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# 2-Phosphaindolizines

Neelima Gupta,[1] Chandra B. Jain,[1] Joachim Heinicke,[1]
Neetu Bharatiya,[2] Raj K. Bansal,[2] and Peter G. Jones[3]

[1]*Institut für Anorganische Chemie, EMA-Universität Greifswald, 17487 Greifswald, Germany E-mail: heinicke@rz.uni-greifswald.de; Telefax(+49-3834-864319)*

[2]*Department of Chemistry, University of Rajasthan, Jaipur 302 004, India Fax (+91-141-652784)*

[3]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany E-mail: p.jones@tu-bs.de*

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ABSTRACT: *Eight new 2-phosphaindolizines* **2** *have been obtained by [4 + 1] cyclocondensation of 1,2-dialkylpyridinium halides* **1** *with* $PCl_3$. *The X-ray structure analysis of* **2a** *is consistent with the integration of the 1,3-azaphosphole ring in the 10π-aromatic system. The charge densities on phosphorus of various representatives as obtained by PM3 calculations correlate approximately with the* $^{31}$*P-NMR shifts. The mass spectral fragmentation of* **2a** *resembles that of its nonphosphorus analog.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:333–339, 1998

## *INTRODUCTION*

The first synthesis of 2-phosphaindolizine by [4 + 1]cyclocondensation of 1,2-dialkylpyridinium salts with $PCl_3$ [1,2] led to the development of an advantageous synthetic method for the preparation of a variety of annulated azaphospholes. The compounds represent heteroaromatic 10π- or, in the case of partly hydrogenated annulated rings, 6π-systems [3,4], as shown by characteristic NMR data and, for 2-phosphaindolizines, by MNDO calculations [1], and by their tendency to undergo electrophilic substitution rather than addition reactions, such as in bromination or substitution by chlorophosphines [5]. To extend the knowledge of the chemistry of these new classes of heterocycles, it is desirable to obtain more detailed information on their structure and reactivity. This prompted us to search for new derivatives of phosphaindolizines that are suitable for X-ray structure analysis and studies of their coordination behavior. The coordination behavior and variety of σ- and π-coordination modes of π-excess aromatic heterocycles are of current research interest [6–8], but annulated 1,3-azaphospholes have been used only sporadically for the preparation of coordination compounds. Few $\eta^1$-P-coordinate and no higher-coordinate (π-mode) transition-metal complexes are known besides formally N- and C(2)-lithiated 1,3-azaphosphole species [9].

In this article, we report the synthesis of new 2-phosphaindolizines, the molecular structure of one representative (**2a**), and spectroscopic data. Experimental and calculated structures of isomeric pyrido- and benzo-annulated 1,3-azaphospholes are compared and discussed in terms of their electronic nature. The mass spectroscopic fragmentation of **2a** is compared with that of the nonphosphorus analog [10].

## *RESULTS AND DISCUSSION*

CH-acidic 1,2-dialkylpyridinium bromides **1a–h** undergo cyclocondensation with one equivalent of $PCl_3$

*Present address: Department of Chemistry, University of Rajasthan, Jaipur, India.
*Correspondence to:* Joachim Heinicke
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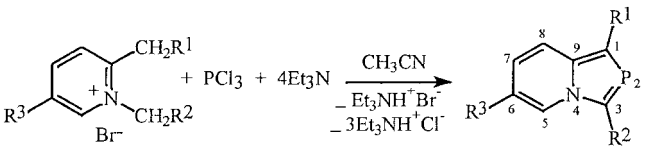
and four equivalents of triethylamine at ambient temperature in acetonitrile to form 2-phosphaindolizines **2a–h** in medium to high yields (Scheme 1). The starting materials **1** are readily accessible by N-alkylation of various 2-alkylpyridines with bromoacetic esters, bromoacetonitrile, or $\alpha$-bromomethyl keto compounds.

The 2-phosphaindolizines **2a–h** are pale yellow to orange-brown solids. Substituents in positions 1, 3, and 6 have been varied to obtain suitable derivatives with different electronic and solubility properties, necessary for studies of coordination behavior and influence of complexation on the charge distribution within the ligand by donor and acceptor interactions with the metal. In this article, we focus on spectroscopic data and the structure of the ligand **2a** in correlation with calculated charge densities and bond lengths, and finally, we describe the fragmentation in EI-mass spectra. The chemical studies of complexes will be published separately [11].

