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Electronic Structure and Reactivity. 8.[1] Iminophosphoranes—Simple Ylide Analogues? An Investigation of Quantitative and Phenomenological Differences

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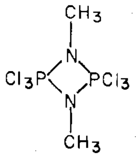
Gas-phase photoelectron spectra of 13 monomeric iminophosphoranes R_3PNX, with substituents R = $-CH_3$ or $-C_6H_5$ and X = $-H$, $-CH_3$, $-C_2H_5$, $-CH(CH_3)_2$, $-C_6H_{11}$, $-C(CH_3)_3$, $-Si(CH_3)_3$, or $-C_6H_5$, have been obtained. Compared to ylides, they show reduced oxidizability (higher IE's) as well as less tendency to split off phosphine. Alkyl substituents lower $n_N{}^{\pi}$ and $n_N{}^{\sigma}$ ionizations to a different degree, thereby reducing the 1-eV $n_N{}^{\pi}/n_N{}^{\sigma}$ energy gap of the parent system $(H_3C)_3PNH$. The trimethylsilyl substituent leaves the $n_N{}^{\pi}$ IE unchanged, inducing a $n_N{}^{\pi}/n_N{}^{\sigma}$ "degeneracy". *P*-Phenyl groups delocalize the P^+ charge, lowering the first IE. *N*-Phenyl groups delocalize the N^- charge, which is demonstrated by characteristic ^{13}C NMR chemical shifts and marked conjugative PE splittings. The high ylidic N^- charge offers a new example of an inductive ~1-eV low-energy shift for the phenyl π_{as} ionization, usually fixed at ~9.25 eV. Together with extensive CNDO calculations for $\geqslant P^{+}\overset{...}{\underset{...}{-}}N^{-}-$, interrelations with the isoelectronic ylides $\geqslant P^{+}\overset{...}{-}C^{-}<$ are differentiated, and connections to the azomethine bond system $>C{=}N-$ are discussed. CNDO/2 geometry optimization for $(H_3C)_3PNH$ gives a 166-pm P–N distance, a sp^2 nitrogen with a staggered N–H bond (C_s symmetry). Contrasting azomethines, we find "isomerization" takes place easiest through rotation. For $(H_3C)_3PNC_6H_5$, the phenyl ring is calculated to rotate rather freely around the N–C bond, some hindrance being imposed by through-space interactions. Calculated dipole moments are of the right order of magnitude. According to CNDO predictions for the protonated parent system $(H_3C)_3P^{+}\overset{...}{-}NH_2$, the pyramidal nitrogen geometry is only slightly favored over the planar form. Proton affinities are predicted for ylidic systems. The ylide-type charge distribution of the aminophosphonium ion explains the sensitivity of such salts toward hydrolysis. Metal coordination is believed to lead to angle widening. Unstable (phosphinimine)chromium and -molybdenum pentacarbonyls have been prepared for the first time. CO stretching frequencies in metal carbonyls document a reduced D/A proportion for phosphinimine ligands compared to ylides. The simple complexes themselves may be considered "stabilized ylides". With *N*-phenylphosphinimines Wittig reaction with coordinated carbon monoxide is observed. $\geqslant P^{+}\overset{...}{\underset{...}{-}}N^{-}-$ systems show bridging ligand character and produce binuclear metal tricarbonyls, approaching the behavior of rarely known deprotonated ylides $[R_3P\overset{...}{\underset{...}{-}}CX]^-$.

Introduction

Phosphinimines (phosphine imides, iminophosphoranes, imidophosphoranes)[2-4] are intermediate in reactivity between the corresponding methylenes (methylides) and oxides, which in turn is strongly influenced through variation of R and X: R_3PCX_2, R_3PNX, R_3PO. While compounds of the type Cl_3PNX are known to be dimers[5-8]



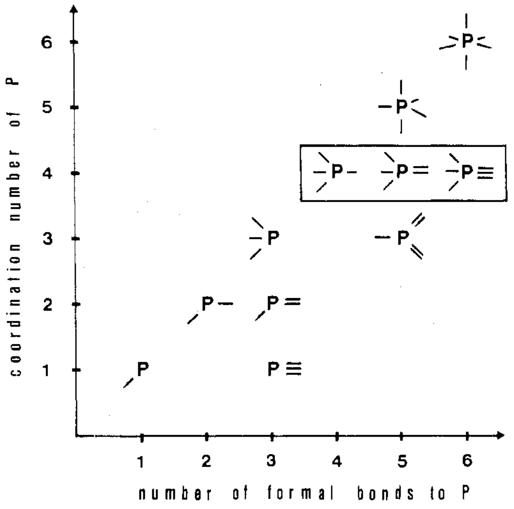
those under investigation in this study with substituents R = methyl or phenyl are monomeric. A detailed knowledge of their electronic structure is essential for a better understanding and manipulating of their chemical behavior. Consequently this also may be important for problems with inorganic oligo- and polymers of the phosphazene (phosphonitrile) type:[9-12] $[-R_2PN-]_n$. In general, phosphorus with the coordination number of 4 and four to six formal bonds to the central atom

$$R_3\overset{+}{P}{-}\overset{\overset{-}{..}}{\underset{..}{N}}X' \leftrightarrow R_3P{=}\ddot{N}X' \leftrightarrow R_3\overset{-}{P}{\equiv}\overset{+}{N}X'$$

$$R_3\overset{+}{P}{-}\ddot{N}XY \leftrightarrow R_3P{=}\overset{+}{N}XY$$

plays a significant role in the context of P chemistry (Scheme I). The following text concentrates on energetic and structural aspects together with charge distribution. Photoelectron (PE), NMR, and IR spectroscopy supported by CNDO calculations are the chosen methods of investigation. Reactivity is mainly discussed in terms of

Scheme I



ionization (oxidizability)

$$R_3PNX \rightarrow R_3PNX^+ + e^-$$

protonation (proton affinity)

$$R_3PNX + H^+ \rightarrow R_3PNX{-}H^+$$

transition-metal coordination (Lewis basicity)

$$R_3PNX + LM(CO)_5 \rightarrow (R_3PNX)M(CO)_n$$

Experimental Section

General Procedure. As in the case of ylides, all possible measures were taken, which enable preparation, purification, and handling of highly sensitive compounds, by rigorously excluding air and water.[1]

Synthesis. (i) Iminophosphoranes (Phosphinimines). In order to avoid explosive hydrazoic acid[3,13] and organic azides,[3] we chose de-

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

iminophosphorane	synthesis method[a]	purificn method[b]	color	state at room temp	PE spectra recording temp, °C	
					gas inlet	heated inlet
$(H_3C)_3PNH$	A	subl	colorless	solid	20	
$(H_3C)_3PNCH_3$	A	dist cond	colorless	liquid	20	
$(H_3C)_3PNC(CH_3)_3$	A	dist cond	colorless	liquid	20	
$(H_3C)_3PNSi(CH_3)_3$[c]	B	dist cond	colorless	liquid	20	
$(H_3C)_3PNC_6H_5$	A, B	dist cond	colorless	solid		45
$(H_5C_6)_3PNH$	C	cryst	colorless	solid		120
$(H_5C_6)_3PNCH_3$	A	cryst	colorless	solid		115
$(H_5C_6)_3PNCH_2CH_3$[d]	A	cryst	colorless	solid		110
$(H_5C_6)_3PNCH(CH_3)_2$[d]	A	cryst	colorless	solid		115
$(H_5C_6)_3PN\text{-c-}C_6H_{11}$[d]	A	cryst	colorless	solid		120
$(H_5C_6)_3PNC(CH_3)_3$	A	cryst	colorless	solid		105
$(H_5C_6)_3PNSi(CH_3)_3$	B	cryst	colorless	solid		75
$(H_5C_6)_3PNC_6H_5$	B	cryst	light yellow	solid		135

[a] See text for explanation of A–C. [b] Key: subl = vacuum sublimation, dist = vacuum distillation, cond = trap-to-trap condensation, cryst = crystallization. [c] Kindly provided by Dr. W. Wolfsberger, University of Würzburg (cf. ref 37). [d] Provided by Dipl. Chem. Halstenberg in the group of Professor Dr. R. Appel, University of Bonn.

protonation of aminophosphonium salts[14] with sodium amide in liquid ammonia (A).[4b,15–17] Subsequent evaporation of the solvent, extraction with ether, sublimation or distillation in high vacuum, or crystallization gave pure iminophosphoranes (Table I). Only in the cases of (phenylimino)-[3] and ((trimethylsilyl)imino)phosphoranes[18–21] was the reaction of phosphine with the corresponding azide under nitrogen evolution (B) used. ((Trimethylsilyl)imino)triphenylphosphorane was desilylated with 2-propanol to yield iminotriphenylphosphorane, recrystallized from hot cyclohexane (C).[22] Identity and purity were established by IR, ^1H NMR, ^{13}C NMR, and PE spectroscopy.

