Heteroatom Chemistry
Volume 5, Number 2, 1994

Study on the Aromaticity and Reactivity of Chlorophosphinines

László Nyulászi*

Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Hungary

György Keglevich

Department of Organic Chemical Technology, Technical University of Budapest, H-1521 Budapest, Hungary

Received 3 November 1993; revised 27 December 1993

ABSTRACT

Aromaticity of phosphinine derivatives, such as 2-, 3-, and 4-chlorophosphinines and 4-chloro-3-methyl- and 3,5-dimethylphosphinine, has been investigated by means of quantum-chemical calculations and photoelectron spectroscopy. The position of the π-bands in the photoelectron spectra of 4-chloro-3-methyl- and 3,5-dimethylphosphinine indicated that the aromaticity of these species is similar to that of the corresponding benzene derivatives.

The MP2/6-31G and the HF/3-21G(*) geometries of the chlorophosphinines, together with the isodesmic reaction energies and Mulliken charge distributions, showed that the electronic system of phosphinine is not significantly perturbed by the chloro-substitution.*

3-methyl-4-chlorophosphinine, similarly to 2-chlorophosphinine, was inert toward nucleophiles even under forced conditions. This unreactivity can more likely be rationalized by kinetic considerations than by thermodynamic arguments (such as increased aromatic stabilization of the chlorophosphinines).

INTRODUCTION

Phosphinine was one of the first examples of aromatic species containing a heavy main group element [1] that "violated" the empirical double bond rule [2]. Its aromaticity has been proven by several different aromaticity criteria [3] and is generally accepted. The aromaticity and corresponding reactivity of substituted phosphinines, however, is much less investigated. In a recent work, Le Floch *et al.* [4] reported that 2-chlorophosphinine was inert in nucleophilic substitution reactions. However, according to Märkl's observation, 3-chloro-5-phenylphosphinine reacted with strong nucleophiles such as lithium-amides [5]. The inertness of 2-chlorophosphinine was interpreted by its increased aromaticity derived from the comparison of the bond lengths of the phosphinine with those of the transition metal complexes of 2-chlorophosphinine and the parent compound. In order to clarify their speculative statement (based on data obtained by gas electron diffraction and X-ray analysis), an appeal was made for theoreticians [4] to investigate further this problem.

By a new synthetic method based on dihydrophosphinine oxides, the hitherto unknown 4-chlorophosphinines became available [6], allowing a complex investigation to be made of the reactivity and aromaticity of all chlorophosphinines from several different aspects. In the present work, nucleophilic reactivity of 4-chlorophosphinines is investigated, together with the HeI and HeII photoelectron spectra of these compounds. For the interpretation of the present (and previous) observations on the reactivity and as an aid to interpret the spectra, ab initio quantum chemical calculations were carried out.

*To whom correspondence should be addressed.

1042-7163/94/$5.00 + .25

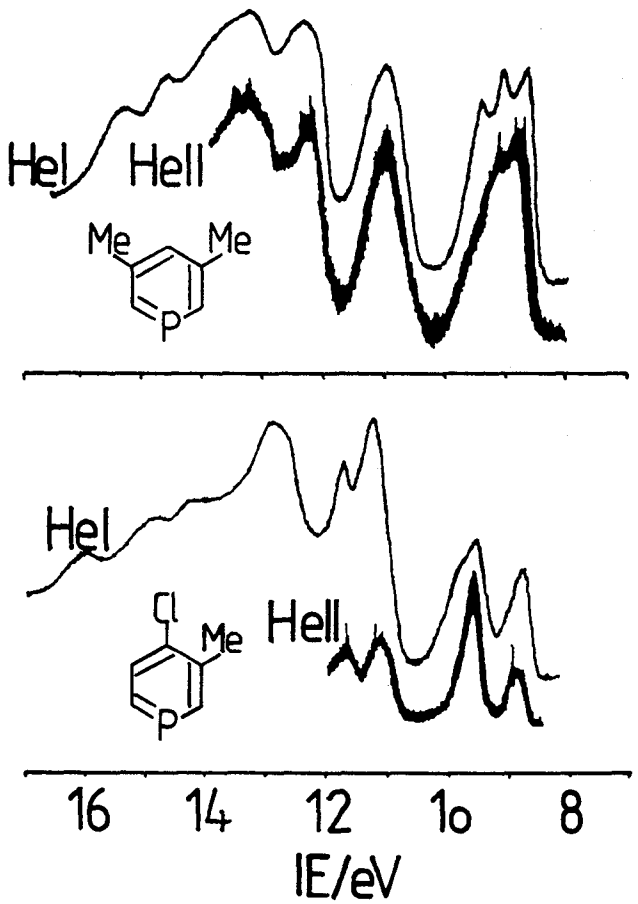
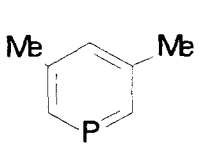
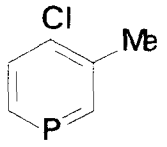


