

## 5-Organyl-5-phosphaSpiro[4.4]nonanes: A Contribution to the Structural Chemistry of Spirocyclic Tetraalkylphosphonium Salts and Pentaalkylphosphoranes

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**Abstract:** Spirocyclic phosphonium salts of the type  $[(\text{CH}_2)_4\text{P}(\text{CH}_2)_4]^+ \text{X}^-$  with  $\text{X} = \text{I}_3$  (**1a**),  $\text{I}$  (**1b**), picrate (**1c**), benzoate (**1d**), and  $\text{Cl}$  (**1e**) were prepared from 1,4-diiodobutane and elemental phosphorus followed by metathesis reactions. The crystal structures of **1b** and **1c** and of **1d**(H<sub>2</sub>O) have been determined by X-ray diffraction methods. In the cations of these salts the phosphorus atoms are shared by two five-membered rings in envelop conformations. In the picrate **1c** the cations show an unsymmetrical ring folding pattern (point group  $C_1$ ), while the geometry of the cations of the iodide **1b** and the benzoate hydrate [**1d**(H<sub>2</sub>O)] approaches the symmetry of point group  $C_2$ . These structures can be taken as models for the as yet unknown molecular geometries of the corresponding hydrocarbon  $(\text{CH}_2)_4\text{C}(\text{CH}_2)_4$  and silane  $(\text{CH}_2)_4\text{Si}(\text{CH}_2)_4$ . Treatment of **1e** with organolithium reagents  $\text{RLi}$  affords spirocyclic pentaorganophosphoranes  $\text{RP}[(\text{CH}_2)_4]_2$  with  $\text{R} = \text{Me, Et, n-Bu, Vi, and Ph}$  (**2a–e**) in good ( $\text{R} = \text{Me, Et, n-Bu}$ ) to low yields ( $\text{R} = \text{Vi, Ph}$ ). The products are isolated as colorless liquids, of which only **2a, 2b,** and **2d** can be distilled without decomposition. Single crystals of **2a** were obtained by low-temperature in situ crystal growth. The molecule has a trigonal bipyramidal configuration with the methyl group in an equatorial position and the two five-membered rings spanning axial/equatorial positions of the polyhedron. Deviations from the standard trigonal bipyramidal geometry are small. The compounds **2a–e** are fluxional in solution as demonstrated by NMR spectroscopy.

### Introduction

Simple pentaalkylphosphoranes  $\text{PR}_5$  with five independent substituents  $\text{R}$  are unknown. Statements to the contrary are in error.<sup>1</sup> All attempts to accomplish pentaalkylation of phosphorus, e.g., by treatment of tetraalkylphosphonium salts  $[\text{R}_4\text{P}]\text{X}$  with alkylmetal reagents  $\text{RM}$ , failed and led to the formation of trialkylphosphonium alkylides (alkylidene trialkylphosphoranes) through  $\alpha$ -deprotonation of a P-bound alkyl group.<sup>2</sup> Ylide formation is also observed with tetraalkylammonium salts,<sup>3</sup> which cannot be converted into compounds with pentacoordinated nitrogen atoms with alkylating agents.<sup>4</sup> By contrast, pentaalkylation of arsenic, antimony, and bismuth has been accomplished and pentamethylarsenic  $\text{AsMe}_5$ , pentamethylantimony  $\text{SbMe}_5$ , and pentamethylbismuth  $\text{BiMe}_5$  have been isolated and fully characterized, while there is no experimental evidence yet for  $\text{NMe}_5$  and  $\text{PMe}_5$ .<sup>5–11</sup>