(ii) Aminophosphonium Salts. These salts were formed in high yields by simultaneous action of ammonia or amines and carbon tetrachloride on phosphines (Me_3P, Ph_3P).[17,23–25] Alternatively, anilinotriorganylphosphonium salts precipitated on dropwise addition of an HCl–ether solution to the corresponding iminophosphorane.

(iii) (Phosphinimine)metal Carbonyls and Related Ylidic System Complexes. On reflux of metal hexacarbonyls and the potential ligand in various solvents, thermal substitution results in penta-, *cis*-tetra-, and/or *fac*-tricarbonyls. The latter are binuclear in the case of iminophosphoranes. Solubility decreases rapidly in the order "penta > tetra > tri" and is least in nonpolar solvents: e.g., $(Ph_3PNSiMe_3)Mo(CO)_5$, $(Ph_3PNSiMe_3)_2Mo(CO)_4$, $(Ph_3PNSiMe_3)_3[Mo(CO)_3]_2$ in benzene; $(Ph_3PNPh)_3[Cr(CO)_3]_2$ in THF; (Me_3PCH_2)(Cr, Mo, W)$(CO)_5$ in THF;[26] $(Ph_3PCH_2)Mo(CO)_5$ in THF; $(Ph_3PCHPh)Cr(CO)_5$ in petroleum ether.[27] Low-temperature (0–20 °C) ligand exchange was carried out with the photochemically generated THF–metal pentacarbonyls: e.g., $(Me_3PNH)Cr(CO)_5$ in THF; $(Ph_3PNH)Cr(CO)_5$ in THF; $(Ph_3PNSiMe_3)Cr(CO)_5$ in THF; $(Me_3PNPh)Cr(CO)_5$ in THF; $(Ph_3PNPh)Cr(CO)_5$ in THF, subsequent heating giving $(Ph_3PNPh)_3[Cr(CO)_3]_2$; $(Me_3PCH_2)Cr(CO)_5$ in THF, $(Ph_3PCH_2)Cr(CO)_5$ in THF; $(Me_3PCHPh)Mo(CO)_5$ in THF;[26] $(Ph_3PC_5H_4)Mo(CO)_3$ in THF; $(Me_3PS)Cr(CO)_5$ in THF; $(Ph_3PS)Cr(CO)_5$ in THF. Also direct UV irradiation has been successfully applied in several cases: e.g., $(Me_3PNPh)Cr(CO)_5$ in Et_2O; $(Me_3PCHPh)Cr(CO)_5$ in THF; $(Me_3PCH_2)Cr(CO)_5$ in THF; $(Me_3PS)Mo(CO)_5$ in THF.

Spectroscopy. (i) He I PE Spectra. Spectra were recorded on Perkin-Elmer PS 16 instruments with 127° electrostatic deflection-type analyzers (He I excitation = 21.21 eV). Xenon (12.13 eV/13.43 eV) and argon (15.76 eV/15.94 eV) were used as standards. The resolution was better than 0.04 eV. A heated inlet equipment was available for high-temperature measurements. A method of introducing air-sensitive compounds into the spectrometer has been described in the preceding publication of this series.[1] At the selected temperatures, given in Table I, thermolysis of iminophosphoranes was not observed. (See Figure 1.)

(ii) ^{13}C NMR Spectra. Proton broad-band decoupled and off-resonance spectra were recorded in FT mode on a Bruker HX 90/4-15 equipped with a Nicolet computer series 290/1083. Chemical shifts are reported in ppm downfield from Me_4Si. The resolution was at least 2.94 Hz corresponding to 0.13 ppm. C_6D_6 served as solvent and heteronuclear lock, Me_4Si as internal standard for trimethylphosphinimines, $CDCl_3/Me_4Si$ (internal) as standard for triphenylphosphinimines, and CD_3OD/Me_4Si (internal) as standard for aminophosphonium salts. Proton NMR spectra of the latter were also recorded in CD_3NO_2/Me_4Si (internal).

(iii) ^1H NMR Spectra. Spectra were recorded on a Varian T-60 spectrometer.

(iv) IR Spectra. Spectra were recorded with Perkin-Elmer Model 325 and 457 spectrophotometers. Spectra for metal carbonyl complexes were run in Nujol suspension or in closed solution cells with KBr windows and typical path lengths of 25 μm (THF) or 100 μm (CS_2, *n*-hexane).

Computational Details. SCF MO calculations with an s,p,d basis set for phosphorus were carried out on a UNIVAC 1108 at the HRZ of the Frankfurt University. The CNDO/2[28] QCPE program 141 and a modified version[29] were used. Eigenvalues of the latter, multiplied by a factor of 0.86, provide an appropriate numerical fit to photoelectron data of iminophosphoranes, as was the case for ylides.[1] In addition, Koopmans deviations[30–32] were approximated[33] for upper π and σ levels of test compounds. A similar magnitude of calculated corrections suggests that the CNDO (ground state) orbital sequence may be used for assignment of the individual radical cation states within the same molecular system as well as for comparison within the series. The calculations were based on standard geometries unless stated otherwise.

Results and Discussion

He I Photoelectron Spectra. When C_{3v}-symmetric trimethylphosphine and singlet nitrene are brought together, with CNDO/2 model calculations, the total energy minimum results at $d_{PN} \sim 166$ pm. Simultaneously n_N^{π} becomes HOMO and the n_N^{π}/n_N^{σ} energy gap (Figure 2) is maximized but does not reach the PE spectroscopic $\Delta IE_{1/2} \sim 1$ eV of iminotrimethylphosphorane $(H_3C)_3PNH$ (Figures 1 and 4). The nitrogen prefers a sp^2 hybridization, the N–H bond being staggered with regard to the tetrahedral R_3P group. "Cis/trans isomerization" (corresponds to eclipsed/staggered) occurs—contrasting azomethines[34,35]—practically unhindered via rotation.[36] A closer numerical fit with PE data is obtained from modified CNDO calculations, as shown in Figure 4. The most characteristic differences in Figure 4 compared to the photoelectron spectrum of the isoelectronic ylide $(H_3C)_3PCH_2$[1,37] are *two* low-energy ionizations separated by ~1 eV and assigned to n_N^{π} and n_N^{σ}, respectively. The s-orbital contribution is considered responsible for the relatively higher n_N^{σ} IE. This sequence is reversed, compared to azomethines,[38,39] where the strong bonding interaction with the p orbital of the sp^2 carbon