FIGURE 1

TABLE 1 Measured and Calculated[a] Ionization Energies of 3,5-Dimethyl- and 3-Methyl-4-chlorophosphinines (Data are Given in eV)

			
Experimental	*HF/3-21G(*)*	*Experimental*	*HF/3-21G(*)*
8.77(8.75[b])	8.59π	8.84(8.84[c])	8.83π
9.16(9.01[b])	9.20π	9.60(9.35[c])	9.88π
9.54	$10.26n_P$	9.8(sh)	$10.76n_P$
11.46	12.44	11.25	$12.40n_{Cl}\sigma$
	12.77π	11.69	$12.47n_{Cl}\pi$
			13.18
			14.48π
12.50	14.33	13.0	

[a]HF/3-21G(*) orbital energies are listed. HF/6-31G*//HF/3-21G(*) data, however, differ by less than 0.1–0.2 eV, while no change in orbital sequence occurs.
[b]π-Ionization energies of 1,3-dimethylbenzene [7] (Note that the symmetries of the uppermost two benzene orbitals are interchanged).
[c]π-Ionization energies of 1-chloro-2methylbenzene [8].

RESULTS AND DISCUSSION

The photoelectron spectra of 4-chloro-3-methyl- and 3,5-dimethylphosphinine are shown in Figure 1, while the observed and calculated (Koopmans) ionization energies are listed in Table 1. Comparing the relative intensities of the corresponding HeI and HeII spectra, bands originating from the removal of an electron from an orbital having a large linear coefficient at phosphorus or chlorine show drastic changes. Thus, in agreement with other phosphorus lone pair ionization energies for related aromatic compounds [9–13], bands at 9.54 and 9.8(sh) eV for 3,5-dimethyl- and 3-chloro-4-methylphosphinine, respectively, should be assigned to ionization from the phosphorus lone pair (n_P). Calculations also support the decision to assign the third IE to n_P, as shown in Table 1.

The first two ionizations of both compounds should be assigned to ionization from π-orbitals, similarly to the case of the parent phosphinine [9] and its 2,4,6-tri-t-butyl derivative [10]. As judged from the calculations, the HOMO (b_1 symmetry in the case of the parent molecule and its symmetrically substituted derivatives) has a relatively large linear coefficient at phosphorus. Accordingly, the intensity of the corresponding band in the HeII spectrum shows a considerable decrease for 3-chloro-4-methylphosphinine, where this band is well separated from the rest of the bands. Similar phenomena were observed in the cases of the parent phosphinine [9] and 1H-1,3-azaphosphole [12] as well. The intense 11.46 eV band of 3,5-dimethylphosphinine should be assigned to two ionizations, viz. to the σ_{CPC} bonding orbital and the lowest lying π-MO. This assignment is based on the calculations and is in agreement with the assigned spectrum of the phosphinine itself [9]. As shown before [14], π-ionization energies of conjugated systems containing the λ^3–P=C bond are similar to those containing the C=C bond, here, we compared the ionization energies of the corresponding benzene derivatives. The assignable π-ionization energies of the corresponding benzene derivatives (in *italics* in Table 1) are nearly the same as those of the phosphinines. This good agreement not only gives further support to our previous findings [14] about the similar conjugative abilities of the C=C and λ^3–P=C bonds (for the similar chemical reactivity of these compounds, see Ref. [15]), but indicates that the aromaticity of the corresponding benzenes and phosphinines is nearly the same. However, π-ionization energies of chloropyridines [16] (9.7–10.0 π_3 and 10.0–10.7 π_2 eV) and 3,5-dimethylpyridine [17] (8.82 π_3 and 9.97 eV π_2) are at higher ionization energies than those of the corresponding phosphinines.