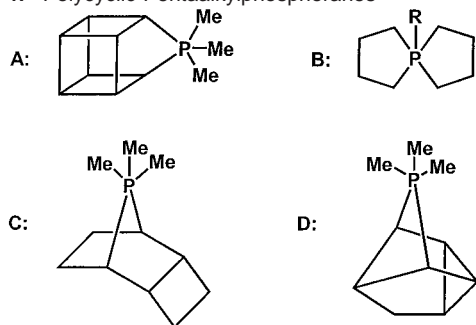
Pentaorganophosphoranes  $\text{PR}_5$  can only be obtained if there is no C–H acidic function in the corresponding phosphonium salt. This is true for tetraarylphosphonium salts, and consequently pentaarylphosphoranes or alkyltetraarylphosphoranes were the first compounds with five P–C bonds to be prepared.<sup>2,4b,12–18</sup> Pentaarylation has also been carried out successfully for the heavier Group V elements (As, Sb, Bi), but not for nitrogen.<sup>4,6,19–22</sup>

Pentaalkylation of the phosphonium center in a  $[\text{PR}_4]^+$  cation is only possible in systems where the corresponding ylides suffer from configurational or conformational strain, or if strain already present in a phosphonium cation is reduced or relieved upon changes in the coordination sphere of the phosphorus atom.<sup>23</sup>

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**Scheme 1.** Polycyclic Pentaalkylphosphoranes

Two polycyclic phosphonium salts have been designed for these purposes (focusing on the latter of the two principles) and yielded the first and only examples of true pentaalkylphosphoranes.

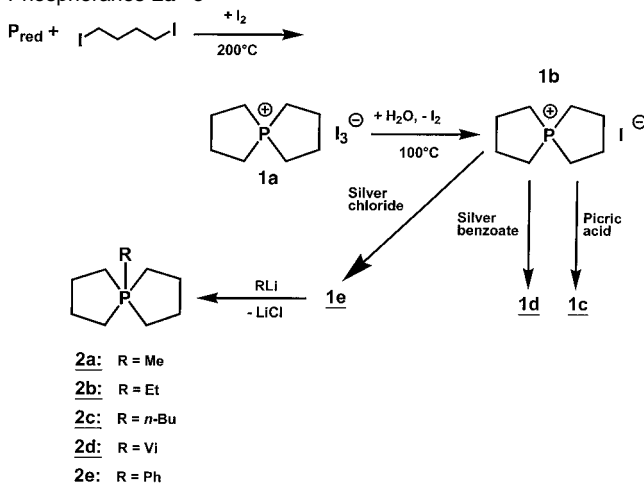
Early work by Katz and Turnblom focused on the homocubyl system **A** shown in Scheme 1.<sup>24,25</sup> The phosphonium atom in the onium precursor is bridging an edge of the cubane and therefore is part of a bicyclic unit of the homocubyl system. This leads to a significant distortion of the tetrahedral geometry at the heteroatom. The imposed strain can be relieved as the phosphorus atom becomes pentacoordinate upon nucleophilic attack of a carbanion. In the resulting trigonal bipyramidal geometry the two fused five-membered rings are assumed to span a pair of axial/equatorial positions of the polyhedron, for which small angles close to 90° are ideal.<sup>26</sup> It is remarkable that the influence of ring strain is so strong that no ylide formation at one of the methyl groups is observed. The structure of **A** has not yet been determined by diffraction methods, but the structure assignment is fully supported by analytical and spectroscopic data.<sup>25</sup>

Pentaalkylated phosphorus also seems to be present in a product **C** obtained from a 9,9-dimethyl-9-phosphoniatricyclo-[4.2.1.0<sup>2,5</sup>]nonane iodide, but the evidence is less comprehensive.<sup>25</sup> Even more strained systems such as **D** are also assumed to give pentaalkylphosphoranes as intermediates upon alkylation, but the products are not stable.<sup>27</sup>

In our own laboratory, similar considerations led to work on the spirocyclic system **B** also presented in Scheme 1. Methylation of the onium salt with MeLi gave good yields of the corresponding phosphorane which may be considered to be the most simple stable pentaalkylphosphorane known to date.<sup>28,29,30</sup>

Accumulation of strongly electronegative groups at the carbon atoms of phosphonium salts can also be used as a concept to increase the acceptor properties of the onium center and to destabilize the corresponding ylide. Thus hexafluorination is a means to stabilize (CH<sub>3</sub>)<sub>3</sub>P(CF<sub>3</sub>)<sub>2</sub>, which has a trigonal-bipyramidal structure with the CF<sub>3</sub> groups in axial positions as inferred from low-temperature NMR data.<sup>31,32</sup>

It should further be noted that tetraalkylphosphonium cations bearing no C–H acidic  $\alpha$ -hydrogen atoms are extremely rare.

