J. Org. Chem. **1996,** *61,* 7808−7812

Phospholes with Reduced Pyramidal Character from Steric Crowding. 2. Photoelectron Spectral Evidence for Some Electron Delocalization in 1-(2,4-Di-*tert*-butyl-6-methylphenyl)-3-methylphosphole

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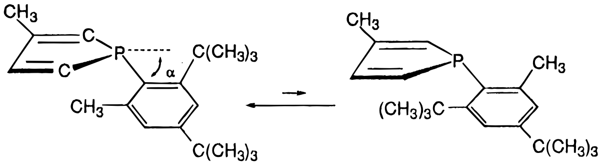
Received April 8, 1996[⊗]

Photoelectron spectroscopy has been explored as a tool to measure the flattening of the phosphorus pyramid in a phosphole as caused by a large, sterically demanding P-substituent. Earlier PE spectra had shown no difference in ionization energies (IE) for simple phospholes and their tetrahydro derivatives (both around 8.0−8.45 eV). Calculations of the Koopmans IE at the Hartree−Fock 6-31G* level for 1-methylphospholane showed that, as is known for nitrogen, planarization at phosphorus markedly reduced the ionization energy value (8.74 to 6.29 eV). A reduction in IE also occurred on planarizing 1-methylphosphole, but to a lesser extent, being offset by increased electron delocalization (8.93 to 7.16 eV). This suggests that experimental comparison of IE for the unsaturated and saturated systems could be used to detect the presence of electron delocalization in the former. The IE experimentally determined for the crowded 1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methylphosphole was 7.9 eV, the lowest ever recorded for a phosphole. The corresponding phospholane had IE 7.55 eV. The difference in the values is attributed to electron delocalization in the phosphole. Calculations performed on the related model 1-(2-*tert*-butyl-4,6-dimethylphenyl)-phosphole showed that the P-substituent adopted an angle of 55.7° (DFT/6-31G* level; 57.6° at the HF/6-31* level) with respect to the C$_2$−P−C$_5$ plane (for P-phenyl, 67.1° and 68.3°, respectively).

In the preceding paper of this issue,[1] we described the synthesis and NMR characterization of a phosphole (**1**) with the sterically demanding 2,4-di-*tert*-butyl-6-methylphenyl substituent at phosphorus. This compound was prepared for the purpose of determining if a large P-substituent, through steric interactions with the phosphole ring, could cause flattening of the normally pyramidal[2,3] phosphorus, with the consequence of enhancing cyclic electron delocalization in the ring system. Computations clearly indicated that large aryl substituents such as this could cause the desired effect, so that the normal angle (designated α; see structure **1A**) by which a P-substituent would fall below the plane of the C−P−C moiety of the phosphole ring (about 68° in 1-methylphosphole) would be reduced by as much as 10−15°. Both the ^{13}C and ^{1}H NMR spectra of **1** showed that the aryl substituent adopted a conformation in which the two ring planes were perpendicular; the conformation (**1A**) with the aryl methyl group, rather than the *tert*-butyl group (as in **1B**), positioned under the plane of the phosphole ring was preferred. Even at low temperatures (−50 °C) there were no spectral indications of conformer **1B**; if a conformational equilibrium is present, the contribution of form **1B** must be very small.



1A **1B**

Photoelectron spectroscopy can be used to determine the stabilization energy of the lone pair in the family of five-membered heterocycles with divalent atoms. As seen in Table 1, all of the lone-pair ionization energy values[4] are higher than are those for the corresponding tetrahydro derivatives,[5] and this provides a measure of the interaction of the lone pair with the π-system. It is the interaction with the unoccupied orbitals, rather than with the occupied orbitals,[6] that is responsible for aromatic stabilization,[7] and indeed thiophene, accepted to be the most aromatic compound of this series,[8] has the largest lone pair stabilization energy. However, with a trivalent heteroatom, as in the case of N in pyrrole and P in phosphole, the geometry of the heteroatom must be taken into consideration. Thus, N is planar in pyrrole, but pyramidal in pyrrolidine, and a comparison of the ioniza-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

[1] Quin, L. D.; Keglevich, G.; Ionkin, A. S.; Kalgutkar, R.; Szalontai, G. *J. Org. Chem.* **1996**, *61,* 7801.