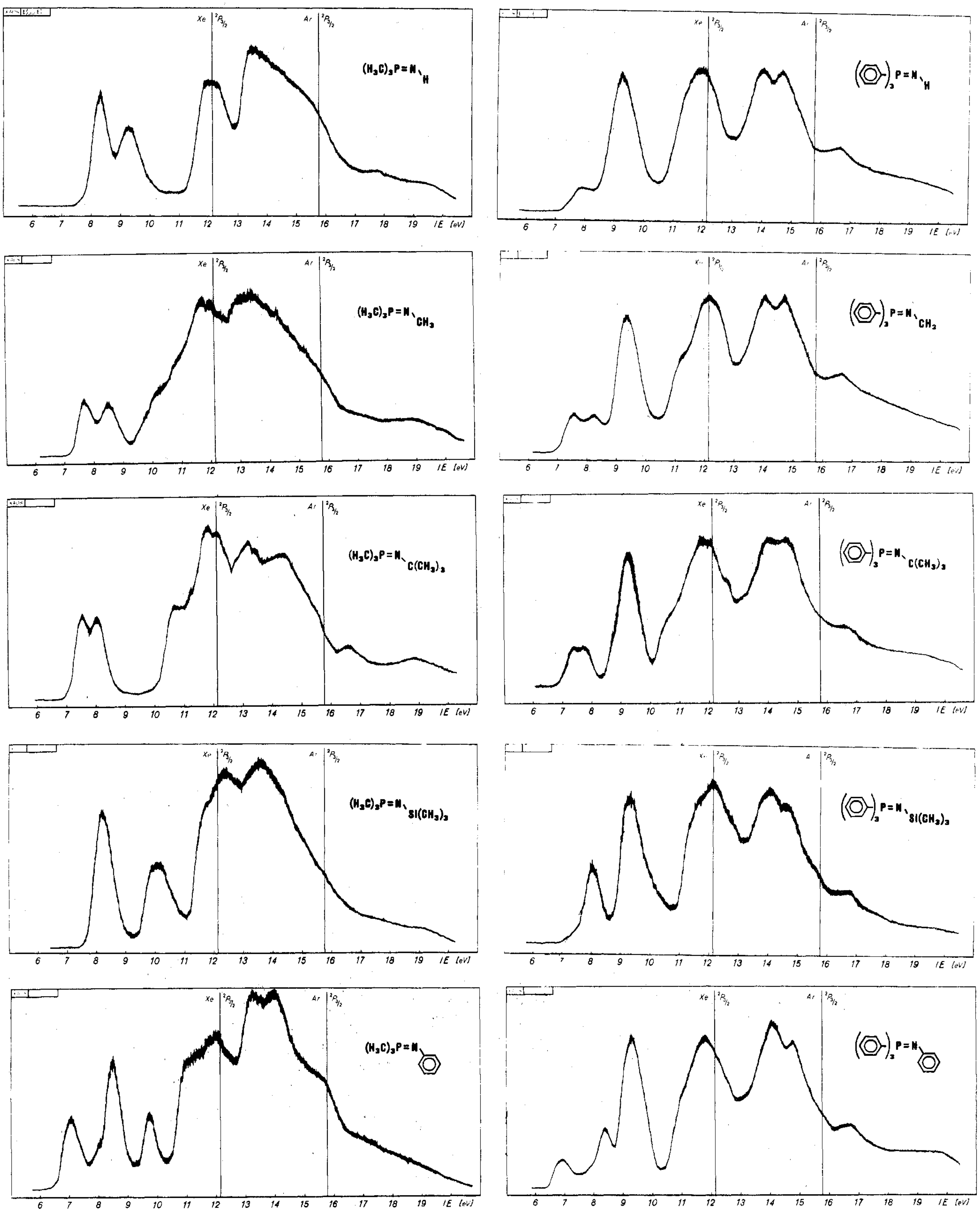


Figure 1. He I PE spectra of corresponding trimethylphosphin- and triphenylphosphinimines.

leads to a stronger stabilization of the π orbital. (See Figure 5.)

N-Alkyl Substituents. *N*-Alkyl substituents in phosphinimines reduce the n_N^σ IE more strongly than the n_N^π IE (Table II). With increasing size and branching in the series H, Me, Et, *n*-Pr, *i*-Pr, c-Hx, and *t*-Bu, IE_1 and IE_2 are not only lowered but also converge. Energetic equivalence, however, is the outstanding feature of the *N*-trimethylsilyl substituent,[20,21,40–44] which leaves the n_N-π ionization unaffected relative to R_3PNH, as was found for n_C-π of ylides (silyl effect toward anion centers)[1,37,45] (Chart I). At the same time n_N^σ (with higher e^- localization and energetic proximity to $SiMe_3$ bond orbitals) is destabilized through hyperconjugative plus inductive interactions and PNSi angle widening[46] up to the level of n_N^π. The

Table II. Vertical Ionization Potentials IE_n^v (eV) of Trimethyl- and Triphenylphosphinimines

R_3PNX	ionization[a]											
	n_N^π	n_N^σ	π_{CC}	σ_{SiC}	$\sigma_{PN}/\sigma_{PC}/\sigma_{CC}/\sigma_{CH}\cdots$[b]							
$(H_3C)_3PNH$	8.29	9.25				(11.8,	12.3)	13.4				17.6
$(H_3C)_3PNCH_3$	7.67	8.47			10.3, 10.7	(11.7,	12.0)	(13.0, 13.4)			16.9	
$(H_3C)_3PNC(CH_3)_3$	7.56	8.06			10.7, 11.3	(11.8,	12.1)	(13.2, 13.5,	14.3,	15.6)	16.6	
$(H_3C)_3PNSi(CH_3)_3$	8.30	8.30		10.3		11.8,	12.4	(13.6)				
$(H_3C)_3PNC_6H_5$[c]	7.05	(8.3)	8.5, 9.75		(10.9,	12.0)		(13.3,	14.0,	15.7)		17.2
$(H_5C_6)_3PNH$	7.95		9.3			11.9			14.0, 14.6		16.6	
$(H_5C_6)_3PNCH_3$	7.54	8.21	9.3		(11.0,	12.1)			14.0, 14.6		16.7	
$(H_5C_6)_3PNCH_2CH_3$	7.43	8.04	9.3		(11.0,	12.0)			14.0, 14.6		16.6	
$(H_5C_6)_3PNCH(CH_3)_2$	7.38	7.88	9.3		(10.8,	12.0)			14.0, 14.6	16.1,	16.6	
$(H_5C_6)_3PN\text{-c-}C_6H_{11}$	7.37	7.88	9.3		(10.9,	11.9,	12.3)		14.0, 14.6		16.6	
$(H_5C_6)_3PNC(CH_3)_3$	7.35	7.70	9.3		(10.7,	11.7,	12.1,	12.6)	14.0, 14.6		16.6	
$(H_5C_6)_3PNSi(CH_3)_3$	8.05	8.05	9.3	(10.3)		(11.7,	12.1)		14.0, 14.6		16.6	
$(H_5C_6)_3PNC_6H_5$[c]	6.95	(8.1)	8.4, 9.3		(10.9,	11.7,	12.2)		14.0, 14.6		16.6	

[a] All well-separated peaks with distinct maxima are listed; values for strongly overlapping bands are in parentheses. [b] Characterized according to main CNDO calculated contribution. [c] See text for assignment.

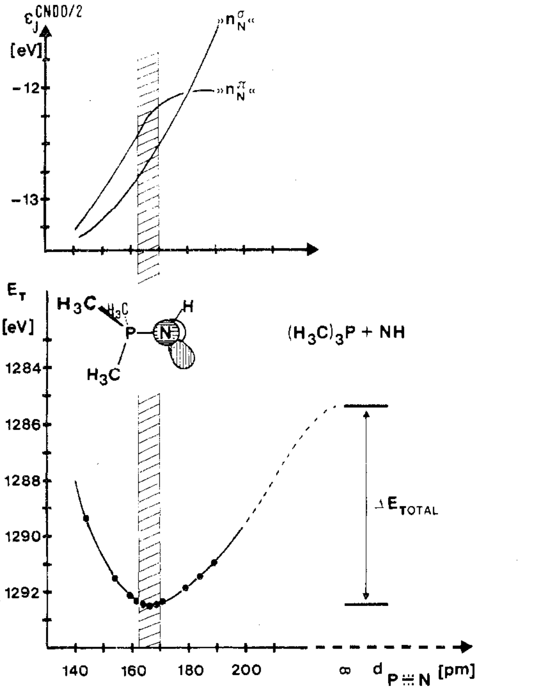


Figure 2. CNDO/2 correlation diagrams: ϵ_j^{CNDO} (HOMO, HOMO-1) and E_{total}^{CNDO} vs. bond distance $d_{P\equiv N}$.

Chart I

	n_N-$^\pi$	n_N-$^\sigma$
Me_3PNH	8.3	9.3
$Me_3PNSiMe_3$	8.3	8.3
	n_C-	
Me_3PCH_2	6.8	
$Me_3PCHSiMe_3$	6.8	

degenerate n_N ionizations thereby appear at higher energies than the center of gravity $^1/_2(IE_1 + IE_2)$ in *N*-alkyl derivatives (cf. extrastabilization by silyl groups).