## *NMR Data*

The structures of the 2-phosphaindolizines **2a–h** have been elucidated by $^1$H-, $^{13}$C-, and $^{31}$P-NMR data. The proton NMR spectra exhibit doublets for 1-H with large $^2J$(PH) values of 35.4–38.6 Hz, characteristic of *cis*-RP=CH(R′) compounds [12]. The signals of 5-H-8-H reveal quite different chemical shifts in the range 6.8 (6-H) to 10.2 ppm (5-H), with multiplicities according to the substitution pattern, and allow an approximate first-order determination of $\delta$ values and coupling constants for ready assignment (Table 1). Typical features in the $^{13}$C-NMR spectra are the doublets for C-3 and C-1 with $^1J$(PC) coupling constants of 53–63 and 37–43 Hz, respectively, indicating the presence of twofold coordinate trivalent phosphorus [13]. $^{31}$P-NMR signals appear in the range $\delta$ 160–183 (Table 1), typical of 2-phosphaindolizines [1,2,14]. The chemical shift depends strongly on the nature of the substituent in the 3-position, which is due to direct conjugative interactions. The connection between the phosphorus chemical shift and group electronegativity [15] of the 3-substituent in 1,2-azaphospholes [16] stimulated us to carry out semiempirical calculations of the parent and some 3-substituted 2-phosphaindolizines using the PM3 method [17] and to seek correlations of calculated charge densities with chemical shifts (Table 2). It is found that $\delta$ $^{31}$P increases approximately linearly with decreasing total charge density at the phosphorus atom in the cases of phenyl, *p*-nitrophenyl, and nitrile groups, whereas the charge values calculated for 3-ester and 3-keto derivatives are a little too high and much too low, respectively. The strong deviations for the two ketones are attributed to a different orientation of the anisotropy cone around the C=O bond compared to those of the axial-symmetric phenyl, *p*-nitrophenyl, and cyano substituents or the less unsymmetrical COOR group with delocalized C(=O)–O bonds. The $^{13}$C chemical shifts are strongly influenced by substitution, annulation, and heteroatom effects, preventing a correlation with charge densities. The shift values will be useful, however, for comparison with the spectra of complexes of the various ligands [11], since the above-mentioned factors are little changed except for the atoms near the coordination site (=P-), and thus $\Delta\delta$ should correlate with variation in the electron density and be useful in assessing the ligand properties.




**1** **2**

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | $CH_3$ | $COC(CH_3)_3$ | H |
| b | $CH_3$ | $COOCH_3$ | H |
| c | $C_6H_5$ | $COOCH_3$ | H |
| d | H | $COOCH_3$ | $C_2H_5$ |
| e | H | $COOC_2H_5$ | $C_2H_5$ |
| f | H | $COC_6H_5$ | $C_2H_5$ |
| g | H | $COC(CH_3)_3$ | $C_2H_5$ |
| h | H | CN | $C_2H_5$ |

**SCHEME 1**

## *X-ray Analysis of* **2a**

The X-ray structure determination of **2a** reveals the planarity and aromaticity of the bicyclic 10$\pi$ system. The mean of the deviations of the ring atoms from the plane is 3 pm. Figure 1 displays the molecular structure. Selected bond lengths and bond angles are given in Table 3. The 3-pivaloyl substituent prefers a coplanar orientation (torsion angle P-C1-C9-O 178°), which is stabilized by conjugation of the carbonyl group with the heterocyclic ring. The bulky *tert.*-butyl group lies on the less hindered *cis* position to phosphorus. C=P–C bond lengths lie between single (185 pm) and double (167 pm) PC bond lengths of phosphaalkenes [18], indicating effective delocalization. In order to compare the structures of the three annulated 1,3-azaphospholo isomers, selected experimental data of **2, 3** [19], and **4** [20], as well as

**TABLE 1** $^{31}P$- and $^{1}H$-NMR Data of 2-Phosphaindolizines **2** ($CDCl_3$)

| *δ J [Hz]* | **a** | **b** | **c** | **d** | **e** | **f** | **g** | **h** |
|---|---|---|---|---|---|---|---|---|
| P | 172.1 | 164.5 | 160.3 | 162.4 | 160.7 | 182.6 | 169.2 | 164.0 |
| 1-H | | | | 7.47 | 7.38 | 7.58 | 7.45 | 7.43 |
| $^{2}J$(P, H) | | | | 35.7 | 35.6[a] | 35.4 | 36.9 | 38.4 |
| 5-H | 10.24 | 9.85 | 9.9 | 9.70 | 9.62 | 10.16 | 10.02 | 8.29 |
| $^{4}J$(P, H) | 1.9 | 0.9 | 0.9 | 0.9 | | 1.8 | 1.5 | 0.9 |
| $^{3}J$(5-H,6-H) | 7.4 | 7.2 | 7.1 | | | | | |
| $^{4}J$(5-H,7-H) | 0.9 | 0.9 | | | | 0.9 | 0.7 | |
| 6-H | 6.86 | 6.88 | 6.91 | | | | | |
| $^{5}J$(P,H) | 1.2 | 1.2 | | | | | | |
| $^{3}J$(6-H,7-H) | 6.3 | 6.4 | 6.3 | | | | | |
| 7-H | 7.17 | 7.12 | 7.12 | 7.0 | 6.45 | 7.17 | 7.0 | 7.03 |
| $^{5}J$(P,H) | 0.8 | 0.7 | | 1.5 | | 9.0 | | 1.4 |
| $^{3}J$(7-H,8-H) | 8.8 | 8.9 | 8.8 | 9.0 | 8.8 | 9.0 | 8.8 | 9.1 |
| 8-H | 7.46 | 7.47 | 7.69 | 7.44 | 7.36 | 7.49 | 7.40 | 7.48 |
| 1-CH3 | 2.60 | 2.62 | [b] | | | | | |
| $^{3}J$(P,H) | 12.4 | 12.1 | | | | | | |
| $R^2$ | | | | | | | | |
| $OCH_3/OCH_2$ | | 3.91 | 3.94 | 3.92 | 4.30 | [c] | | |
| $CH_3$ | | | | | 1.33 | | | |
| $C(CH_3)_3$ | 1.56 | | | | | | 1.50 | |
| $R^3$ | | | | | | | | |
| $CH_2$[d] | | | | 2.67 | 2.58 | 2.73 | 2.59 | 2.69 |
| $CH_3$[d] | | | | 1.28 | 1.20 | 1.33 | 1.21 | 1.29 |