[2] Mathey, F. *Chem. Rev.* **1988**, *88,* 437.

[3] Hughes, A. N. In *Handbook of Organophosphorus Chemistry;* Engel, R., Ed.; Marcell Dekker: New York, 1992.

[4] The π-type p orbital of the heteroatom has the largest contribution in the uppermost doubly filled b$_1$ orbital: (a) Distefano, G.; Pignatoro, S.; Innorta, G.; Fringuelli, F.; Marino, G.; Taticchi, A. *Chem. Phys. Lett.* **1973**, *22,* 132. (b) Schäfer, W.; Schweig, A.; Gronowitz, S.; Taticchi, A.; Fringuelli, F. *J. Chem. Soc., Chem. Commun.* **1973**, 541.

[5] Pignatoro, S.; Distefano, G. *Chem. Phys. Lett.* **1974**, *26,* 356.

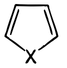
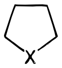
[6] The lone pair orbital of tetrahydrofuran analogues has been shown to interact with the σ CH$_2$ orbitals.[5] This (destabilizing) interaction was shown to be the most effective for tetrahydrofuran, thus without this destabilization an even higher lone pair IE should be expected for the oxygen lone pair.

[7] Epiotis, N. D.; Cherry, W. R.; Bernardi, F.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98,* 4361.

[8] (a) Katritzky, A. R.; Barczynsky, P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111,* 7. (b) Schleyer, P. v. R.; Freeman, P. K.; Jias, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 337. (c) Nyulászi, L.; Várnai, P.; Veszprémi, T. *THEOCHEM,* in press.

S0022-3263(96)00641-X CCC: $12.00

Table 1. Heteroatom Lone Pair (n_X) Ionization Energies (IE, in eV) of Some Heterocyclic Systems

X			ΔIE
O	10.32 [a]	9.53 [c]	0.79
S	9.52 [a]	8.42 [c]	1.10
Se	9.19 [a]	8.14 [c]	1.05
Te	8.40 [a]	7.73 [c]	0.67
NH	9.22 [b]	8.77 [d]	0.45

[a] Reference 4. [b] Derrick, P. J.; Asbrink, L.; Edqvist, O.; Lindholm, E. *Spectrochim. Acta* **1971**, *27A*, 2525. [c] Reference 5. [d] Yoshikawa, K.; Hashimoto, M.; Morishima, I. *J. Am. Chem. Soc.* **1974**, *96*, 288.

tion energies of the two molecules will not give a useful measure of the stabilization energy of the former. In fact the difference is only 0.45 eV, less than that of any of the divalent heteroatom systems, yet the aromaticity of pyrrole is comparable to that of thiophene.[8] Flattening of the N pyramid in an amine is known to reduce the ionization energy by about 0.9 eV; compare the value of 7.05 eV for manxine, a cage compound with planar N, with that (7.92 eV) for tri-*n*-propylamine.[9] In a simple phosphole, P is pyramidal,[2,3] as it is in the tetrahydro derivatives. Early PES studies[10,11] showed no difference in the ionization energies of these molecules, and the conclusion was drawn that there was little interaction between the lone pair and the π-system of the phosphole. Epiotis and Cherry[12] later emphasized that the energy of the phosphorus lone pair orbital for a planar phosphole would be determined by its interaction with the occupied and unoccupied π-orbitals; if these interactions happen to be of equal strength, the orbital energy would remain at the same value as for the unperturbed lone pair. Although less explicity expressed, a similar observation can be found in an earlier paper.[11]

