization by forming a 6π electron system, i.e., the largest $^{13}C_\alpha$ NMR downfield chemical shift (Figure 8).

Numerous other observations concerning ylide reactivity can also be easily incorporated in the carbanion charge concept. To quote just a few examples: Many reactions at the γ position of allylic ylides are known in the meantime,[34] in full accord with the considerable CNDO net charge (Figure 6) or the ^{13}C NMR chemicalshift (Figure 8). The same argument would predict allylidenephosphoranes to be bidentate and π-type ligands[35,36] as proven, e.g., by the x-ray structure determination[37] of $(OC)_4MO(R_3PCHCH{=}CH_2)$. The cyclopentadienylidenephosphorane expectedly reacts as a tridendate ligand and its 6π electron system forms sandwich complexes like $(OC)_3MO(R_3PC_5H_4)$.[38]

Conclusions drawn from a simplifying model, and especially, regarding an overall reactivity without corroborative mechanistic information should only be accepted with reservation. Nevertheless, several predictions of our model concerning, e.g., carbene generation from phosphoranes, proved to be quite valuable in the meantime.

Acknowledgment. Our work has been supported by Fonds der Chemischen Industrie and by Hoechst AG. Thanks are also expressed to H. Schmidbaur (Technical University Munich) for the stimulation to investigate the PE spectra of ylides and to H. tom Dieck (University Frankfurt) for helpful advice in synthesis and handling of the sensitive and unstable compounds.

References and Notes

(1) Part 57: B. Solouki, P. Rosmus, and H. Bock, *Angew. Chem.* **88**, 381 (1976); *Int. Ed. Engl.*, **15**, 384 (1976).

(2) Part of the thesis of K. A. Ostoja Starzewski, University Frankfurt, 1976.

(3) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).

(4) G. Wittig and G. Geissler, *Justus Liebigs Ann. Chem.*, **580**, 44 (1953), cf. the review by U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(5) (a) A. W. Johnson "Ylide Chemistry", Academic Press, New York, N.Y., 1966; (b) H. J. Bestmann und R. Zimmermann, *Fortschr. Chem. Forsch.*, **20**, 1 (1971) as well as in (c) "Organophosphorus Chemistry", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., (1972); (d) H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975).

(6) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.

(7) K. Siegbahn, C. Nordling, A. Fahlmann, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy", Almquists and Wiksells, Uppsala, 1967; as well as K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelins, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North Holland Publishing, Amsterdam, 1969.

(8) H. Bock and B. G. Ramsey, *Angew. Chem.*, **85**, 773 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 734 (1973).

(9) H. Bock, *Int. Pure Appl. Chem.*, **44**, 343 (1975), and literature quoted.

(10) The He(II) spectrum has kindly been measured by J. P. Mayer, Institute of Physical Chemistry, University of Basel (Switzerland).

(11) S. C. Avanzino, W. L. Jolly, M. S. Lazarus, W. B. Perry, R. R. Rietz, and T. F. Schaaf. *Inorg. Chem.*, **14**, 1595 (1975).
(12) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 595 (1968).
(13) T. Koopmans, *Physica* (*Utrecht*), **1**, 104 (1934); cf. also ref 8 or E. Heilbronner "Ups and Downs in UPS," in the Proceedings of the First International Congress of Quantum Chemistry, R. Daudel and B. Pullman, Ed., D. Reidel Publishing, Dordrecht, Holland, 1974, and literature quoted.
(14) K. A. Ostoja Starzewski, W. Richter, and H. Schmidbaur, *Chem. Ber.*, **109**, 473 (1976).
(15) J. C. J. Bart, *J. Chem. Soc. B*, 350 (1969).
(16) R. Köster, D. Simic, and M. A. Grassberger, *Justus Liebigs Ann. Chem.*, **739**, 211 (1970).
(17) W. Malisch, D. Rankin, and H. Schmidbaur, *Chem. Ber.*, **104**, 145 (1971).
(18) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **100**, 1032 (1967).
(19) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 6167 (1957).
(20) K. A. Ostoja Starzewski and H. tom Dieck *Phosphorus*, **6**, 177 (1976).
(21) J. Kroner, D. Proch, W. Fuss, and H. Bock, *Tetrahedron*, **28**, 1585 (1972).
(22) Thesis, K. Wittel, University of Frankfurt, 1974; cf. also B. T. Pickup and O. Goscinski, *Mol. Phys.*, **26**, 1013 (1973); B. Kellerer, L. S. Cederbaum, and G. Hohlneicher, *J. Electron Spectrosc.*, **3**, 107 (1974).
(23) Cf., e.g., W. Ensslin and H. Bock, *J. Am. Chem. Soc.*, **96**, 2757 (1974), and literature quotations given.
(24) J. L. Daly, *J. Chem. Soc.*, 3799 (1964).
(25) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Che. Soc.*, **94**, 1451 and 1466 (1972).
(26) K. A. Ostoja Starzewski, H. Bock, and H. tom Dieck, *Angew. Chem.*, **87**, 197 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 173 (1975).
(27) The corresponding cyclopentadienylidenetrimethylphosphorane has been prepared in the meantime and its PE spectrum recorded by K. Schwerdtfeger (Diplomarbeit University, Frankfurt, 1976).
(28) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(29) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).
(30) E. E. Astrup, H. Bock, K. Wittel, and P. Heimbach, *Acta Chem. Scand., Ser. A*, **29**, 827 (1975).
(31) Cf., e.g., ref. 28 p 102 ff, and literature quoted.
(32) The ^{13}C NMR spectrum of allylidenetrimethylphosphorane has kindly been recorded by A. Walter, University of Frankfurt (cf. ref 20).
(33) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).
(34) Cf., e.g., S. Tripett, "Ylides and Related Compounds" in Specialist Report "Organophosphorus Chemistry", The Chemical Society, London, 1975, p 161 ff.
(35) K. A. Ostoja-Starzewski, H. tom Dieck, K. D. Franz, and F. Hohmann, *J. Organomet. Chem.*, **42**, C35 (1972).
(36) A. Greco, *J. Organomet. Chem.*, **43**, 351 (1972).
(37) I. W. Bassi and R. Scordamaglia, *J. Organomet. Chem.*, **51**, 280 (1973).
(38) E. W. Abel and G. Wilkinson, *Chem. Ind.* (*London*), 1067(1959).