[a] $^{4}J$(H,H) = 0.8 Hz.
[b] 1-$C_6H_5$; δ 7.3–7.6
[c] $COC_6H_5$; *o* ~ δ 7.9, *m* ~ δ 7.4, *p* ~ δ 7.5.
[d] $^{3}J$(H, H) = 7.5 Hz.

of the geometry-optimized unsubstituted representatives, calculated by the PM3 method, are assembled in Table 3. In principle, by symmetry reasons, the extent of the delocalization should diminish in the order 2-phosphaindolizine > 1-phosphaindolizine > 1,3-benzazaphosphole. The presence of a strongly electron-withdrawing group with a −M effect at a carbon atom α to phosphorus, e.g., C(O)R in **2a,** disturbs the π-delocalization within the ring, causing the CP bond **a** to become a little shorter and the CP bond **b** somewhat longer. The effect of the nature of the 3-substituent on the two CP bond lengths of 2-phosphaindolizines is confirmed by the results of PM3 calculations (Table 2), which, however, overemphasize these changes. The endocyclic angle at phosphorus (91.9°) is controlled by steric factors of the five-membered ring and lies in the range characteristic of azaphospholes [9].

### *Mass Spectral Fragmentation of* **2a**

In the mass spectrum of **2a** (Scheme 2), the base peak is observed at *m*/*z* 176, indicating that the primary decomposition pathway of the molecular ion (*m*/*z* 233) involves the loss of the *tert*-butyl group. Peaks at *m*/*z* 57, 41, and 29, typical for the *tert*-butyl group, are also present. The loss of CO generates an $C_8H_7PN$ ion having the basic skeleton of 2-phosphaindolizine. Further fragmentation proceeds in close analogy to the related nitrogen heterocycles, with [21] or without [10] the presence of phosphorus. The loss of HCN from species ***A,*** typical of 1,3-azaphospholes [22], gives the ion at *m*/*z* 121, which may lose either HCP or acetylene. Moreover, ring expansion has been observed in the mass fragmentation of methyl substituted indolizines [23]. Similar behavior is also indicated in the present case, where the generation of the ions *m*/*z* 117 and 104 seems to occur via the intermediacy of species ***B*** formed by ring expansion of species ***A***.

## *EXPERIMENTAL*

All reactions involving phosphorus compounds were carried out under a dry nitrogen or argon atmosphere using the Schlenk technique. NMR spectra have been recorded on a Bruker ARX 300 ($^{31}P$ NMR at 121.5 MHz, $^{1}H$ NMR at 300 MHz, and $^{13}C$ NMR at 75.5 MHz) spectrometer or a JEOL FX 90Q ($^{31}P$ NMR at 36.23 MHz, $^{1}H$ NMR at 89.55 MHz) spectrometer. The chemical shifts refer to 85% $H_3PO_4$ (ex-

**TABLE 2** $\delta$ $^{31}$P and Selected data obtained by PM3 calculations of 3-Substituted 2-Phosphaindolizines **2**

| ($R^1$ = H) $R^2$ | $\delta$ $^{31}$P (*Exp.*)[a] | Total Charge Density on P | Angle C=P-C (°) | CP Bond Lengths (*pm*) | | CN Bond Lengths (*pm*) | |
|---|---|---|---|---|---|---|---|
| | | | | *a* | *b* | *c* | *d* |
| H | — | +0.4109 | 92.4 | 171.5 | 172.3 | 137.1 | 141.8 |
| $C_6H_5$ | 120 | +0.4253 | 92.1 | 170.4 | 175.8 | 137.9 | 141.7 |
| $C_6H_4$-$NO_2$-*p* | 132 | +0.4631 | 92.3 | 169.7 | 176.3 | 138.0 | 141.4 |
| $COOCH_3$ | 162 | +0.5792 | 92.6 | 167.7 | 177.3 | 139.3 | 140.6 |
| $COOC_2H_5$ | 162 | +0.5757 | 92.6 | 167.7 | 177.3 | 139.3 | 140.6 |
| CN | 164 | +0.5525 | 92.1 | 169.1 | 175.2 | 139.0 | 141.2 |
| $COC(CH_3)_3$ | 170 | +0.4950 | 93.0 | 169.4 | 177.5 | 139.0 | 140.7 |
| $COC_6H_5$ | 183 | +0.5112 | 93.4 | 167.1 | 177.7 | 139.2 | 140.7 |

[a]Ref. [1,2].