We have performed calculations of the Koopmans ionization energy of 1-methyl- and 1-phenylphosphole at the Hartree–Fock 6-31G* level, as a function of the degree of flattening of the phosphorus pyramid (Table 2). It is clearly seen that, as the angle of deflection (α in **1A**) of the methyl substituent in 1-methylphosphole decreases from the natural pyramidal value of 68.0° to planarity at 0°, the calculated IE decreases from 8.93 eV to 7.16 eV, therefore suggesting that the experimental determination of the ionization energy could provide a measure of the approach to planarity induced by the bulk of a substituent on P. In this table, the pyramidalization angle[13] ($\theta_{\sigma\pi} - 90$, discussed in the preceding paper of this issue[1]), is also given. The calculated values for IE of 1-phenylphosphole show the same trend and range from 9.03 eV to 7.18 eV at planarity. Also of importance is the effect of flattening the P atom in the tetrahydro derivative; just as is seen in amines,[9] flattening of 1-methylphospholane causes a decrease in the ionization energy (Table 3), from 8.74 eV for the natural pyramid to 6.29 eV in the planar form. On comparing the natural pyramidal structures for 1-methylphosphole and 1-methylphospholane, it is seen that there is little difference (0.19 eV) in their n_p energies, just as had been observed in early experiments on the PES of unhindered phospholes.[10,11] Thus, even though the calculated values do tend to be on the high side of experimental (1-phenylphosphole, calcd 9.03 and 8.45 ± 0.05 expt[10]; for 1-methylphosphole, calcd 8.93, compared to expt 8.45 for 1-butylphosphole in the absence of data for 1-methyl; 1-methylphospholane, calcd 8.74, compared to expt 8.25[11] for 1-butyl), it can be concluded that flattening of phosphorus will have a greater effect on the lone pair ionization energy of the phospholane than on the phosphole, there being some offset of the effect of planarization by electron delocalization. The maximum difference of 0.87 eV for 1-methylphosphole is achieved at planarity. A role for PES in the study of partially flattened phospholes is therefore clearly established.

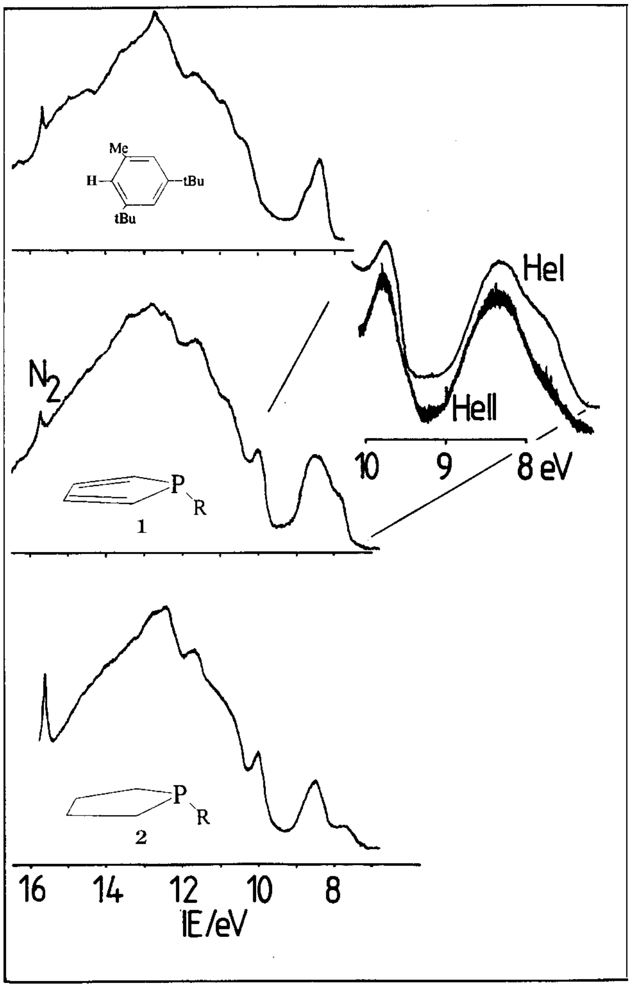


Figure 1. Photoelectron spectra of compounds **1** and **2**.