Regarding 3-methyl-4-chlorophosphinine, chlorine nonbonding ionizations can be assigned

to the 11.25/11.69 eV bands based on the decreasing HeII/HeI intensity ratio and the splitting (0.44 eV). This splitting is the usual value for chloro-substituted aromatic systems [18–21]. (These bands are obviously superimposed by the σ_{CPC} and π_1 ionizations, as judged from the increased relative intensity of the bands in the 11–12 eV region.) This assignment is further supported by the calculated IE-*s* (see Table 1) and by the similar n_{Cl} ionization energies of chlorobenzene [18] and other chlorinated aromatic systems [8,16,18–21] (11–12 eV, see Table 2). As seen from the data presented in Table 2, chlorine lone pair ionization energies of the chlorophosphinine are again closer to the corresponding chlorobenzene ionization energies than to those of any other heteroaromatics.

In the prediction of the extent of the aromaticity of phosphinines, the structural characteristics of these compounds are of special importance. One of the most important arguments in considering the increased aromaticity of 2-chlorophosphinine [4] was that the bond lengths of the 2-chlorophosphinine · $W(CO)_5$ complex [4] were similar to those of the parent phosphinine [22] but differed from those reported for the phosphinine · $Mo(CO)_5$ complex. In the latter case, the difference between C–C bond lengths was bigger than in the other two structures and the chloro-compound exhibited the largest equalization. One must, however, be very careful with the conclusion of increased aromaticity as, on one hand, different complexes cannot generally be compared and, on the other hand, structures determined by different methods *may* be different (crystal forces, effects of large amplitude motions). To clarify the situation, we evaluated the structures of phosphinine and chlorophosphinines by means of ab initio methods, at two different levels of theory.

Calculated geometries of the chloro-substituted phosphinine derivatives at the HF/3-21G(*) and MP2/6-31G* levels of theory are shown in Table 3. To study the effect of chloro-substitution in detail, all possible monosubstituted isomers have been considered. Structural data for the corresponding pyridine and benzene derivatives calculated at the HF/3-21G(*) level are listed in Table 4. As seen, the chloro-substituent has practically no effect on the geometry, neither on the phosphinine nor on the pyridine ring. The C–Cl bond length is ca. 1.75 Å in each case (being somewhat larger for phosphinines than for pyridine derivatives), while changes in the bond lengths of the ring are less than 0.01 Å, if the different isomers are compared to each other or to the corresponding parent compound. As for the parent rings, the present results are in agreement with those published earlier [12]. In the case of phosphinines, MP2/6-31G* calculations have also been carried out. Bond lengths for the parent phosphinine and chlorophosphinines again show close resemblance at this level of theory.

On the basis of the calculated geometries (Table 3), no increased aromaticity of chlorophosphinines (including also 2-chlorophosphinine) can be assumed. Although direct comparison of X-ray structures obtained from the solid phase with calculated structures is meaningless, it is worth noting that the calculated structure of 2-chlorophosphinine is very close to that obtained for its tungstate complex by X-ray analysis [4]. In contrast with the good agreement between the experimental and the calculated structures of 2-chlorophosphinine, the calculated difference of the two C–C bond lengths (ΔCC) for the parent phosphinine was less than 0.005 Å at the HF/3-21G(*) [23], HF/4-31G(*) [12], HF/6-31G* [24], and the MP2/6-31G* levels of theory, while 0.029 ± 0.023 Å was reported in the combined electron diffraction (ED) and microwave spectroscopy (MW) analysis [22]. At the highest level of theory used here, such a difference is unusual, even if we consider that the calculated and the ED structures to the equilibrium geometry and to the r_g structure, respectively. Considering the uncertainty given (for 2.5σ) in the ED work [22], reinvestigation of the experimentally determined structure of phosphinine seems to be desirable.

In order to study the conjugative interaction between the chlorine substituent and the ring, isodesmic reactions have been investigated. Energies of these reactions for the different compounds, including chlorobenzene and chloropyridines, are listed in Table 5. (Ar refers to an aromatic ring.)