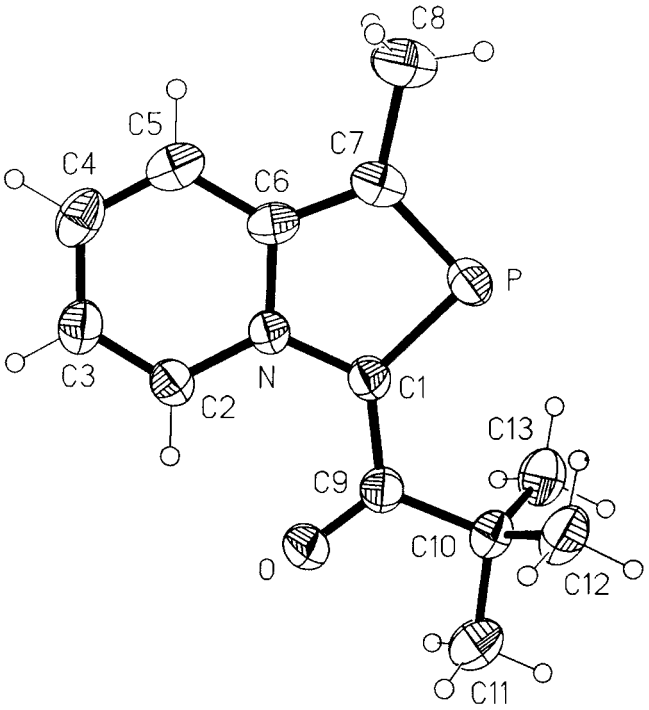



**FIGURE 1** Structure of **2a** in the crystal. Ellipsoid represents 50% probability levels.

ternal) or TMS (internal). Mass spectra have been recorded on an AMD 40 (intectra) instrument.

1,2-Dialkylpyridinium bromides **1** were prepared by stirring equimolar amounts of a 2-alkylpyridine and a suitably substituted methyl bromide in diethyl ether for 24–48 hours. The white to cream-colored solid thus obtained in each case was filtered off, washed with ether, and dried.

**1a:** Yield 82%, mp 181–184°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.36 (s, 9H, *t*Bu), 1.40 (t, 3H, $^3J_{HH}$ = 7.4 Hz, $CH_3$), 3.02 (q, 2H, $^3J_{HH}$ = 7.4 Hz, 2-$CH_2$), 6.79 (s, 2H, $NCH_2$), 7.83 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 3-H), 7.88 (t, 1H, $^3J_{HH}$ = 6.3 Hz, 5-H), 8.40 (td, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, 4-H), 9.74 (dd, 1H, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.3 Hz, 6-H).

**1b:** Yield 78%, mp 188–191°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.42 (t, 3H, $^3J_{HH}$ = 7.5 Hz, $CH_3$), 3.21 (q, 2H, $^3J_{HH}$ = 7.5 Hz, 2-$CH_2$), 3.84 (s, 3H, $OCH_3$), 6.30 (s, 2H, $NCH_2$), 7.83 (d, 1H, $^3J_{HH}$ = 7.0 Hz, 3-H), 8.0 (t, 1H, $^3J_{HH}$ = 7.0 Hz, 5-H), 8.60 (t, 1H, $^3J_{HH}$ = 7.0 Hz, 4-H), 9.87 (d, 1H, $^3J_{HH}$ = 6.5 Hz, 6-H).

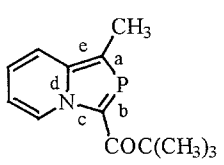
**1c:** Yield 65%, mp 184–186°C; $^1$H NMR ($CDCl_3$): $\delta$ = 3.73 (s, 3H, $OCH_3$), 4.66 (s, 2H, 2-$CH_2$), 6.42 (s, 2H, $NCH_2$), 7.27–7.61 (m, 5H, $C_6H_5$), 7.64 (dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.1 Hz, 3-H), 7.97 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, 5-H), 8.40 (td, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, 4-H), 9.90 (dd, 1H, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.3 Hz, 6-H).

**1d:** Yield 87%, mp 197–199°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.36 (t, 3H, $^3J_{HH}$ = 7.6 Hz, $CH_3$), 2.89 (q, 2H, $^3J_{HH}$ = 7.6 Hz, 5-$CH_2$), 2.92 (s, 3H, 2-$CH_3$), 3.84 (s, 3H, $OCH_3$), 6.28 (s, 2H, $NCH_2$), 7.96 (d, 1H, $^3J_{HH}$ = 7.9 Hz, 3-H), 8.28 (dd, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.1 Hz, 4-H), 9.74 (d, 1H, $^4J_{HH}$ = 1.1 Hz, 6-H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.4 ($CH_3$), 20.7 (5-$CH_2$), 25.5 (2-$CH_3$), 53.7 ($OCH_3$), 58.7 ($NCH_2$), 166.2 (CO).