**Scheme 2.** Preparation of the Phosphonium Salts **1a–e** and Phosphoranes **2a–e**

In the prototype of the series, the tetra(*tert*-butyl)phosphonium cation, the steric crowding is so severe that no alkylation is possible. Deprotonation by strong base leads to reductive  $\beta$ -elimination of propene leaving tri(*tert*-butyl)phosphine.<sup>33</sup> Treatment of tetra(isopropyl)phosphonium salts with alkylmetal agents affords only the ylide (iPr)<sub>3</sub>P=CMe<sub>2</sub>,<sup>34</sup> and even tetra-(cyclopropyl)phosphonium salts give tri(cyclopropyl)phosphonium cyclopropylides.<sup>35</sup> The metalalkyls thus act as a base (in deprotonation) and not as a nucleophile (at the phosphorus atom).

In the present study we have resumed and extended our earlier work from the 1970s to improve the preparative methods for compounds R–P[(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>, **B**, to add data on simple homologues with R other than methyl, and to provide for the first time structural data on the precursor phosphonium salts and the phosphorane products.

It should be pointed out that hydrocarbon and organosilicon analogues of the phosphonium salts considered here in the course of our structural studies have not been structurally characterized, e.g., the structures of spiro[4.4]nonane (CH<sub>2</sub>)<sub>4</sub>C–(CH<sub>2</sub>)<sub>4</sub> and the corresponding silicon spiro-compound (CH<sub>2</sub>)<sub>4</sub>–Si(CH<sub>2</sub>)<sub>4</sub> are unknown. Because of the close analogy between C/Si and P<sup>+</sup> units the results of the present investigation also shed light on the conformational characteristics of the neutral carbon and silicon species.

## Preparations and Properties of the Compounds

**5-Phosphoniaspiro[4.4]nonane Salts [(CH<sub>2</sub>)<sub>4</sub>P(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> X<sup>–</sup> (**1a–e**).** The spirocyclic phosphonium salts of type **1** are accessible from a “direct process”, such as the reaction of 1,4-diiodobutane, red phosphorus, and iodine at 200 °C.<sup>36</sup> The triiodide **1a** is obtained as the primary product, which can be converted into the monoiodide **1b** by steam distillation.<sup>36</sup> Metathesis reactions of the iodide with picric acid<sup>36</sup> in ethanol or silver benzoate in methanol give the corresponding picrate **1c** or benzoate **1d**, respectively, and transhalogenation with AgCl affords the chloride salt **1e** (Scheme 2).<sup>30</sup>

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Salt **1a** is insoluble in water but readily soluble in alcohols, dichloromethane, and chloroform. The salts **1b–e** can be dissolved in both water and polar organic solvents. The solutions show very similar NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ), indicating that the cations are independent of the anions in the solvated state. The  $^{31}\text{P}$  signals appear at very low field in the narrow range of  $\delta$  72.0–72.7 ppm. Owing to the flexibility of the two five-membered rings (envelope conformations, below), virtual (averaged)  $D_{2d}$  symmetry can be assumed for the cations in solution with four equivalent  $\alpha\text{-CH}_2$  and four equivalent  $\beta\text{-CH}_2$  groups. The FAB mass spectra of all four salts show monomeric cations as the parent ions. Elemental analyses are in agreement with the proposed formulas for solvent-free compounds (after drying in a vacuum).