The photoelectron spectra of hindered phosphole **1** and its tetrahydro derivative **2**[1] are given in Figure 1 and Table 4, together with the spectrum of the aromatic hydrocarbon (3,5-di-*tert*-butyltoluene) corresponding to the P-substituent. This allows the recognition of the signals arising from the aryl ring system (8.3–8.4 eV) in all of the spectra. That this value is the same in the phosphole implies no π-electron interaction between the two ring systems, a fact already reported[10,11] for the 1-phenyl derivative and consistent with the conforma-

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(9) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136.

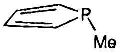
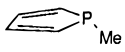
(10) Schäfer, W.; Schweig, A.; Märkl, G.; Hauptmann, H.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 145.

(11) Schäfer, W.; Schweig, A.; Mathey, F. *J. Am. Chem. Soc.* **1976**, *98*, 407.

(12) Epiotis, N. D.; Cherry, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 4365.

(13) (a) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385. (b) Haddon, R. C. *Science* **1993**, *261*, 1545.

Table 2. Calculated (Koopmans) Ionization Energies [IE, $b_1/a'(n_p)$] in eV and Relative Energies (ΔE) in kcal/mol for 1-Methylphosphole

					
α[a]	68.0	50.0	30.0	10.0	0.0
$\theta_{\sigma\pi}$-90[b]	27.6	20.3	12.0	5.0	0.0
$b_1/a'(n_p)$[c]	8.93	8.16	7.51	7.19	7.16
a_2/a''[d]	8.71	8.59	8.38	8.16	8.13
b_2/a'' (σ_{CPC})	12.57	12.71	12.84	12.88	12.88
b_1/a'[c]	11.95	12.36	12.68	12.89	12.91
ΔE	0	4.42	14.70	22.04	22.80

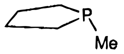
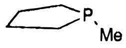
[a] The deflection angle of the methyl group from the C–P–C plane; see **1A**.

[b] The degree of pyramidalization calculated by the POAV method, as discussed in the preceding paper.[1]

[c] b_1/a' refers to the symmetry of the phosphorus lone pair (n_p) orbital in the C_{2v} (planar) structure, and C_s (nonplanar structure) point groups.

[d] a_2/a'' refers to the symmetry of the butadienic π-orbital in the C_{2v} (planar structure) and C_s (nonplanar) structure point groups.

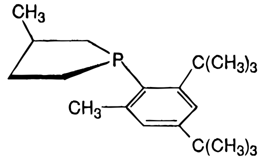
Table 3. Calculated (Koopmans) Ionization Energies [IE, $b_1/a'(n_p)$] in eV and Relative Energies (ΔE) in kcal/mol for 1-Methylphospholane

				
α[a]	67.2	50.0	30.0	0.0
$\theta_{\sigma\pi}$-90[b]	29.3	20.0	14.4	0.0
n_p	8.74	7.83	7.07	6.29
σ_{CPC})	11.62	11.64	11.65	11.72

[a] The deflection angle of the methyl group from the C–P–C plane; see **1A**.

[b] The degree of pyramidalization calculated by the POAV method, as discussed in the preceding paper.[1]

tional preference for phosphole **1** with perpendicular ring planes which would prevent such interaction. This conformational preference is supported by calculations for 1-phenylphosphole, 1-mesitylphosphole, and 1-(2-*tert*-butyl-4,6-dimethylphenyl)phosphole. At the HF/6-31G* and DFT/6-31G* levels this conformation was the minimum according to the second derivative calculations. The ionization energy of phosphole **1** is 7.9 eV, seen as a shoulder on the aryl π-band. This is the lowest energy ever recorded for a phosphole; it is some 0.5−0.6 eV below that for 1-phenylphosphole, indicating that **1**, as predicted, has partial flattening of the phosphorus pyramid.[14] The signal shows a somewhat decreased HeII intensity in agreement with this involvement of the lone pair in the α′ MO.[15] For the assignment of the photoelectron spectrum HF/6-31G* calculations were carried



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(14) The effect of placing a methyl substituent at the β-position, as in **1**, has not been considered. The effect of this substitution should be to lower the ionization energy by 0.1−0.2 eV. The observed band position[10] as well as the position of the 7.9 eV shoulder of **1** can be given with an uncertainty of about 0.05 eV.