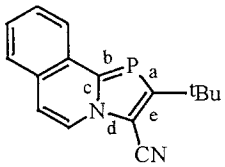
**1e:** Yield 83%, mp 203–205°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.24 (t, 3H, $^3J_{HH}$ = 7.5 Hz, 5-$CH_2\underline{CH_3}$), 1.33 (t, 3H, $^3J_{HH}$ = 7.5 Hz, $OCH_2\underline{CH_3}$), 2.79 (s, 3H, 2-$CH_3$), 2.82 (q, 2H, $^3J_{HH}$ = 7.5 Hz, 5-$CH_2$), 4.22 (q, 2H, $^3J_{HH}$ = 6.9 Hz, $OCH_2$), 6.1 (s, 2H, $NCH_2$), 7.78 (d, 1H, $^3J_{HH}$ = 8.3 Hz, 3-H), 8.12 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.4 Hz, 4-H), 9.61 (d, 1H, $^4J_{HH}$ = 1.4 Hz, 6-H).

**1f:** Yield 85%, mp 187–189°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.37 (t, 3H, $^3J_{HH}$ = 7.8 Hz, 5-$CH_2\underline{CH_3}$), 2.78 (s, 3H, 2-$CH_3$), 2.89 (q, 2H, $^3J_{HH}$ = 7.8 Hz, 5-$CH_2$), 7.16 (s, 2H, $NCH_2$), 7.51 (m, 2H, *m*-H), 7.65 (t, 1H, $^3J_{HH}$ = 7.4 Hz, *p*-H), 7.77 (d, 1H, $^3J_{HH}$ = 8.2 Hz, 3-H), 8.15 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.8 Hz, 4-H), 8.26 (d, 2H, $^3J_{HH}$ = 7.3 Hz, *o*-H), 9.50 (d, 1H, $^4J_{HH}$ = 1.6 Hz, 6-H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.4 ($CH_2\underline{CH_3}$), 20.6 (5-$CH_2$), 25.7 (2-$CH_3$), 65.0 ($NCH_2$), 190.3 (CO).

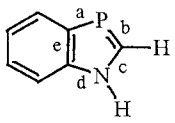
**TABLE 3** Selected Bond Lengths (pm) and Bond Angles (°) of Azaphosphole Ring in 2-Phosphaindolizine (**2**), 1-Phosphaindolizine (**3**), and 1,3-Benzazaphosphole (**4**)




**2a**




**3**




**4**

| | **2a** (*Exp.*) | **2a** (*optimized*) | *Unsubstituted 2-Phosphaindolizine* (*optimized*) | **3** (*Exp.*) *[16]* | *Unsubstituted 1-Phosphaindolizine* (*optimized*) | **4** (*Exp.*) *[17]* | *Unsubstituted 1,3-Benzazaphosphole* (*optimized*) |
|---|---|---|---|---|---|---|---|
| a(C–P) | 170.8(4) | 169.4 | 171.5 | 175.4(3) | 173.2 | 180.7(7) | 180.3 |
| b(C–P) | 174.7(3) | 177.5 | 172.3 | 173.4(4) | 177.3 | 169.5(9) | 169.3 |
| c(C–N) | 140.0(4) | 139.8 | 137.1 | 136.5(4) | 139.9 | 135.1(11) | 137.9 |
| d(C–N) | 139.5(4) | 140.7 | 141.8 | 137.2(4) | 139.4 | 137.1(9) | 140.6 |
| ∠P | 91.9(2) | 93.0 | 92.4 | 89.9(2) | 90.8 | 88.2(4) | 91.3 |