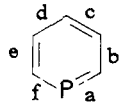
$$ArCl + CH_4 = ArH + CH_3Cl$$

As seen from the data, the conclusion is again sim-

TABLE 2 Chlorine Lone Pair Ionization Energies in eV for Chloro-Substituted Heteroaromatic Systems

											
$n_{Cl}\sigma$	11.25	11.09	11.34	11.53	11.82	11.74	11.98	11.46	11.42	11.34	10.86
$n_{Cl}\pi$	11.69	11.53	11.70	12.08	12.45	12.60	12.47	11.85	11.93	11.70	11.24
Ref.	—	[8]	[18]	[16]	[16]	[16]	[19]	[20]	[20]	[21]	[21]

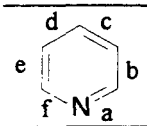
TABLE 3 Bond Lengths for Phosphinine and for the Chloro-Substituted Derivatives in Å at Different Levels of Theory



	ED[22]	MP2[g]	HF[h]	2Cl MP2[g]	2Cl HF[h]	3Cl MP2[g]	3Cl HF[h]	4Cl MP2[g]	4Cl HF[h]
a	1.733	**1.739**	1.719	**1.749**	1.726	**1.739**	1.720	**1.740**	1.719
b	1.413	**1.393**	1.382	**1.392**	1.383	**1.389**	1.381	**1.391**	1.383
c	1.384	**1.396**	1.385	**1.394**	1.386	**1.395**	1.382	**1.395**	1.381
d	1.384	**1.396**	1.385	**1.395**	1.381	**1.394**	1.383	**1.395**	1.381
e	1.413	**1.393**	1.382	**1.392**	1.383	**1.393**	1.382	**1.391**	1.383
f	1.733	**1.739**	1.719	**1.739**	1.715	**1.737**	1.716	**1.740**	1.719
C–Cl	—	—	—	**1.746**	1.763	**1.747**	1.759	**1.740**	1.752

[g]MP2/6-31G*; [h]HF/3-21G(*); ED: structure determined from interpreting microwave spectra and electron diffraction data.

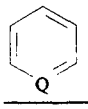
TABLE 4 Bond Lengths (in Å) for Pyridine and Its Chloro-Derivatives Together with the Data for Benzene and Chlorobenzene at HF/3-21G(*) Level of Theory



		2-Cl-	*3-Cl-*	*4-Cl-*	*Benzene*	*Cl-Benzene*[g]
a	1.330	1.311	1.327	1.330	1.385	1.380
b	1.382	1.376	1.375	1.381	1.385	1.383
c	1.384	1.380	1.379	1.379	1.385	1.384
d	1.384	1.387	1.384	1.379	1.385	1.384
e	1.382	1.378	1.382	1.383	1.385	1.383
f	1.330	1.335	1.331	1.330	1.385	1.380
C–Cl	—	1.743	1.741	1.742	—	1.749

[g]The chlorine atom is situated in position 1 (between a and f bonds).

TABLE 5 Energies of Isodesmic Reactions (in kcal/mol)



	2Cl, Q=P	*3Cl, Q=P*	*4Cl, Q=P*	*2Cl, Q=N*	*3Cl, Q=N*	*4Cl, Q=N*	*Q=CCl*
HF[a]	−0.37	+2.13	+2.05	+2.12	+3.04	+2.49	+3.92
MP2[b]	+4.45	+6.28	+5.25	+7.25	+5.07	+5.81	+6.20
MP2[c]	+7.13	+8.82	+8.55	—	—	—	—

[a]HF/3-21G(*)//HF/3-21G(*) + ZPE
[b]MP2/6-31G*//HF/3-21G(*) + ZPE
[c]MP2/6-31G*//MP2/6-31G* + ZPE
[-]Negative energy means destabilization; zero point energy (ZPE) is calculated at the HF/3-21G(*) level of theory.

ilar to the one drawn from the geometries and the photoelectron spectra; i.e., there is no significant difference between the conjugative interactions (between the π-system and the chlorine lone pair) when the chloro-substituent is attached to any of the aromatic rings investigated here. (The somewhat smaller stabilization shown by 2-chlorophosphinine is within the expected error [25] of the calculations.) In agreement with our expectations, inclusion of electron correlation increases somewhat the stabilization energies of the isodesmic reaction. The reaction energies calculated at the MP2/6-31G*//MP2/6-31G* + ZPE level (for phosphinines only) show some further increase. In order to assess whether the stabilization observed is due to increased aromaticity or is a result of the conjugative interaction between the chlorine lone pair and the π-system, the same reaction has been investigated for vinyl chloride and 2-chlorophosphaethylene (Cl–CH=PH). The stabilization energies for these compounds at the MP2/6-31G*//MP2/6-31G* + ZPE level of theory are close to the values obtained for chlorophosphinines at the same level of sophistication (6.78 and 5.76 kcal/mol, respectively), indicating that the stabilization cannot be attributed to the increase of aromaticity.