(15) The ionization cross section of phosphorus s-type orbitals, which have a large contribution in the a′ MO involved in the ionization, is known to decrease under HeII conditions. Eland, J. H. D. *Photoelectron Spectroscopy*; 2nd ed.; Butterworths: London, 1983; p 73.

Table 4. Measured Ionization Energies and Assignments of Some Phospholes and Phospholanes in eV

compound	ionization energy	assignment
1-phenylphosphole[a]	8.45	n_P
	8.45	π (diene)
	9.25	π (phenyl)
	9.25	π (phenyl)
1-phenylphospholane[a]	8.35	n_P
	9.30	π (phenyl)
	9.30	π (phenyl)
1	7.9 (sh)	n_P
	8.35	π (diene)
	8.35	π (phenyl)
	8.35	π (phenyl)
2	7.54	n_P
	8.27	π (phenyl)
	8.27	π (phenyl)

[a] See ref 10.

out for **1**. As a basis for the structure the HF/6-31G*-optimized geometry of 1-(2-*tert*-butyl-4,6-dimethyl-phenyl)phosphole was used. The methyl substituent at the β-position of the phosphole ring and the methyl groups of the second *t*-Bu moiety were attached with standard geometrical features (CC, 1.54; CH, 1.08 Å; tetrahedral angles). The HOMO obtained from the calculations was the n_p orbital, in agreement with the HeII intensity. The Koopmans ionization energy was 8.19 eV. This value is lower by 0.8 eV than the one calculated for 1-phenylphosphole, while the difference in the observed IE is 0.5−0.6 eV. Thus it seems that the calculated 10° opening of angle α (*vide infra*) is reasonable.

To confirm the significance of the observed value of 7.9 eV for phosphole **1**, it should be compared to the experimental value for the tetrahydro derivative **2**, which is 7.55 eV. This value also indicates substantial flattening of the pyramid in **2**. This is the first experimental observation of a considerable difference between the energies of a phosphole and its tetrahydro derivative, clearly pointing to the presence of a stabilizing interaction between the lone pair and the π^*-orbital. The difference in ionization energy (0.3^5 eV, 8 kcal/mol) for the 1-phenyl derivative is a measure of the additional delocalization in the phosphole caused by the partial flattening of the pyramid.

It would be of value to know the degree of flattening of the phosphorus pyramid in **1A** that is associated with the lowered experimental ionization energy. We have approached this question by performing *ab initio* calculations on the preferred geometry of the phosphole and from that the ionization energy associated with this structure. To facilitate these calculations, some simplifications of the structures were made; the 3-methyl group on the phosphole ring was not included, and the 4-*tert*-butyl group of phosphole **1A** was replaced by methyl. None of these simplifications should have significant effects on the parameters of the phosphole ring; semiempirical MNDO calculations on several substituted phospholes showed that adding a 3-substituent caused a change in α of only a few tenths of a degree. The results of calculations for 1*H*-phosphole, 1-phenylphosphole, and 1-(2-*tert*-butyl-4,6-dimethyl-phenyl)phosphole are given in Table 5. The calculated value for α in the case of 1-(2-*tert*-butyl-4,6-dimethylphenyl)phosphole at the HF/6-31G* level is 57.4° (55.7° at the DFT/6-31G* level), and the calculated value for the ionization energy is 8.19 eV, in reasonable agreement with the experimental value. On comparing the value for α to that calculated for 1-phenylphosphole (67.1° and 68.3° at DFT/6-31G* and HF/6-31G* levels, respectively), the extent of the flattening can be seen clearly. A relationship between the degree of flattening and electron delocalization was observed by calculating the full molecular geometry associated with the structure having the calculated value for $\alpha = 57.4°$. These calculations revealed that replacing H by phenyl caused practically no change in bond lengths, even though the values for α differ, but replacing phenyl by the larger trisubstituted phenyl group caused quite pronounced changes. The internal P−C bond was shortened by 0.02 Å, the $C_2{-}C_3$ double bond was decreased by 0.009 Å, and the $C_3{-}C_4$ single bond was lengthened by 0.010 Å. Similar conclusions can be drawn from the HF/6-31G* calculations (Table 5). All of these bond-length changes are consistent with increased electron delocalization in the substituted-phenyl phosphole. Our conclusion is that the concept of increasing the electron