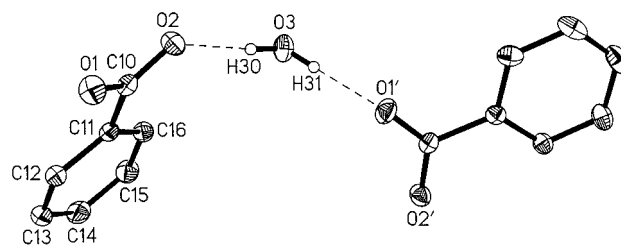
**5-Alkyl-, 5-Vinyl-, and 5-Phenyl-5-phosphoniaspiro[4.4]nonanes, 2a–e.** For the preparation of the phosphoranes **2a–e** the phosphonium chloride **1e** was treated with the corresponding organolithium reagent (Scheme 2). The methylphosphorane **2a** is obtained from the reaction of the chloride **1e** with equimolar quantities of methyllithium in diethyl ether at  $-60$  °C.<sup>29</sup> The product can be purified by distillation in a short-path apparatus and is isolated in 43% yield as a mobile, colorless liquid that solidifies at  $-36$  °C.

The ethyl homologue **2b** is formed in low yield (16%) on treatment of the chloride salt **1e** with ethyllithium in diethyl ether at  $-50$  °C. It can also be purified by distillation and is received as a colorless, viscous liquid. The reaction of **1e** with *n*-butyllithium under similar conditions gives much higher yields (46%) of the *n*-butyl compound **2c**, which is also isolated as a colorless viscous liquid.

The vinylphosphorane **2d** and the phenylphosphorane **2e** are generated in the reactions of **1e** with vinylithium or phenyllithium, respectively, in diethyl ether at  $-50$  °C, with yields of 33% for **2d** and 6.5% for **2e**. **2d** is a colorless liquid, while **2e** is a yellow viscous product. All attempts to produce the corresponding ethynylphosphorane by using the lithium acetylide ethylenediamine complex as the reagent for **1e** were not successful. Upon workup of the reaction mixture the residues quickly turned to intractable brown tars.

All products (**2a–e**) were identified by their NMR and mass spectra. The  $^{31}\text{P}$  resonances are shifted to very high field as compared to the values for the signals of the precursor cations in **1a–e**. The resonance of **2a** appears at  $-89.3$  ppm and is thus displaced by more than 160 ppm (**1e** vs **2a**). The data for **2b** ( $-81.2$  ppm) and **2c** ( $-84.3$  ppm) are very similar, and even for the vinyl and phenyl compounds the signals remain at high field (**2d**,  $-79.1$  ppm; **2e**,  $-72.5$  ppm). In the EI mass spectra all phosphoranes show the molecular ions as the parent peaks.

The phosphorane molecules **2a–e** are chiral owing to the trigonal-bipyramidal configuration at the phosphorus atoms with the two rings spanning axial/equatorial positions and leaving the independent substituent in the remaining equatorial position (see crystal structure below). This ground-state structure is fluxional in solution, rendering not only the two ring systems equivalent but also equilibrating the four  $\alpha$ -carbon and the four  $\beta$ -carbon atoms by pseudorotation.<sup>37</sup> With hydrogen decoupling, only two signals are observed for the ring carbon atoms, both



**Figure 1.** Structure of a representative part of the chains formed by the benzoate anions and the solvent water molecules in crystals of compound **1d**, with atomic numbering.

split into doublets through phosphorus coupling. The ring hydrogen atoms give  $(A_2A'_2B_2B'_2)X$  spin systems owing to magnetic inequivalence. The  $^1\text{H}$  NMR spectrum of **2a** is virtually independent of temperature in the range of  $+25$  to  $-90$  °C (in dichloromethane). The resonances of the independent ligand R are as expected. Note that only the phenyl group in compound **2e** allows for a symmetry element (point group  $C_2$ ), while all other compounds (**2a–d**) belong to point group  $C_1$ .