Mulliken charge distribution shown in Figure 2 (for the heavy atoms only, for hydrogens, the calculated charge is about +0.18–0.20) is different for the pyridine and phosphinine rings. The presence of the chlorine atom in the ring does not change considerably the charge distribution relative to that of the parent compound (only the charge of the carbon atom attached to chlorine being changed somewhat, mainly due to the inductive effect of the substituent). This behavior indicates that the aromatic system is not effected significantly by the chloro-substituent.

To describe chemical reactivity, not only thermodynamical considerations (like aromatic stabilization of the reactant [4]), but also the barrier of the transition state (estimated by the powerful method of perturbation theory [26]) is of importance. It is well known that nucleophilic aromatic substitution has a transition state (σ-complex) in which the cyclic conjugation is interrupted. The energy of the transition state is mainly dependent on the five-electron five-centered nonbonding molecular orbital (NBMO) which is stabilized if one of the carbon atoms is replaced (especially in position α or γ) by electron-withdrawing atoms like nitrogen [26,27]. As σ^2,λ^3-phosphorus behaves similarly to a carbon atom in conjugative interactions [14], it is reasonable to conclude that the corresponding NBMO in the transition state will be similar for chlorobenzenes and phosphinines. Chlorobenzene is known to take part only under drastic conditions in nucleophilic substitution reactions; thus, chlorophosphinines are not expected to be very reactive either. Indeed, 2-chlorophosphinine was found to be inert in nucleophilic substitution reactions [4]. On consideration of the previously discussed geometries (Table 3), isodesmic reactions (Table 5), and charge distributions (Figure 2) of different chlorophosphinines, neither can the 4-chloro-derivative show reactivity in similar reactions. Accordingly, it was not surprising that the halogen atom in 4-chloro-3-methylphosphinine failed to undergo substitution with nucleophiles, such as lithium diisopropylamide and sodium methylate/methanol.

Considerable decomposition was observed in both cases, and in the reaction with sodium methylate, some of the starting material was recovered unchanged. The ^{1}H NMR spectrum of the distillate revealed also the presence of several minor byproducts which were not aromatic (the shifts of the methyl-protons were between δ 1.2 and 1.9) and may have come from nucleophilic attack at the phosphorus atom of the phosphinines (cf. with Ref. [28]). The presence of another species, 1,1-dimethoxy-3-methyl-λ^5-phosphinine, also could not be excluded. ^{1}H NMR data (δ_{Me} = 2.15 (s), δ_{MeO} = 3.50 (s) with a 1:2 intensity ratio), attributable to this species, could be well identified, especially in the initial stage of the reaction. The observation of