Table 5. Selected Bond Lengths for Some Phospholes, as Optimized by the Density Functional Method Using the B3LYP Functional and the 6-31G* Basis Set (DFT/6-31G*) and by the Hartree−Fock Method (HF/6-31G*), and Pyramidalization Effects

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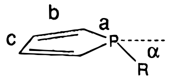
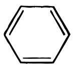
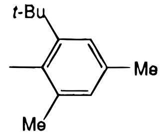
	H					
	DFT	HF	DFT	HF	DFT	HF
a, Å	1.817	1.821	1.816	1.817	1.796	1.802
b, Å	1.355	1.332	1.356	1.333	1.365	1.339
c, Å	1.460	1.471	1.461	1.479	1.451	1.463
α, °	73.6	74.3	67.1	68.3	55.7	57.6
$\theta_{\sigma\pi}-90$[a]	29.4	29.6	27.0	27.5	22.5	23.3

[a] Pyramidalization angle.[13b]

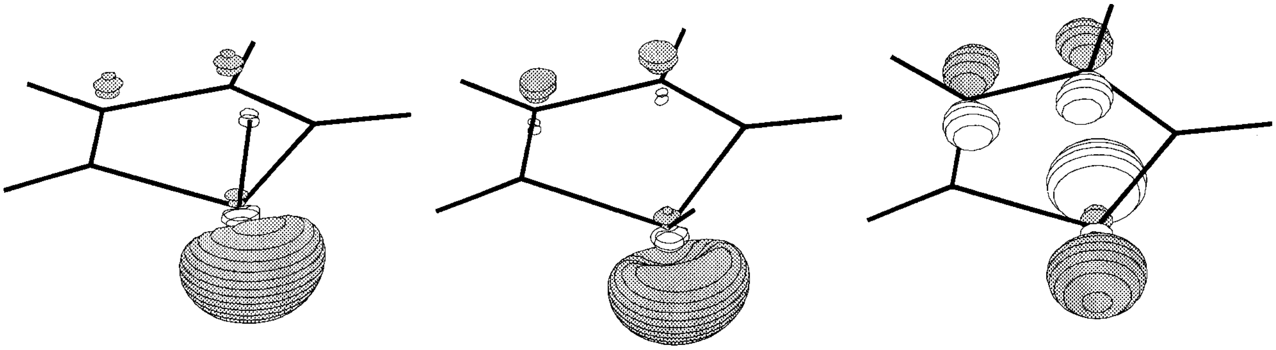


Figure 2. The shape of the phosphorus nonbonding MO for 1-methylphosphole calculated with deflection angles (see **1A**) of 68° (A), 50° (B), and 0° (C), as plotted by the MOLDEN[21] program.

delocalization in a phosphole by reducing the pyramidal character at phosphorus is valid. It would, of course, be important to confirm the bond parameters by X-ray diffraction analysis, but attempts to perform this experiment have been unsuccessful with the crystals of **1** available. We are proceeding to prepare other phospholes with large P-substituents in hopes of obtaining better crystals for the X-ray study, and even further flattening at phosphorus.