**TABLE 4** Bond Lengths (pm) and Bond Angles (°)

| | | | |
|---|---|---|---|
| P–C (7) | 170.8 (4) | P–C (1) | 174.7 (3) |
| N–C (2) | 138.4 (4) | N–C (6) | 139.5 (4) |
| N–C (1) | 140.0 (4) | O–C (9) | 122.8 (4) |
| C(1)–C(9) | 146.1 (4) | C(2)–C(3) | 135.7 (5) |
| C(3)–C(4) | 139.7 (5) | C(4)–C(5) | 135.6 (5) |
| C(5)–C(6) | 140.9 (5) | C(6)–C(7) | 139.5 (5) |
| C(7)–C(8) | 150.8 (5) | C(9)–C(10) | 154.8 (5) |
| C(10)–C(13) | 152.4 (5) | C(10)–C(11) | 153.2 (5) |
| C(10)–C(12) | 153.6 (5) | | |
| C(7)–P–C(1) | 91.9 (2) | C(2)–N–C(6) | 119.5 (3) |
| C(2)–N–C(1) | 127.2 (3) | C(6)–N–C(1) | 113.3 (2) |
| N–C(1)–C(9) | 121.8 (3) | N–C(1)–P | 110.1 (2) |
| C(9)–C(1)–P | 128.0 (2) | C(3)–C(2)–N | 120.5 (3) |
| C(2)–C(3)–C(4) | 121.3 (3) | C(5)–C(4)–C(3) | 118.8 (3) |
| C(4)–C(5)–C(6) | 121.2 (3) | C(7)–C(6)–N | 112.6 (3) |
| C(7)–C(6)–C(5) | 128.6 (3) | N–C(6)–C(5) | 118.8 (3) |
| C(7)–C(6)–C(8) | 122.1 (3) | C(6)–C(7)–P | 112.0 (2) |
| C(8)–C(7)–P | 125.9 (3) | O–C(9)–C(1) | 121.5 (3) |
| O–C(9)–C(10) | 118.0 (3) | C(1)–C(9)–C(10) | 120.5 (3) |
| C(13)–C(10)–C(11) | 108.3 (3) | C(13)–C(10)–C(12) | 110.8 (3) |
| C(11)–C(10)–C(12) | 107.8 (3) | C(13)–C(10)–C(9) | 111.2 (3) |
| C(11)–C(10)–C(9) | 107.9 (3) | C(12)–C(10)–C(9) | 110.7 (3) |

**TABLE 5** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$). *U*(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

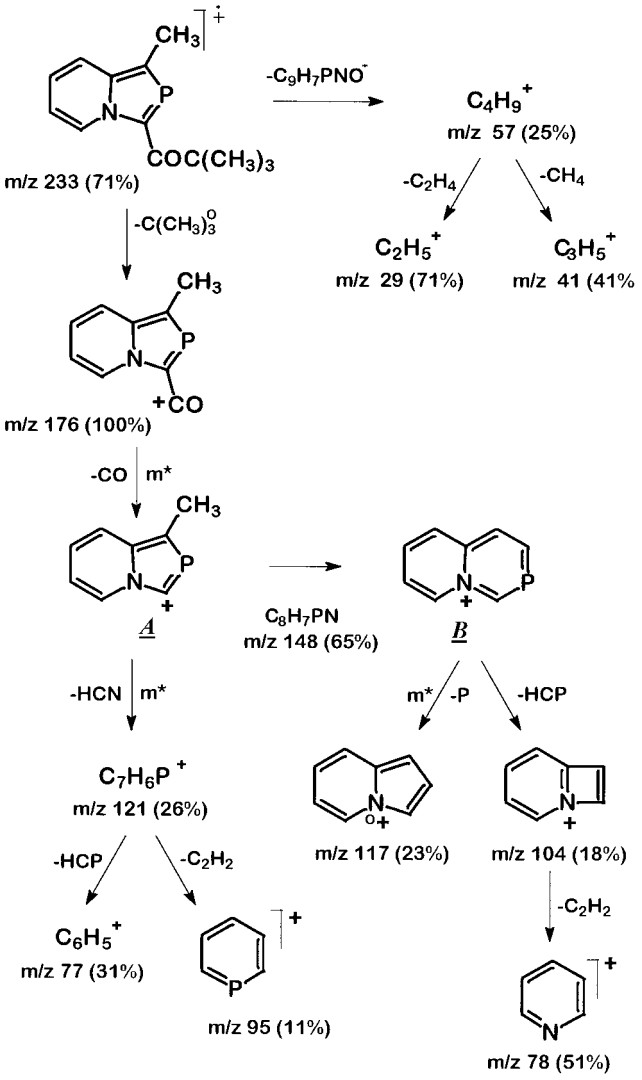
| | *x* | *y* | *z* | *U* (*eq*) |
|---|---|---|---|---|
| P | 3785.0 (11) | 3848.4 (4) | 4714.2 (14) | 39.5 (3) |
| N | 5221 (3) | 2877.9 (10) | 5451 (4) | 30.0 (6) |
| O | 8666 (3) | 3292.7 (10) | 7347 (4) | 54.3 (7) |
| C (1) | 5663 (4) | 3440.8 (13) | 5695 (5) | 32.0 (7) |
| C (2) | 6346 (4) | 2429.9 (13) | 6035 (5) | 34.9 (7) |
| C (3) | 5720 (5) | 1904.2 (14) | 5695 (5) | 41.6 (8) |
| C (4) | 3938 (5) | 1799.4 (15) | 4735 (5) | 44.5 (9) |
| C (5) | 2827 (5) | 2235.0 (14) | 4145 (5) | 40.9 (8) |
| C (6) | 3433 (4) | 2785.4 (14) | 4505 (4) | 33.3 (7) |
| C (7) | 2476 (4) | 3276.8 (15) | 4019 (5) | 39.8 (8) |
| C (8) | 515 (5) | 3280.2 (18) | 2999 (6) | 54.4 (10) |
| C (9) | 7467 (4) | 3625.2 (13) | 6664 (5) | 34.9 (7) |
| C (10) | 7918 (5) | 4251.3 (14) | 6861 (6) | 42.3 (8) |
| C (11) | 9907 (5) | 4307.6 (16) | 7873 (7) | 58.2 (11) |
| C (12) | 6935 (5) | 4539.4 (15) | 8235 (6) | 53.6 (10) |
| C (13) | 7501 (5) | 4529.1 (15) | 4782 (6) | 52.4 (10) |