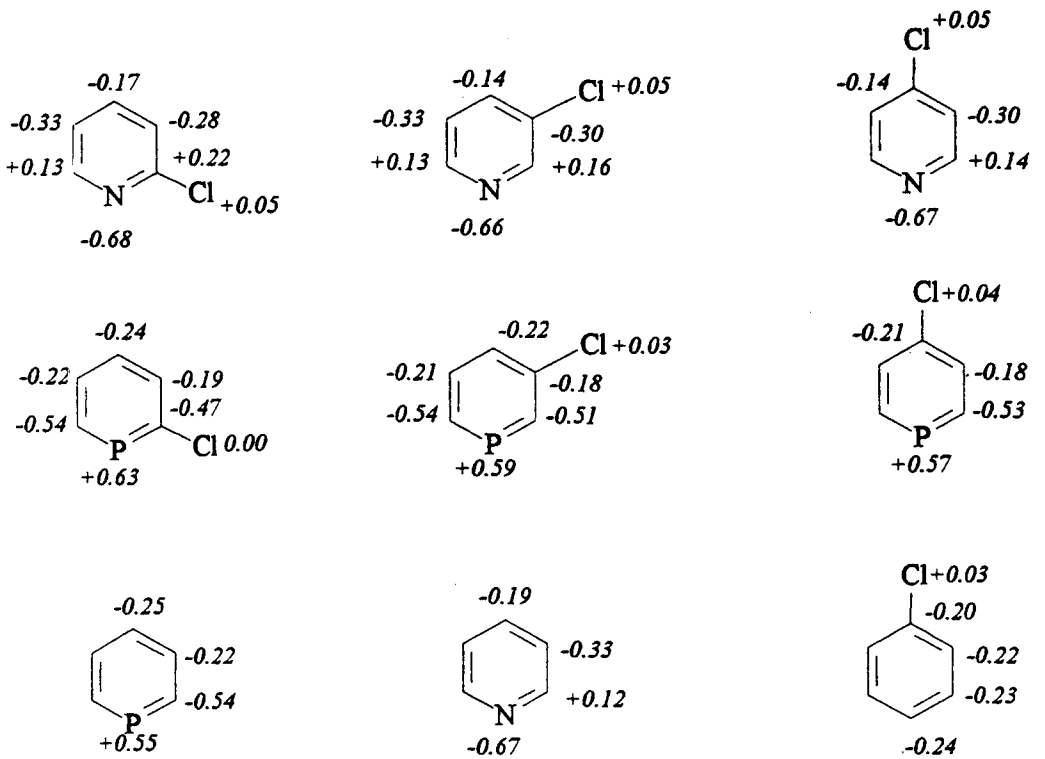


FIGURE 2

Teunissen and Bicklehaupt [29] that 1,1-diethoxy-λ^5-phosphinine is formed in the reaction of 2-iodophosphinine with sodium ethylate/ethanol [29] at least coincides with our assumption. The λ^5-phosphinine may be formed in a consecutive series of reactions starting with an attack on the phosphorus atom of the phosphinine by the alkoxide anion followed by protonation in position 4, departure of the chlorine atom as an anion, and attachment of a second alkoxy group to the phosphorus atom [29]. The unreactivity of the 4-chlorophosphinine in nucleophilic substitution reactions is probably further increased by the presence of the methyl group in position 3.

In view of the previous results on the similar aromaticity of all chlorophosphinines, Märkl's observation that 3-chloro-5-phenylphosphinine reacted with lithium diisopropylamide [5] seems somewhat surprising. This is not the case, however, if we consider the beneficent presence of the electron-withdrawing phenyl group in position 5, which may stabilize the NBMO and thus the transition state. The somewhat electropositive phosphorus in position β with respect to chlorine (no linear coefficient in the NBMO) might provide an additional argument to explain Märkl's observations [5].

EXPERIMENTAL CALCULATIONS

Photoelectron spectra have been recorded on a spectrometer described earlier [30] using both HeI and HeII resonance lines. The resolution of the spectrometer under working conditions was 45 meV (FWHM) at the $Ar^2P_{3/2}$ line. For calibration, MeI was used as an internal standard.

Quantum-chemical calculations have been carried out by use of the MICROMOL package [31] and by the Gaussian 90 suite of programs [32] on an IBM 3090 mainframe computer. For geometry optimization, the economical 3-21G(*) basis set was used. At the optimized geometries, analytical second derivatives have been calculated. As all harmonic frequencies were positive, the structures obtained are real minima at the respective potential energy surfaces. In order to account for the effect of electron correlation, improved energies at the MP2/6-31G* level of theory (MP2/6-31G*//HF/3-21G(*) energies) have been calculated as well. These data have been used to obtain isodesmic reaction energies. In the case of chlorophosphinines, the structures have been reoptimized at the MP2/6-31G* level, but since they have similar structures as those at the HF/3-21G(*) level, no second derivatives have been calculated.

ACKNOWLEDGMENT

Financial support from OTKA 642 and 1170 is gratefully acknowledged.