By exchange of H for different alkyl groups, varying degrees of hyperconjugation become evident, when looking at changes in n_N- ionization energies. In going from the *tert*-butyl derivatives $R_3PN{-}C(CH_3)_3$ to $R_3PN{-}Si(CH_3)_3$ IE_1 and IE_2 *increase*—a difference in n_N^π and n_N^σ is no longer perceivable. Although important interactions between R_3PN– and –$Si(CH_3)_3$ are obvious, the "e"-type ionizations *move together* by reducing IE(SiC) relative to $t_2^{SiC}(Me_4Si)$. Such an influence on the nitrogen substituent by the negative end of the iminophosphoranyl group is characterized best by investigating its "benzene perturbation".[1,47]

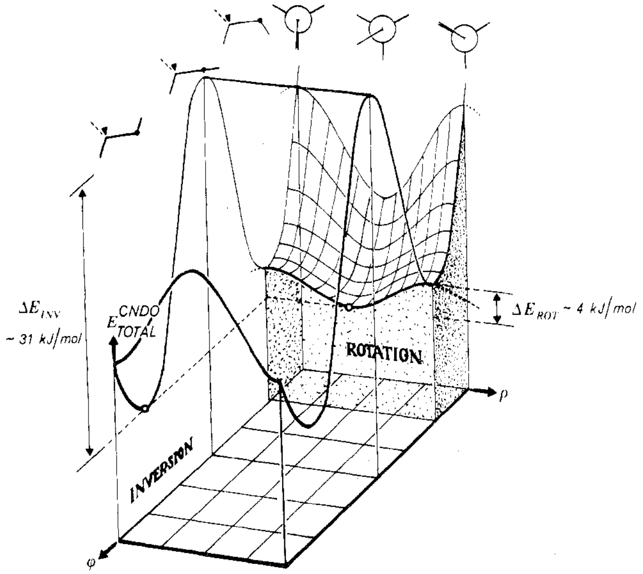


Figure 3. Segment of the CNDO/2 potential surface for iminotrimethylphosphorane $(H_3C)_3PNH$, which reflects total energy changes on N inversion (φ = bond angle PNH) and NH rotation (ρ = dihedral angle CPNH).

***N*-Phenyl Substituents.** (*N*-Phenylimino)trimethylphosphorane (trimethylphosphine *N*-phenylimide) shows—as expected—four low-energy ionizations (Figure 1), two of which are N localized. The remaining two may be related to the e_g state of the benzene radical cation. The fact that none of them appears near—but instead three of them appear below—9.25 eV proves an ylide-like bond system,[1,47] part of which approaches the limiting azabenzyl anion situation. X-ray data, which are available for $(H_5C_6)_3PNC_6H_4Br$, show a dihedral angle of 35° between the PNC plane and the C_6H_4Br ring.[48] Within the CNDO/2 approximation, a staggered geometry for $(H_3C)_3PNC_6H_5$ and an idealized 120° PNC angle lead to a favored perpendicular arrangement (90° rotamer). Its total energy is only 7 kJ/mol below the coplanar form (0° rotamer) but ~60 kJ/mol below a 35° arrangement. For the

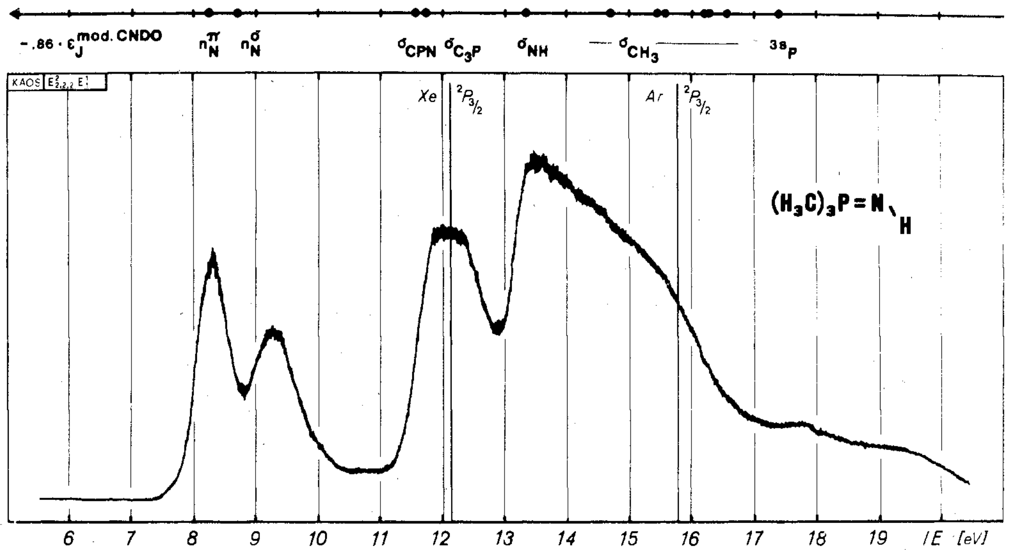


Figure 4. He I PE spectrum of iminotrimethylphosphorane with CNDO eigenvalues (modified CNDO values multiplied by 0.86)[1] and dominant contribution of corresponding MO's.

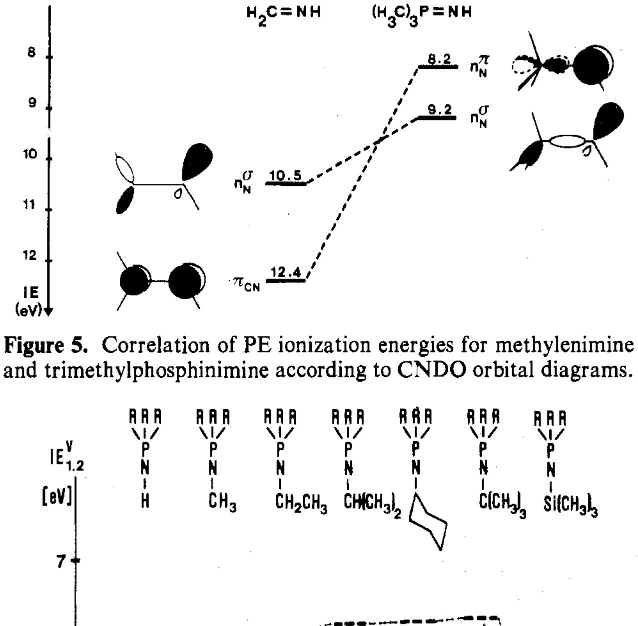


Figure 5. Correlation of PE ionization energies for methylenimine and trimethylphosphinimine according to CNDO orbital diagrams.

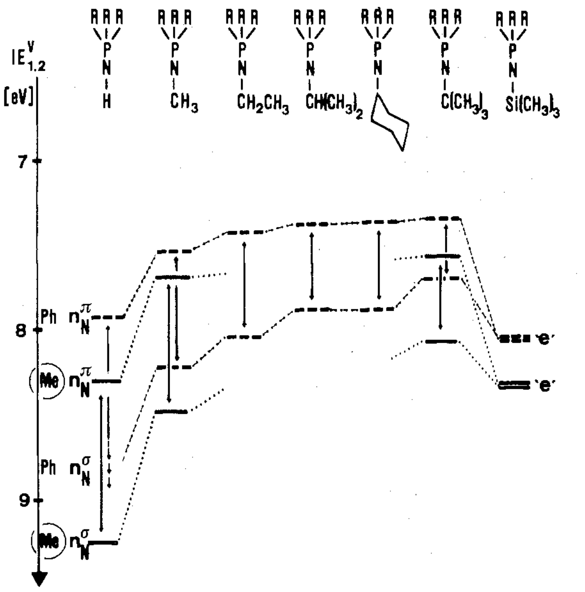


Figure 6. Iminophosphorane n_N^π and n_N^σ PE ionization energies as a function of P substituents (methyl (—), phenyl (- - -)) and N substituents (H, alkyl, trimethylsilyl).

real gas-phase molecule the rotational barrier should be lower due to adjusting methyl groups and possible angle deviations. A modified CNDO diagram (Figure 7) for the five highest occupied molecular orbitals shows changes in energies and sequence, which result from rotating the phenyl group. Applying Koopmans theorem,[30] the overall low-energy ionization pattern remains essentially the same and therefore a definite gas-phase geometry is not to be singled out by comparing the ionization potentials. Along with this, the position of π_{as} (IE_2 or IE_3) remains uncertain. Intensity considerations do, however, justify the following assignment.

At the elevated measurement temperatures, where a whole range of rotational isomers may well have similar statistical weight, the second ionization is broadened and appears as a low-intensity shoulder on the high-intensity, narrow, third ionization peak. The latter, IE_3 at 8.5 eV, is therefore assigned π_{as}, which is not affected by the substituent mobility.