**1g:** Yield 92%, mp 170–172°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.30 (s, 9H, *t*Bu), 1.30 (t, 3H, $^3J_{HH}$ = 7.5 Hz, 5-$CH_2\underline{CH_3}$), 2.69 (s, 3H, 2-$CH_3$), 2.79 (q, 2H, $^3J_{HH}$ = 7.5 Hz, 5-$\underline{CH_2}$), 6.6 (s, 2H, $NCH_2$), 7.59 (d, 1H, $^3J_{HH}$ = 8.3 Hz, 3-H), 7.99 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.4 Hz, 4-H), 9.48 (d, 1H, $^4J_{HH}$ = 1.4 Hz, 6-H).

**1h:** Yield 73%, mp 160–163°C; $^1$H NMR ($CDCl_3$): $\delta$ = 1.27 (t, 3H, $^3J_{HH}$ = 7.5 Hz, 5-$CH_2\underline{CH_3}$), 2.79 (q, 2H, $^3J_{HH}$ = 7.5 Hz, 5-$CH_2$), 3.01 (s, 3H, 2-$CH_3$), 6.69 (s, 2H, $NCH_2$), 7.78 (d, 1H, $^3J_{HH}$ = 8.0 Hz, 3-H), 8.12 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 4-H), 9.67 (d, 1H, $^4J_{HH}$ = 1.4 Hz, 6-H).

## *2-Phosphaindolizines: General Procedure*

A 0.05 mol amount of 1,2-dialkylpyridinium bromide was suspended in 200 mL of acetonitrile under argon/nitrogen. To the well-stirred suspension (at 0–5°C), 28 mL (0.2 mol) of triethylamine was added, and the reaction mixture turned yellow. After about 10–20 minutes, a solution of 4.35 mL (0.05 mol) $PCl_3$




**SCHEME 2** Mass spectral fragmentation of **2a,** abundance of various ions given in parentheses and fragmentation steps supported by metastable ion marked m*.

in 10 mL $CH_3CN$ was added dropwise over 45–60 minutes. The mixture turned from orange-brown to deep brown and was then allowed to warm to ambient temperature. After 4–5 hours of stirring, the mixture was filtered and the solid thoroughly washed with 2 × 20 mL portions of acetonitrile. The solvent was removed in vacuo to complete dryness and the residue extracted with diethyl ether (2 × 100 mL) at room temperature. On leaving the concentrated ethereal extract in the refrigerator, pale yellow to orange-brown crystals separated. Alternatively, the ether was removed completely in vacuo to obtain spectroscopically pure powders **2a–h.** For $^{31}P$- and $^{1}H$-NMR data, see Table 1.

**2a:** Yield 68%, mp 58–59°C. Anal. calcd. for $C_{13}H_{16}NPO$ (233.2): C, 66.94; H, 6.92; N, 6.01. Found: C, 66.93; H, 7.10; N, 6.02; $^{13}C$ NMR ($CDCl_3$): $\delta$ = 12.9 ($^2J_{CP}$ = 25.9 Hz, 1-$CH_3$), 30.5 ($^4J_{CP}$ = 11.2 Hz, C($\underline{C}H_3)_3$), 45.0 [$^3J_{CP}$ = 3.4 Hz, $\underline{C}(CH_3)_3$], 113.9 ($^4J_{CP}$ = 4.4 Hz, C-6), 116.3 ($^3J_{CP}$ = 7.4 Hz, C-8), 123.8 ($^4J_{CP}$ = 2.5 Hz, C-7), 131.0 ($^3J_{CP}$ = 4.2 Hz, C-5), 136.0 ($^1J_{CP}$ = 37.8 Hz, C-1), 139.5 ($^1J_{CP}$ = 62.4 Hz, C-3), 142.8 ($^2J_{CP}$ = 9.1 Hz, C-9), 199.9 ($^2J_{CP}$ = 20.3 Hz, CO).