### Crystal and Molecular Structures

**The Spirocyclic Phosphonium Salts (1b–d).** Single crystals suitable for structure determination by X-ray diffraction have been obtained for the iodide **1b** (from acetonitrile/diethyl ether), the picrate **1c** (from chloroform/hexane), and the benzoate **1d** as a monohydrate **1d(H<sub>2</sub>O)** from moist chloroform. Crystals of the triiodide **1a** and the chloride **1e** were always twinned or of low quality otherwise.

Crystals of the iodide **1b** and picrate **1c** are both monoclinic, space groups  $P2_1/c$  and  $P2_1/n$ , respectively, with  $Z = 4$  formula units in the unit cell. The cations and anions are well separated with no conspicuous sub-van der Waals contacts. The structure of the picrate anion is very similar to that reported for other salts containing this anion.<sup>38</sup> Detailed data for this unit have been deposited and are not discussed here any further. The structures of the cations in **1b** and **1c** are described and discussed below.

Crystals of **1d(H<sub>2</sub>O)** are monoclinic, space group  $P2_1/c$ , with  $Z = 4$  formula units in the unit cell. The lattice contains onium cations well separated from meandering chains of benzoate anions which are linked via hydrogen bonds with the water molecules. The hydrogen bonding is almost fully symmetrical as shown by equidistant lengths C10–O1 and C10–O2 [ $1.255(1)/1.258(1)$  Å]. The angle at the oxygen atom of the water molecule O3 is  $106(2)^\circ$ . The carboxylate group of the anion is almost coplanar with the phenyl ring with dihedral angles O1–C10–C11–C16 and O2–C10–C11–O16 of  $3.8^\circ$  and  $-5.0^\circ$ , respectively (Figure 1).

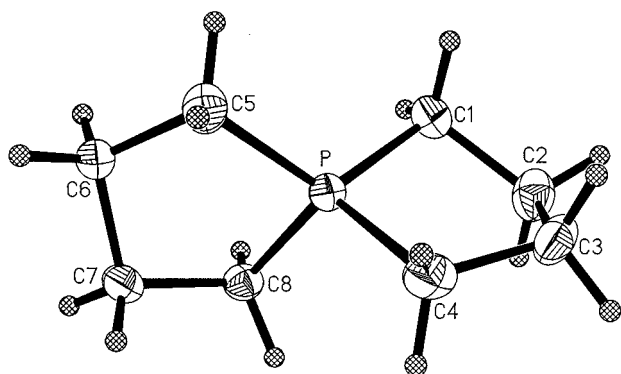
The structures of the spirocyclic phosphonium cations in the salts **1b**, **1c**, and **1d(H<sub>2</sub>O)** are very similar. Selected bond lengths and angles are summarized in Table 1. Figure 2 shows the cation of the picrate **1c** as a representative example. The five-membered rings are in envelope conformations with two small endocyclic C–P–C angles at the spiro center in the narrow range  $97.4(1)$ – $97.9(1)^\circ$ . Accordingly, the four exocyclic C–P–C angles are larger than the tetrahedral reference and appear in the range  $112.34(6)$ – $119.58(6)^\circ$ , taking all three cations together.

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**Table 1.** Bond Lengths [Å] and Angles [deg] in the Cations [(CH<sub>2</sub>)<sub>4</sub>P(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>

	1b	1c	1d
P1–C1	1.773(10)	1.795(2)	1.815(1)
P1–C4	1.773(8)	1.809(2)	1.809(1)
P1–C5	1.785(10)	1.807(2)	1.822(1)
P1–C8	1.784(10)	1.808(2)	1.803(1)
C1–P1–C4	97.9(5)	97.9(1)	97.37(6)
C1–P1–C5	112.0(7)	118.6(1)	119.58(6)
C1–P1–C8	119.3(7)	114.2(1)	116.95(6)
C4–P1–C5	117.5(5)	117.0(1)	112.34(6)
C4–P1–C8	115.8(5)	112.7(1)	113.72(6)
C5–P1–C8	95.7(6)	97.4(1)	97.85(6)