***P*-Phenyl Derivatives.**[15] *P*-Phenyl derivatives—mostly white solids and less sensitive compounds—are often preferred in synthetic procedures because they are easier to handle as are also their phosphine precursors and also because they are phosphine precursors themselves. Their gas-phase spectra are obtainable without sign of thermolytic phosphine evolution, even at high temperatures. Contrary to the phosphorus ylide carbene dissociation,[1] a possible nitrene dissociation of phosphinimines obviously occurs less readily. Assignment of the spectra is straightforward and analogous to that for the *P*-methyl derivatives, where a series of related compounds and SCF results provide assuring evidence.

The already known ionizations from the aza anion part appear at somewhat lower energies with phenyl groups delocalizing the P^+ charge. In addition, six phenyl ionizations (3 π_{as}, 3 π_s) produce a structureless band centered near 9.3 eV—similar to ylides.[1] The high-intensity peak often obscures other bands (e.g., Ph_3PNH, n_N^σ; Ph_3PNPh, $\pi_s + n_N$; $Ph_3PNSiMe_3$, σ_{SiC}), so that investigation of trialkylphosphinimines was essential. The region above 11 eV is nearly completely dominated by the aromatic ring ionization pattern as evidenced by comparison with the benzene spectrum.

n_N- and σ_{PC}- valence ionizations, as well as those being mainly localized in the substituents of N and P, confirm a $\geqslant P^+ \text{⩶} N^-$– bond system. The calculated charge distribution (Figure 8) is also in accord with ESCA results, where the higher P_{2p} binding energy points to a more positive P^+ charge in R_3PNH (137.4 eV) than in R_3PCH_2 (137.0 eV).[49] Similar conclusions may be drawn for the mainly P_{3s} localized ionization at 17.7 eV (Figure 4), which was localized in the spectrum of R_3PCH_2 at 17.1 eV.

To our knowledge no dipole moments of trimethylphosphinimines have been measured. Similar experimental values of the related phosphine oxides, however, show only small differences for trimethyl and triphenyl derivatives.

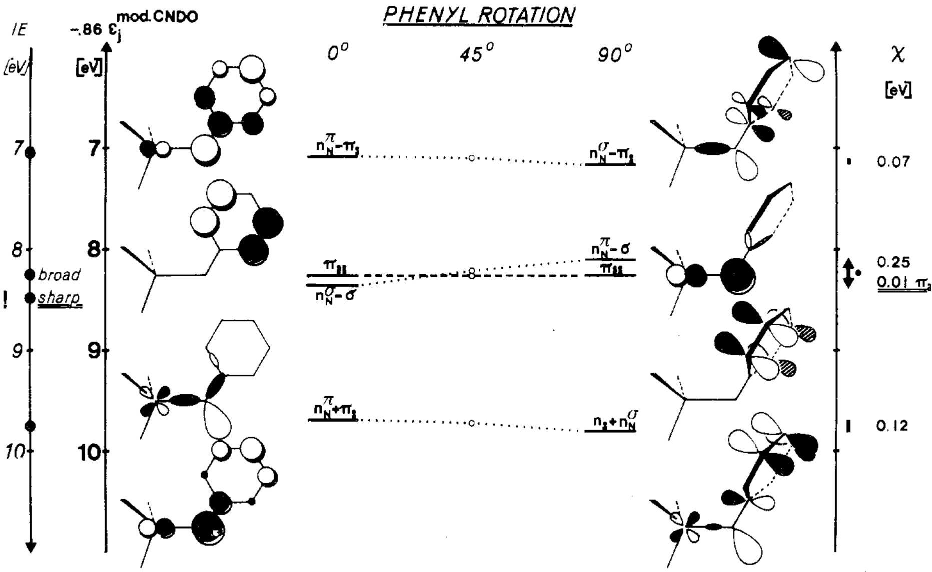


Figure 7. Comparison of PE IE_1–IE_4 and different band shapes (left), CNDO results including phenyl rotation (center), and maximum calculated energy change per orbital (χ) (right).

Table III. ^{13}C NMR Chemical Shift (ppm) Relative to Me_4Si and ^{31}P–^{13}C Coupling Constants (Hz) of Iminophosphoranes

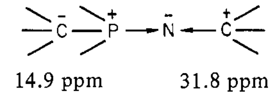
R_3PNX	C-1 ($^1J_{PC}$)	C-β ($^2J_{PC}$)	C-γ ($^3J_{PC}$)	C-δ	C-ε
$(H_3C)_3PNH$	20.0 (62)				
$(H_3C)_3PNCH_3$	14.9 (65)	31.8 (6)			
$(H_3C)_3PNC(CH_3)_3$	20.4 (65)	51.4 (5)	35.9 (12)		
$(H_3C)_3PNSi(CH_3)_3$	22.2 (69)		6.1 (4)		
$(H_3C)_3PNPh$	15.3 (65)	152.3 (3)	122.2 (21)	128.6	116.3

R_3PNX	C-4 ($^4J_{PC}$)	C-3/5 ($^3J_{PC}$)	C-2/6 ($^2J_{PC}$)	C-1 ($^1J_{PC}$)	C-β ($^2J_{PC}$)	C-γ ($^3J_{PC}$)	C-δ	C-ε
$(H_5C_6)_3PNH$	131.3	128.3 (12)	132.0 (9)	132.7 (106)				
$(H_5C_6)_3PNCH_3$	130.9	128.3 (12)	132.6 (10)	132.9 (93)	32.2 (5)			
$(H_5C_6)_3PNCH_2CH_3$	131.0 (2)	128.3 (11)	132.5 (9)	132.1 (95)	40.0 (5)	21.1 (18)		
$(H_5C_6)_3PNCH(CH_3)_2$	130.9	128.1 (11)	132.5 (10)	132.9 (95)	45.8 (4)	28.8 (12)		
$(H_5C_6)_3PN\text{-c-}C_6H_{11}$	130.9	128.1 (11)	132.5 (9)	133.1 (95)	54.2 (5)	39.5 (12)	26.1	26.1
$(H_5C_6)_3PNC(CH_3)_3$	130.5 (2)	128.0 (11)	132.6 (10)	135.4 (96)	51.7 (2)	35.4 (10)		
$(H_5C_6)_3PNSi(CH_3)_3$	131.3	128.7 (12)	132.6 (10)	136.4 (102)		6.1 (3)		
$(H_5C_6)_3PNC_6H_5$	131.5	128.4 (12)	132.4 (10)	131.2 (99)	151.0 (2)	123.4 (18)	128.5	117.3

Therefore, comparison of calculated and experimental values for corresponding phosphinimines seems reasonable and obviously the CNDO/2 method provides sufficiently accurate results.

Me_3PO	Me_3PNH	$Me_3PNC_6H_5$
4.3 D (exptl)[50]	4.4 D (calcd)	4.8 D (calcd)
Ph_3PO	Ph_3PNH	$Ph_3PNC_6H_5$
4.5 D (exptl)[50]	4.2 D (exptl)[51]	4.4–4.8 D (exptl)[51]

^{13}C **NMR Spectra.** ^{13}C NMR spectra have been demonstrated to be especially useful in combination with photoelectron spectra to provide complementary information on bonding properties, e.g., of ylides, where charge effects are dominant.[1,26] Methyl and phenyl ^{13}C NMR data are discussed as representative examples. In tetramethylphosphinimine two doublets (due to one-bond and two-bond ^{31}P coupling) are separated by ~17 ppm. Charge alternation is enforced by the electron-attracting nitrogen.