REFERENCES

[1] G. Märkl, *Angew. Chem., 78*, 1966, 907; *Angew. Chem. Int. Ed. Engl.*, 5, 1966, 846.
[2] K. S. Pitzer, *J. Am. Chem. Soc., 70*, 1948, 2140.
[3] G. Märkl: *λ^3-Phosphinines, λ^3-Aza-phosphinines and λ^3,λ^3-Diphosphinines in Multiple Bonds and Low Coordination in Phosphorus Chemistry*, M. Regitz, O. J. Scherer, (eds), G. Thieme Verlag, Stuttgart, Germany, 1990.
[4] P. Le Floch, L. Ricard, F. Mathey, *Polyhedron, 9*, 1990, 991.
[5] G. Märkl, K. Hock, *Tetrahedron Lett., 24*, 1983, 5055.
[6] Gy. Keglevich, K. Újszászy, A. Kovács, L. Töke, *J. Org. Chem., 58*, 1993, 977.
[7] M. Klessinger, *Angew. Chem., 84*, 1972, 544.
[8] S. Fujisawa, I. Oonishi, S. Masuda, K. Ohno, Y. Harada, *J. Phys. Chem., 95*, 1991, 5742.
[9] C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe, III, D. T. Clark, U. T. Cobley, D. Kilcast, I. Scanlan, *J. Am. Chem. Soc., 95*, 1973, 928; A. J. Ashe, B. Fritz, N. Y. El-Sheik, E. Heilbronner, J. P. Maier, J. F. Muller, *Helv. Chim. Acta. 59*, 1976, 1944.
[10] H. Oehling, W. Schäfer, A. Schweig, *Angew. Chem., 83*, 1971, 723.
[11] L. Nyulászi, G. Csonka, J. Réffy, T. Veszprémi, J. Heinicke, *J. Organomet. Chem., 373*, 1989, 49.
[12] T. Veszprémi, L. Nyulászi, J. Réffy, J. Heinicke, *J. Phys. Chem., 96*, 1992, 624.
[13] L. Nyulászi, T. Veszprémi, J. Réffy, B. Burkhardt, M. Regitz, *J. Am. Chem. Soc., 114*, 1992, 9080.
[14] L. Nyulászi, T. Veszprémi, J. Réffy, *J. Phys. Chem., 97*, 1993, 4011.
[15] F. Mathey, *Acc. Chem. Res., 25*, 1992, 90; R. Appel, *Pure and Appl. Chem., 59*, 1987, 977.
[16] A. Modelli, G. Distefano, *J. El. Spectr. Rel. Phen., 23*, 1981, 323.
[17] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata: *Handbook of HeI Photoelectron Spectra of Organic Compounds*, Halsted Press, New York, 1980.
[18] W. von Niessen, L. Åsbrink, G. Bieri, *J. El. Spectr. Rel. Phen., 26*, 1982, 173.
[19] L. Nyulászi, T. Veszprémi, J. Réffy, Gy. Zsombok, T. Cvitaš, B. Kovač, L. Klasinc, S. P. McGlynn, *Int. J. Quant. Chem. Quant. Chem. Symp., 25*, 1991, 479.
[20] T. Veszprémi, L. Nyulászi, Gy. Zsombok, *J. El. Spectr. Rel. Phen., 46*, 1988, 269; T. Veszprémi, L. Nyulászi, Gy. Zsombok, T. Cvitaš, B. Kovač, L. Klasinc, *J. Mol. Struct. (THEOCHEM), 202*, 1989, 227.
[21] F. Fringuelli, G. Marino, A. Taticchi, G. Distefano, F. P. Colonna, S. Pignatoro, *J. Chem. Soc. Perkin II*, 1976, 276.
[22] T. C. Wong, L. S. Bartell, *J. Chem. Phys., 61*, 1976, 2840.
[23] K. K. Baldridge, M. S. Gordon, *J. Am. Chem. Soc., 110*, 1988, 4204.
[24] C. W. Bock, M. Tratchman, P. George, *Struct. Chem., 1*, 1990, 345.
[25] W. J. Hehre, L. Radom, P. V. R. Schleyer, J. A. Pople: *Ab Initio MO Theory*, J. Wiley, New York, 1986.
[26] M. J. S. Dewar, R. C. Dougherty: *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
[27] H. E. Mertel: *The Chemistry of Heterocyclic Compounds Vol II Pyridine and its Derivatives*, Interscience, New York, 1961; A. J. Boulton, A. McKillop: *Reactivity of Six-Membered Rings in Comprehensive*

Heterocyclic Chemistry Vol 2a, A. R. Katritzky, C. W. Rees (eds), Pergamon Press Ltd., Oxford, 1984.
[28] G. Märkl, F. Lieb, A. Merz, *Angew. Chem., 79*, 1967, 59.
[29] H. T. Teunissen, F. Bicklehaupt, *Bull. Soc. Chim. Belg., 101*, 1992, 609.
[30] T. Veszprémi, Gy. Zsombok, *Magy. Kém. Folyóirat., 92*, 1986, 39.
[31] S. Colwell, R. Amos: MICROMOL mark 4.0, 1987.
[32] M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople: [GAUSSIAN 90, Revision J.] Gaussian, Inc., Pittsburgh, PA, 1990.