**2b:** Yield 75%, mp 85–87°C. Anal. calcd. for $C_{10}H_{10}NPO_2$ (207.2): C, 57.97; H, 4.86; N, 6.76. Found: C, 58.13; H, 4.75; N, 6.89; $^{13}C$ NMR ($CDCl_3$): $\delta$ = 13.1 ($^2J_{CP}$ = 24.7 Hz, 1-$CH_3$), 51.3 ($OCH_3$), 113.6 ($^4J_{CP}$ = 4.5 Hz, C-6), 116.8 ($^3J_{CP}$ = 7.1 Hz, C-8), 122.4 ($^4J_{CP}$ = 3.4 Hz, C-7), 129.3 ($^3J_{CP}$ = 3.8 Hz, C-5), 137.1 ($^1J_{CP}$ = 38.8 Hz, C-1), 143.5 ($^1J_{CP}$ = 56.4 Hz, C-3), 144.0 ($^2J_{CP}$ = 10.2 Hz, C-9), 164.3 ($^2J_{CP}$ = 20.8 Hz, CO).

**2c:** Yield 64%, mp 92–93°C.

**2d:** Yield 72%, mp 82–83°C; $^{13}C$ NMR ($CDCl_3$): $\delta$ = 14.9 ($CH_3$), 26.1 ($CH_2$), 51.4 ($OCH_3$), 119.2 ($^3J_{CP}$ = 6.8 Hz, C-8), 124.9 ($^1J_{CP}$ = 41.7 Hz, C-1), 125.2 ($^4J_{CP}$ = 2.7 Hz, C-6), 126.5 ($^4J_{CP}$ = 4.4 Hz, C-7), 129.9 ($^3J_{CP}$ = 4.2 Hz, C-5), 135.9 ($^1J_{CP}$ = 53.5 Hz, C-3), 145.2 ($^2J_{CP}$ = 10.8 Hz, C-9), 164.4 ($^2J_{CP}$ = 22.2 Hz, CO).

**2e:** Yield 42%, oily.

**2f:** Yield 78%, mp 115–17°C. Anal. calcd. for $C_{16}H_{14}NPO$ (267.3): C, 71.90; H, 5.28; N, 5.24. Found: C, 72.28; H, 5.35; N, 5.03; $^{13}C$ NMR ($CDCl_3$): $\delta$ = 14.9 ($CH_3$), 26.1 ($CH_2$), 118.9 ($^3J_{CP}$ = 7.1 Hz, C-8), 126.7 ($^1J_{CP}$ = 42.7 Hz, C-1), 127.6 ($^3J_{CP}$ = 3.0 Hz, C-6), 127.8 (*m*-C), 128.2 ($^4J_{CP}$ = 4.7 Hz, C-7), 129.7 ($^4J_{CP}$ = 7.3 Hz, *o*-C), 130.7 ($^3J_{CP}$ = 4.3 Hz, C-5), 137.0 (*p*-C), 142.0 (*i*-C), 144.3 ($^1J_{CP}$ = 57.6 Hz, C-3), 146.1 ($^2J_{CP}$ = 10.5 Hz, C-9), 187.9 ($^2J_{CP}$ = 25.9 Hz, CO).

**2g:** Yield 48%, mp 58–60°C.

**2h:** Yield 53%, mp 120–22°C; $^{13}C$ NMR ($CDCl_3$): $\delta$ = 14.7 ($CH_3$), 25.7 ($CH_2$), 116.2 ($^2J_{CP}$ = 24.7 Hz, C-9), 116.8 ($^1J_{CP}$ = 52.2 Hz, C-3), 119.8 ($^3J_{CP}$ = 5.9 Hz, C-8), 123.5 ($^1J_{CP}$ = 45.7 Hz, C-1), 124.8 ($^4J_{CP}$ = 4.7 Hz, C-6), 125.8 ($^4J_{CP}$ = 2.2 Hz, C-7), 130.8 ($^3J_{CP}$ = 3.7 Hz, C-5), 143.1 ($^2J_{CP}$ = 11.7 Hz, CN).

## *X-ray Structure Analysis of* **2a**

*Crystal Data.* $C_{13}H_{16}NOP$, $M_r$ = 233.24, monoclinic, space group $P2_1/c$, $a$ = 786.0(3), $b$ = 2411.8(8), $c$ = 683.7(3) pm, $\beta$ = 105.90(3)°, $V$ = 1.2465 $pm^3$, $Z$ = 4, $D_{calc}$ = 1.243 Mg $m^{-3}$, $\mu$(Mo $K\alpha$) = 0.20 $mm^{-1}$, $F$(000) = 496, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $T$ = −130°C.

*Data Collection and Reduction.* A yellow plate 0.65 × 0.4 × 0.15 mm was mounted in an inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4). By use of $\omega/\theta$ scans, 2378 intensities were collected to $2\theta_{max}$ 50°, of which 2190 were independent ($R_{int}$ 0.018).

*Structure Solution and Refinement.* The structure was solved with direct methods and refined anisotropically on $F^2$ using the program SHELXL-93 (G.M. Sheldrick, University of Göttingen), methyls being treated as rigid groups, other H riding. The final $wR(F^2)$ was 0.173 for all reflections, with conventional $R(F)$ 0.060; 149 parameters; $S(F^2)$ 1.06, max. $\Delta\rho$ 494 e $nm^{-3}$. Complete crystallographic data (except structure factors) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-406866.

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