The N–CH_3 signal appears ~21 ppm to lower field than the corresponding methyl carbon in ylides R_3PCH–CH_3.[26,52] It is, however, shifted upfield by ~8 ppm as compared to azomethines >C=N—CH_3,[53] where the N charge is less negative (Figure 8). When benzene is substituted by an iminophosphoranyl group (R_3PN–), C-δ remains essentially unaffected while C-γ is shifted upfield, sensing an increased electron density. An even higher shielding is found for C-ε (Table

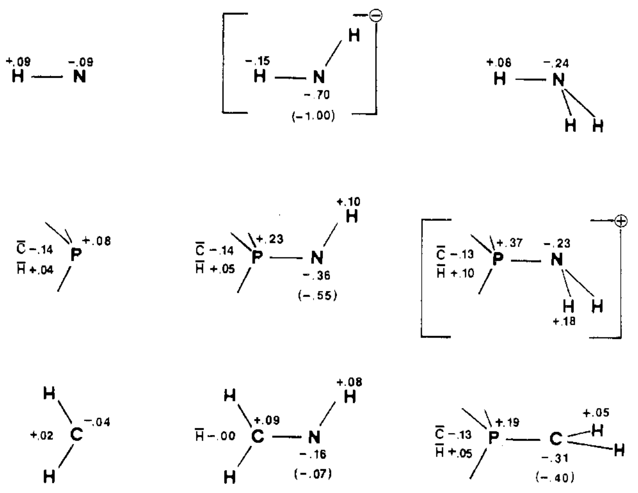
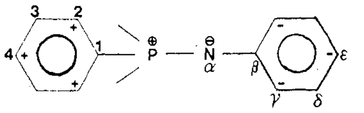


Figure 8. CNDO/2 charge distribution (π charges in parentheses) of iminotrimethylphosphorane, aminotrimethylphosphonium ion, and related molecules nitrene, amide ion, ammonia, trimethylphosphine, singlet carbene, methylenimine, and methylenetrimethylphosphorane.

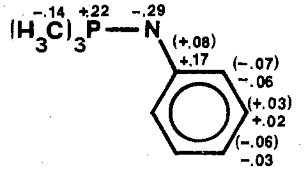
Table IV. ^{13}C NMR Chemical Shifts (ppm) Relative to Me_4Si and ^{31}P–^{13}C Coupling Constants (Hz) of Aminophosphonium Salts

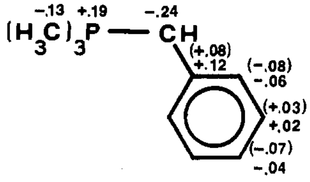
R_3PNHX	Hal^-	C-4 ($^4J_{PC}$)	C-3/5 ($^3J_{PC}$)	C-2/6 ($^2J_{PC}$)	C-1 ($^1J_{PC}$)	C-β ($^2J_{PC}$)	C-γ ($^3J_{PC}$)	C-δ	C-ε
$(H_3C)_3\overset{+}{P}NHH$	Cl^-				13.6 (67)				
$(H_3C)_3\overset{+}{P}NHCH_3$	Cl^-				11.2 (65)	26.9			
$(H_3C)_3\overset{+}{P}NHC(CH_3)_3$	Cl^-				14.7 (65)	54.4 (4)	31.9 (5)		
$(H_5C_6)_3\overset{+}{P}NHC(CH_3)_3$	Cl^-	135.6	130.6 (14)	134.5 (11)	123.3 (102)	56.2 (4)	31.9 (5)		
$(H_3C)_3\overset{+}{P}NHC_6H_5$	Cl^-				12.1 (65)	139.0	122.1	130.7	125.1

III), which does not quite parallel the CNDO/2 charge distribution.



Both values (C-γ and C-ε) are not quite as extreme as in the corresponding benzylidenetrimethylphosphorane ($R_3PCHC_6H_5$)[26]





consistent with a reduced delocalization into the ring. On the other hand the most sensitive C-β signal appears at very low field, the strongly P^+–N^-–C^+ alternating π charges being even enhanced by the σ-withdrawing properties of the nitrogen atom. The NMR pattern of the ring is similar to that of sodium phenolate.[54]

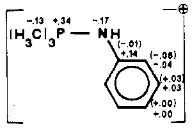
The picture changes drastically for phenyl groups connected to P. As expected, C-1 appears upfield from its *N*-phenyl counterpart C-β, while C-2/6 and especially C-4 move downfield due to P^+ delocalization. Characteristically alternating ^{31}P–^{13}C coupling constants support the assignment.

Protonation. A common feature of phosphinimines and ylides is the pronounced affinity toward protons, cations, and other electrophiles. According to CNDO/2 calculations for the proton adduct $(H_3C)_3PNH_2^+$, a pyramidal (sp^3) nitrogen geometry is slightly, ~3 kJ/mol, favored over the planar form. Following the charge distribution (Figure 8) it should not be called an iminium ion but rather onium-substituted ammonia or aminophosphonium ion.

The still residing $\gg P^+$–$N^{\delta-}<$ charge separation makes it comparable to isoelectronic and isosteric ylides $\gg P^+$–$C^-<$ or $\gg As^+$–$C^-<$.[45] Sensitivity toward hydrolysis underlines such relations.

A major difference, however, is the dramatic energetic stabilization which results from protonation. While one n_N orbital is turned over into a bonding σ_{NH} orbital, the other one is stabilized by ~8 eV (HOMO!) due to the additional positive charge—consistent with a loss in oxidizability. Simultaneously an increased energy separation between ground and excited states[56] may be responsible for different slopes in q_C vs. $\delta(^{13}C)$ correlations, which indicate a reduced sensitivity toward changes in electron density for salts. An approximately linear relationship between CNDO π charges $q_C{}^\pi$ and ^{13}C NMR shifts was discovered for ylides. In the case of the PN compounds, however, a reasonable ordering of carbon chemical shifts according to charge distribution is only observed, when net atomic charges $q_C{}^T$ are used—thereby including σ effects. For example, C-β in the anilinotrimethylphosphonium ion (CNDO/2: $q^T{}_{C\text{-}\beta} = q^\pi + q^\sigma = -0.01 + 0.15 = +0.14$) nicely reflects the situation of a dominant σ charge.

Under the premise of reliable CNDO electron distributions, one may consider "local ΔE values" for ylidic systems. Those would explain not only different ($q^T{}_C$ vs. $\delta(^{13}C)$) slopes for P^+ and N^- or C^- substituents but also the downfield chemical shift of the P-connected carbon, which appears at higher field, when the anion center is protonated.



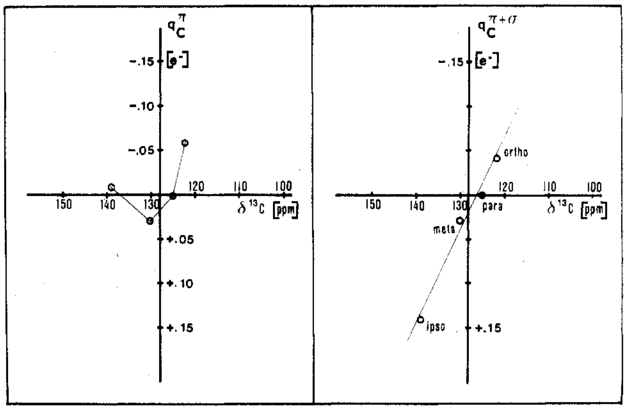
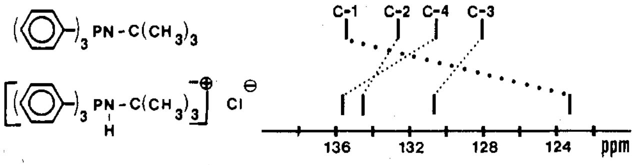


Figure 9. Linear correlation of ^{13}C NMR shift vs. CNDO/2 total charge (right) and "noncorrelation" with π-only charges (left).



The overall energy gain on protonation, as given by the difference in total energies between aminophosphonium ion and phosphinimine $E_T(Me_3P^+NH_2) - E_T(Me_3PNH)$, amounts to ~16.5 eV. But CNDO/2-calculated proton affinities[57] are likely to be exaggerated by 40%. Therefore one could expect a PA value near 10 eV, corresponding to 960 kJ/mol. Although the necessary ICR information is not yet available, one should derive reasonable values from the measured ionization potentials, which are thermodynamically related to proton affinities.

$$\begin{tikzcd}
 & (H_3C)_3\overset{+}{P}NH + e^- + \overset{+}{H} \arrow[dr, "IE(H)"] & \\
(H_3C)_3PNH + \overset{+}{H} \arrow[ur, "IE"] \arrow[dr, "PA"'] & & (H_3C)_3\overset{+}{P}NH + H \\
 & (H_3C)_3\overset{+}{P}NH_2 \arrow[ur, "DH^\circ"'] &
\end{tikzcd}$$

By approximating the unknown bond dissociation enthalpies[61,62] $DH^\circ(Me_3P^+X\text{–}H)$, we calculated proton affinities (PA) of isoelectronic ylidic systems Me_3PX ($X = CH_2$, NH, O, S) according to the following equation and compared them to those of the related anions[61,62] (CH_3^-, NH_2^-, OH^-, SH^-).

$$PA(Me_3PX) = IE(H) - IE(Me_3PX) + DH^\circ(Me_3\overset{+}{P}X\text{–}H) \quad (1)$$

Table V. Ionization Energies and Proton Affinities of Isoelectronic Ylidic Systems and Corresponding Anions

ylidic system	IE-(R_3PX),[a] kJ/mol	$DH°$-(R_3P^+XH),[b] kJ/mol	PA-(R_3PX),[c] kJ/mol	PA(XH^-),[d] kJ/mol
R_3PCH_2	657	435	1090	1732 (CH_3^-)
R_3PNH	800	460	972	1703 (NH_2^-)
R_3PO	953	498	857	1632 (OH^-)
R_3PS	818	377	871	1464 (SH^-)

[a] Vertical ionization potentials IE_1^V from PES; 1 eV corresponds to 96.49 kJ/mol. [b] Values for CH_4, NH_3, H_2O, and H_2S;[62] 1 kcal corresponds to 4.184 kJ. [c] Calculated according to eq 1. [d] Reference 61.