Finally, we consider the effect of flattening on the phosphorus lone pair orbital, as depicted in Figure 2 for deflection angles of 68°, 50°, and 0°. With the largest angle, which corresponds to the minimum on the potential energy surface for a 1-alkylphosphole,[16] the orbital is almost entirely localized at phosphorus. As the angle decreases, the involvement with the p_z orbitals on carbon increases. The shape of the orbital with an angle of 20−30° is quite similar to that of the planar form and to the corresponding MO in thiophenes,[17] indicating that even slightly nonplanar phospholes could exhibit chemical character like that in the planar, aromatic form. The synthesis of other phospholes with smaller α values than that for **1** will allow a test of this prediction.

Experimental Section

Photoelectron Spectral Measurements. Photoelectron spectra were recorded at the HeI and HeII resonance lines, using an instrument described earlier.[18] For calibration purposes, MeI was introduced simultaneously with the sample. Lone pair ionization [$b_1/a'(n_p)$] energies were 7.9 eV (sh) (**1**) and 7.55 (**3**); the ionization energy for aryl was 8.35 eV for both **1** and **2**.

Calculations. For the quantum chemical calculations the GAUSSIAN 92/DFT[19] suite of programs was used. Geometry optimizations were carried out under the specified constraint at the HF/6-31G* level of theory, as well as using the density functional method with the B3LYP functional of Becke[20] (referred to as DFT/6-31G* in the text). For the structures obtained, second derivatives were calculated. When no structural constraint was imposed during the course of the optimization, all the frequencies were real, while for the structures with fixed deflection angle (see **1A**) a single imaginary frequency was obtained. Koopmans ionization energies refer to the optimized structures.

Synthesis of 1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methylphospholane (2). To 1.0 g (0.00314 mol) of 1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methyl-3-phospholene 1-oxide in 30 mL of absolute ethanol was added 0.2 g of 5% palladium on carbon, and the suspension was then hydrogenated at 450 kPa and room temperature with 1 equiv of hydrogen. The mixture was filtered, and solvent was evaporated. The residue was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford 0.98 g (98%) of the diastereomers of phospholane oxide (^{31}P NMR ($CDCl_3$) δ +64.4 (79%) and +63.9 (21%): MS, *m/z* (rel int) 320 (M^+, 19), 305 (100), 250 (63), 57 (36): HR-MS, calcd for $C_{20}H_{33}OP$: 320.2269; found: 320.2206. Phenylsilane (0.15 mL, 0.00122 mmol) was added to a solution of the phospholane oxide in 20 mL of dichloromethane and the mixture stirred at reflux for 24 h under nitrogen. Evaporation of solvent left 0.88 g (95%) of the phospholane **2** as an air-sensitive oil: ^{31}P NMR ($CDCl_3$) δ −25.6 (70%), and −25.0 for the minor (30%) diastereomer: MS, *m/z* (rel int) 304 (M^+, 54), 289 (42), 248 (100), 233 (59), 57 (73): HR-MS, calcd for $C_{20}H_{33}P$: 304.2320; found: 304.2270.

Acknowledgment. L.N. and Gy.K. gratefully acknowledge the support from OTKA T014955 and TO14917, respectively, and L.D.Q. thanks the Exxon Education Foundation for a Research Award that enhanced this international collaboration.

JO9606416

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(16) Nyulászi, L. *J. Phys. Chem.* **1995**, *99*, 586.

(17) Nyulászi, L.; Veszprémi, T. *Acta Chim. Hung. (Models in Chemistry)* **1993**, *130*, 809.

(18) Veszprémi, T.; Zsombok, Gy. *Magy. Kém. Foly.* **1986**, *92*, 39.

(19) GAUSSIAN 92/DFT, Revision F.3. Frish, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, M.; Andrews, J. A.; Ragchavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, J.; Baker, J.; Stewart, J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1993.

(20) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; (b) Lee, C.; Young, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785; (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(21) Schaftenaar, G. *MOLDEN 2.5*; Caos/Camm Center: Nijmegen, The Netherlands, 1994.