Preparation, Structure, and Role of Tetrakis(methoxycarbonyl)palladiacyclopentadiene Cyclic Diolefin Complexes in Selective Palladium-Catalyzed Cyclocotrimerization of Acetylenes with Olefins

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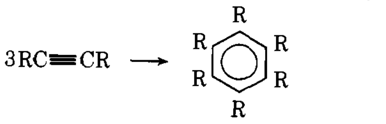
Abstract: Tetrakis(methoxycarbonyl)palladiacyclopentadiene cyclic diolefin complexes, $Pd[C_4(COOCH_3)_4]L$, for L = 1,5-cyclooctadiene and norbornadiene have been prepared. The latter complex has been characterized crystallographically. The material crystallizes with two molecules in space group C_i^1-$P\bar{1}$ in a cell of dimensions a = 10.560 (2), b = 10.583 (2), c = 9.710 (2) Å, α = 99.33 (1), β = 113.24 (1), and γ = 85.53 (2)°. The structure has been refined by standard methods to a conventional R index of 0.027, based on 3646 reflections above background. There is a nearly symmetrical coordination of the diolefin to the palladium atom of the metallocycle. The olefinic C=C bond lengths of 1.352 (4) Å in the norbornadiene fragment together with spectroscopic results suggest a net transfer of electrons from the electron-rich norbornadiene to the metallocycle which has electron-withdrawing substituents. The fact that the diolefin bonds more strongly to the metallocycle than does an activated acetylene is brought to bear on mechanisms of cyclotrimerization of acetylenes and cyclocotrimerization of two acetylene and one olefin molecule. The parent oligomeric $Pd[C_4(COOCH_3)_4]$ complex is an efficient catalyst for the cyclocotrimerization of two dimethylacetylenedicarboxylate molecules with norbornadiene to give 1,2,3,4-tetrakis(methoxycarbonyl)benzene. Use of norbornene in place of norbornadiene leads to the palladium-catalyzed stereoselective production of a cyclohexa-1,3-diene derivative in 94% yield.

The catalytic cyclotrimerization of acetylenes to form benzene derivatives (reaction 1) has been intensively investigated.[2-4] The cyclocotrimerization of two acetylene molecules with an olefin molecule to form cyclohexa-1,3-diene derivatives (reaction 2) has also been the subject of a number of studies,[5-9] but apparently no highly selective, catalytically efficient reactions have been found. This is because reaction 1 is commonly a competitive, fatal side reaction for (2). These two reactions have been postulated to proceed, at least in some instances, via a metallocyclopentadiene complex as the key intermediate,[4,7] as shown in Scheme I. Thus, in principle, high selectivity for the cyclocotrimerization reaction of acetylenes and an olefin may be achieved if the olefin binds much more strongly to the metallocyclopentadiene than does the acetylene. Indeed, Chalk[5] has reported the selective cyclocotrimerization between terminal or conjugated acetylenes and N-substituted maleimides. Such activated olefins are expected to bond very strongly to the metallocycle.



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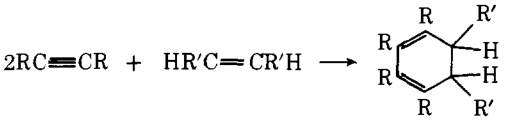

(2)

Another approach for preventing reaction 1, the cyclo-