According to Table V ionization potential and proton affinity of trimethylphosphinimine are midway between those of ylide and oxide. Its PA is above that of ammonia (845 kJ/mol)[60] and well below that of NH_2^-. On substitution of H for R_3P^+ the anion proton affinity (corresponding to 100%) is reduced by ~40–50% as is the electron density at the center of protonation (Figure 8).

Metal Coordination. As was suggested in the foregoing discussion, $R_3PNH_2^+$ is related to R_3PNH and R_3PCH_2 through isoelectronic and approximately isosteric properties. Furthermore it may be looked at as a parent system for phosphinimine coordination compounds: (a) $R_3PNX \rightarrow H^+$, (b) $R_3PNX \rightarrow$ metal. (a) represents the conjugate Brönstedt acids of phosphinimines and (b) is a Lewis acid–base complex. They may be charged when phosphinimines are coordinated to metal ions,[63,64] e.g., Cu^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, or Ni^{2+} or uncharged as in adducts to BX_3, AlX_3, GaX_3, or InX_3[65,66] (X = H, alkyl, phenyl, halogens).

In this study zerovalent (6B) metal carbonyl–PN complexes are compared to ylide analogues and other related systems.

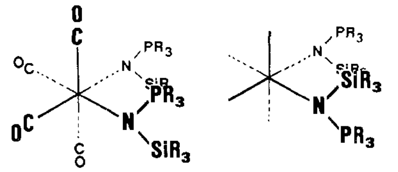
Carbonyl stretching frequencies (ν_{CO}) provide information on "complex architecture" and ligand characteristics, based on steric requirements and electronic structure.

(Phosphinimine)chromium pentacarbonyls can be prepared by low-temperature (0–20 °C) ligand exchange from photochemically generated THF–$Cr(CO)_5$. The infrared absorption pattern (Figure 10) suggests a more or less unperturbed square-pyramidal arrangement for the $Cr(CO)_5$ fragment (C_{4v} local symmetry; 2 A_1 + E modes). Despite shorter bond lengths ($d_{PN} < d_{PS}$ and $d_{NCr} < d_{SCr}$) no splitting of the "E" mode is detected, while one finds 5(!) well-separated bands (removed E degeneracy, active B_1 mode) for $Me_3PSM(CO)_5$.[67] A possible reason for this could be P–N–Cr angle widening. In fact P–O–metal structures have been observed with angles of 140–150° and larger.[68-70] The P–S–Cr angle of 112.5° has been determined for $Me_3PSCr(CO)_5$.[71]

Analogous ylide complexes (Table VI, Figure 10) also show an active B_1 mode and E splitting (solvent dependent), indicating symmetry lowering. Comparison of wavenumbers allows ordering of the ligands with increasing donor/acceptor (D/A) ratio: $R_3PS < R_3PNH < R_3PCH_2$. This parallels the energetic availability of the outermost electrons as measured by photoelectron spectroscopy (IE_1) and calculated proton affinities (Table V). The ionization potential of CH_3^- (electron affinity of $CH_3\cdot$) is expected between ~0.1 and ~0.3 eV and therefore ~6.5 eV below that of the ylide together with a correspondingly higher proton affinity. In accordance with spectroscopic and calculated properties of the free ligands, a comparable complex $(OC)_5WCH_3^-$ shows the D/A ratio of the ylide to be exceeded by that of the unsubstituted carbanion.[72] This in turn demonstrates the charge-stabilizing effect of the R_3P^+ substituent—in this case toward complexed anions.

Besides simple pentacarbonyls through monosubstitution (i), phosphinimines yield various reaction products especially at elevated temperatures. (ii) Disubstitution gives *cis*-$(R_3PNX)_2M(CO)_4$ derivatives with nearly identical CO stretching frequencies for X = H,[73] $SiMe_3$. In the silyl case the B_1 mode shows a shoulder at 1872 cm^{-1} and B_2 is broadened, which may hint at two rotamers (Chart II). (iii) Trisubstitution produces $(R_3PNX)_3[M(CO)_3]_2$, a coordination type which is unique in the R_3PX series. Simple ylides and sulfides preferentially yield pentacarbonyls, which are labile for phosphinimines and even more so for phosphine oxides. Both lead to multiple substitution, either mononuclear $L_2M(CO)_4$ complexes or *fac*-tricarbonyls. These are binuclear[74] solely with R_3PNX ligands (Chart III). Singly coordinated, the nitrogen obviously has still one more electron pair of high energetic availability. This also agrees with the tendencies to form onium units, which are reflected by changes in proton affinities PA:[60,75]

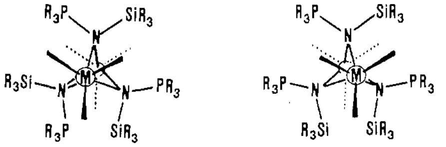
Chart II[a]



	A_1^1	B_1	A_1^2	B_2
$(Ph_3PNSiMe_3)_2Mo(CO)_4$	2000	1866	1841	1789
$(Ph_3PNH)_2Mo(CO)_4$	2000	1863	1840	1787

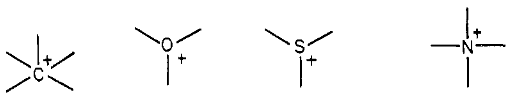
[a] Local symmetry C_{2v}. Units in cm^{-1}. Samples taken in Nujol.

Chart III[a]



	A	E
$(Ph_3PNSiMe_3)_3[Mo(CO)_3]_2$	1892	1770/1750
$(Me_3PNPh)_3[Cr(CO)_3]_2$	1902	1770/1750
$(Ph_3PNH)_3[Mo(CO)_3]_2$	1894	1770

[a] Local symmetry C_{2v}. Units in cm^{-1}. Samples taken in Nujol.



(CH_4) 523 (H_2O) 695 (H_2S) 728 (NH_3) 845 kJ/mol

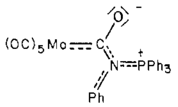
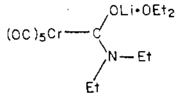
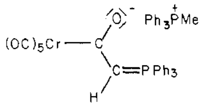
Obviously it is useful to compare property changes for isoelectronic ylides and imines with those for analogous reactions and reaction products. Thanks to additional isosteric conditions, ensuring a constant number of "lone pairs", the ylide anion $[R_3P{\cdots}CX]^-$ should, and indeed does, act as bridging ligand.[76] Vice versa, $R_3P^+{\cdots}N^-X{\cdots}M(CO)_5$ can be considered a stabilized ylide itself, which is able to bind another $M(CO)_n$ fragment. (iv) Nucleophilic addition to metal coordinated CO, which generates $(OC)_5MC(O)N(X)PR_3$, is a low-temperature alternative to substitution. The ν_{CO} pattern from the reaction with Ph_3PNPh is thought to characterize an aminocarbene complex (Chart IV, no. 1) because of similarities with complex no. 2 (Chart IV). The analogous ylide adduct has been shown to transfer protons onto excess ylide, yielding complex no. 3 (Chart IV). This offers one more example of the $R_3P^+{\cdots}N^-X/R_3P{\cdots}CX^-$ relationship. No such follow-up reaction is possible for complex no. 1 (Chart IV). However, we did find (phenyl isocyanide)chromium pentacarbonyl ($\tilde{\nu}_{CN}$ 2135 cm^{-1}; $\tilde{\nu}_{CO}(A_1^1)$ 2053, $\tilde{\nu}_{CO}(E, A_1^2)$ 1962 cm^{-1}) when the imine was Me_3PNPh. This indicates a Wittig reaction with coordinated carbon monoxide (v), which has also been dis-