**Figure 2.** Molecular structure of the cation in compound **1c** (ORTEP drawing with 50% probability ellipsoids).

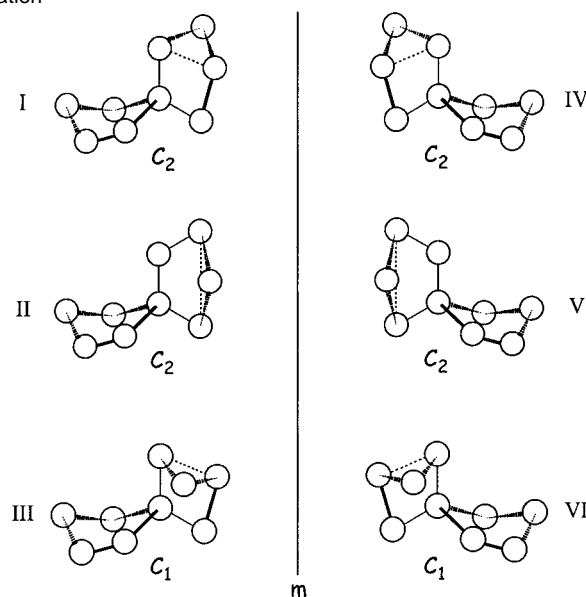
These wide exocyclic C–P–C angles are probably responsible for the susceptibility of the cations to nucleophilic attack at the phosphorus center by carbanions. In the course of such an attack the five-membered rings with their small endocyclic C–P–C angles are shifted into positions where the methylene chains can span axial and equatorial positions in an almost strainless way.

The variations in the P–C bond lengths are small [1.795(1)–1.822(1) Å for **1c** and **1d**; the results for **1b** have larger standard deviations and are less accurate].

Four ring atoms including the phosphorus atom, its two neighboring  $\alpha$ -carbon atoms, and one  $\beta$ -carbon atom are generally found to be roughly coplanar, while a remaining  $\beta$ -carbon atom is positioned above or below this reference plane. In a given cation, the two reference planes are approximately at right angles. In Figure 2 the reference planes contain the atoms C1, P, C4, C3 and C5, P, C8, C7 while the carbon atoms C2 and C6 are those on the tip of the envelop flaps.

With the folding of the five-membered rings the cations become necessarily chiral (point groups  $C_1$  or  $C_2$ ).  $C_2$  is the maximum attainable symmetry in a conformation with appropriate folding of the two rings compatible with a 2-fold axis passing through the P atom and bisecting two exocyclic C–P–C angles. Scheme 3 gives a graphic representation of the four possible folding alternatives for  $C_2$  symmetry and the two conformers with  $C_1$  symmetry derived on the basis of these restraints. Note that two conformers appear in pairs of enantiomers (related by a mirror plane). Since no conformational analysis of spiro[4.4]nonane or its sila-analogue (CH<sub>2</sub>)<sub>4</sub>Si(CH<sub>2</sub>)<sub>4</sub> has previously been carried out, the present study is representative of all species of this type.

For the iodide **1b** and the benzoate **1d** the folding is found to be symmetrical (**I** and **II**) such that the geometry of the

**Scheme 3.** The Six Possible Conformers of the [(CH<sub>2</sub>)<sub>4</sub>P(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> Cation<sup>a</sup>

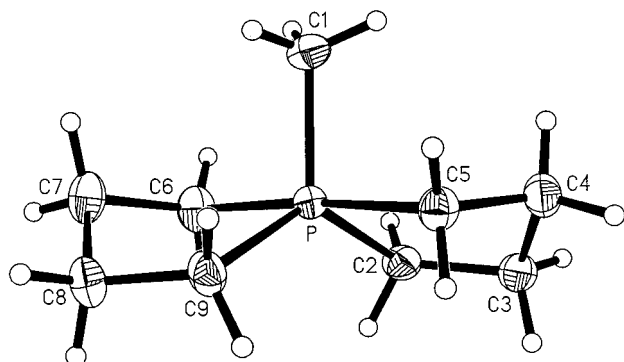
<sup>a</sup> The two five-membered rings have strain-free envelop conformations with the phosphorus atoms in the two perpendicular envelop planes. Two conformers with  $C_1$  symmetry (**III** and **VI**) and four conformers with  $C_2$  symmetry (**I**, **II**, **IV**, **V**) are mirror images.