Table VI. Carbonyl Stretching Frequencies (cm^{-1}) of (Phosphinimine)metal Pentacarbonyls and Related Ylidic System Complexes

	$\tilde{\nu}_{CO}$, cm^{-1}				
(ylidic system)$M(CO)_5$[i]	A_1^1	B_1	E	A_1^2	solvent[a-f]
$(Me_3PNH)Cr(CO)_5$	2059		1933	1895	*b*
	2061		1927	1895	*d*
$(Ph_3PNH)Cr(CO)_5$	2061		1928	1896	*b*
	2062		1922	1885	*d*
$(Me_3PNPh)Cr(CO)_5$	2050		1924	1870	*a*
$(Ph_3PNSiMe_3)Cr(CO)_5$	2044		1911	1883	*d*
$(Ph_3PNSiMe_3)Mo(CO)_5$	2064		1927	1890	*b*
$(Me_3PCH_2)Cr(CO)_5$	2048	1962	1918/1912	1887	*b*
	2046	1958	1907	1881	*e*
	2049	1959	1916/1902	1883	*d*
	2042	1964	1912/1898	1873	*f*
$(Me_3PCH_2)Mo(CO)_5$	2060	1968	1924/1914	1886	*f*
$(Me_3PCH_2)W(CO)_5$	2060	1978	1913/1904	1880	*f*
$(Ph_3PCH_2)Cr(CO)_5$	2048		1916	1882	*a*
$(Ph_3PCH_2)Mo(CO)_5$	2062		1922	1882	*f*
$(Me_3PCHPh)Cr(CO)_5$	2048	1962	1915/1905	1883	*e*
$(Ph_3PCHPh)Cr(CO)_5$	2049	1970	1908	1862	*a*
$(Me_3PS)Cr(CO)_5$[g]	2062	1984	1944/1927	1909	*c*
$(Me_3PS)Mo(CO)_5$	2069	*h*	1946/1928	1910	*b*
$(Ph_3PS)Cr(CO)_5$[g]	2062	1981	1942/1932	1910	*c*

[a] Nujol. [b] *n*-Hexane. [c] Cyclohexane. [d] CS_2. [e] CCl_4. [f] THF. [g] Reference 67. [h] B_1 is probably hidden by the molybdenum hexacarbonyl T_{1u} CO absorption at 1989 cm^{-1}. [i] Local symmetry C_{4v}.

Chart IV[a]

		ν_{CO}, cm^{-1}				
no.		A_1^1	B_1	E	A_1^2	medium
1		2023 w	1924 m	1890 s	1870 m	Nujol
2		2034 m	1939 w	1897 vs	1870 s	THF[77]
3		2015 w	1985 m	1890 s	1859 m	THF[78]

[a] Local symmetry C_{4v}.

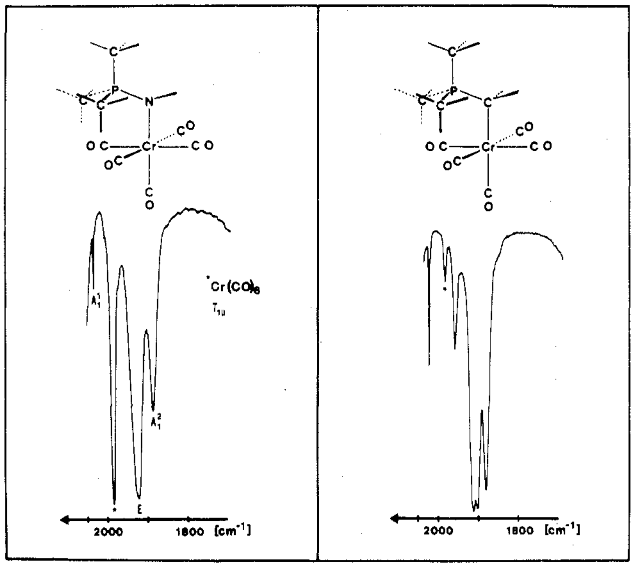


Figure 10. Infrared spectra in the carbonyl stretching region of ((trimethylphosphine)methylene)chromium pentacarbonyl and of (trimethylphosphinimine)chromium pentacarbonyl in CS_2 (100 μm).

covered for iron pentacarbonyl and $Ph_3PN(Tol)$[79] as well as for tungsten hexacarbonyl and the bis ylide $Ph_3P—C—PPh_3$.[80]

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Registry No. $(H_3C)_3PNH$, 15107-02-5; $(H_3C)_3PNCH_3$, 42437-75-2; $(H_3C)_3PNC(CH_3)_3$, 71328-66-0; $(H_3C)_3PNC_6H_5$, 57114-54-2; $(H_5C_6)_3PNH$, 2240-47-3; $(H_5C_6)_3PNCH_3$, 17986-01-5; $(H_5C_6)_3PNC(CH_3)_3$, 13989-64-5; $(H_5C_6)_3PNSi(CH_3)_3$, 13892-06-3; $(H_5C_6)_3PNC_6H_5$, 2325-27-1; $(H_3C)_3PNSi(CH_3)_3$, 6063-72-5; $(H_5C_6)_3PNCH_2CH_3$, 47182-04-7; $(H_5C_6)_3PNCH(CH_3)_2$, 40168-14-7; $(H_5C_6)_3PN$-c-C_6H_{11}, 66949-28-8; $(H_3C)_3P^+NHHCl^-$, 15729-41-6; $(H_3C)_3P^+NHCH_3Cl^-$, 71328-67-1; $(H_3C)_3P^+NHC(CH_3)_3Cl^-$, 71328-68-2; $(H_5C_6)_3P^+NHC(CH_3)_3Cl^-$, 799-52-0; $(H_3C)_3P^+NHC_6H_5Cl^-$, 71328-69-3; $(CH_3)_3PCH_2$, 14580-91-7; $(CH_3)_3PNH$, 15107-02-5; $(CH_3)_3PO$, 676-96-0; $(CH_3)_3PS$, 2404-55-9; $(Me_3PNH)Cr(CO)_5$, 71341-50-9; $(Ph_3PNH)Cr(CO)_5$, 71341-49-6; $(Me_3PNPh)Cr(CO)_5$, 71341-48-5; $(Ph_3PNSiMe_3)Cr(CO)_5$, 71486-16-3; $(Ph_3PNSiMe_3)Mo(CO)_5$, 71369-99-8; $(Me_3PCH_2)Cr(CO)_5$, 71359-57-4; $(Me_3PCH_2)Mo(CO)_5$, 62152-54-9; $(Me_3PCH_2)W(CO)_5$, 71359-58-5; $(Ph_3PCH_2)Cr(CO)_5$, 52615-02-8; $(Ph_3PCH_2)Mo(CO)_5$, 71359-59-6; $(Me_3PCHPh)Cr(CO)_5$, 71359-60-9; $(Ph_3PCHPh)Cr(CO)_5$, 38317-58-7; $(Me_3PS)Mo$-

$(CO)_5$, 71341-47-4; $(Ph_3PNSiMe_3)_2Mo(CO)_4$, 71341-46-3; $(Ph_3PNH)_2Mo(CO)_4$, 71392-34-2; $(Ph_3PNSiMe_3)_3[Mo(CO)_3]_2$, 71382-08-6; $(Me_3PNPh)_3[Cr(CO)_3]_2$, 71341-45-2; $(Ph_3PNH)_3[Mo(CO)_3]_2$, 71341-44-1; $(Ph_3PNPh(CO))Mo(CO)_5$, 71369-78-3; $(H_3C)_3PNH_2(Cl)$, 17663-95-5; $(H_3C)_3P(NHCH_3)Cl$, 71328-70-6; $(H_3C)_3P(NHC(CH_3)_3)Cl$, 71359-30-3; $(H_5C_6)_3P(NHC(CH_3)_3)Cl$, 71359-31-4; $(H_3C)_3P(NHC_6H_5)Cl$, 71328-71-7.

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