cations, although not imposed crystallographically, approaches quite closely  $C_2$  symmetry. However, the cation in the picrate salt **1c** is of lower symmetry (point group  $C_1$ , **III**), because the folding follows the alternative direction. It may be concluded that the three conformers are close in energy and that packing forces depending on the nature of the anion may induce a low-symmetry conformation. In all three cases (**1b–d**), the asymmetric unit contains only one enantiomer, but the counterparts (**IV–VI**)—related by a symmetry operation—are also present in the unit cell. In summary all possible conformations (**I–VI**) have been confirmed experimentally for [(CH<sub>2</sub>)<sub>4</sub>P(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>.

Our results also suggest that the spirocyclic phosphonium cation [(CH<sub>2</sub>)<sub>4</sub>P(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> is highly flexible and can adopt quite easily to an environment of different counterions. It should thus be employed for the precipitation of sensitive anions.

**The Spirocyclic Phosphorane 2a.** Crystals of this phosphorane, which is a liquid at room temperature (mp –36 °C), have been grown from the melt in a capillary mounted on the diffractometer. The specimen obtained was monoclinic, space group  $P2_1/c$ , with  $Z = 4$  formula units in the unit cell. The molecule has the expected spirocyclic structure with a five-coordinate phosphorus atom at the spiro-center (Figure 3). The molecule has no crystallographically imposed symmetry, but the geometry can be interpreted as based on a trigonal-bipyramidal configuration that approaches the symmetry requirements of a 2-fold axis passing through the unique methylene carbon atom and the phosphorus atom (ignoring the hydrogen atoms of the methyl group).

The two four-membered methylene chains are spanning axial and equatorial positions leaving one equatorial site for the methyl group. As suggested by conventional VSEPR models, the axial P–C bonds are found distinctly longer [P–C5 1.944(2) Å, P–C6 1.939(2) Å] than the equatorial P–C bonds [P–C1 1.833(2) Å, P–C2 1.873(2), P–C9 1.878(2) Å]. The two axial P–C bonds form an angle of 175.0(1)°, close to the expected



**Figure 3.** Molecular structure of compound **2a** (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [deg]: P–C1 1.833(2), P–C2 1.873(2), P–C5 1.944(2), P–C6 1.939(2), P–C9 1.878(2); C1–P–C2 115.6(1), C1–P–C5 92.0(1), C1–P–C6 92.9(1), C1–P–C9 114.7(1), C2–P–C5 87.4(1), C2–P–C6 91.0(1), C2–P–C9 129.7(1), C5–P–C6 175.0(1), C5–P–C9 90.3(1), C6–P–C9 87.1(1).

180°. The angles between the methyl carbon atom and the other equatorial ring carbon atoms are small [C1–P–C2 115.6(1) and C1–P–C9 114.7(1)°], but still close to the 120° standard. Together with C2–P–C9 129.7(1)° there is a sum of equatorial angles very close to 360°. The two endocyclic angles at phosphorus C2–P–C5 87.4(1)° and C6–P–C9 87.1(1)° are near the 90° norm assigned to axial–equatorial edges of a trigonal bipyramid, which suggests a largely strain-free connection to the spiro-center for the two rings, which are in an envelop conformation. The carbon atoms C4 and C7 are out of the planes formed by the phosphorus atom, its two  $\alpha$ -carbon atoms, and one  $\beta$ -carbon atom. The folding with dihedral angles of 7.4(1)° for C5–P–C2–C3 and 7.0(2)° for C6–P–C9–C8 is more pronounced than in the phosphonium salt precursors (above).

As to be derived from the virtually temperature-independent NMR spectra (+100 to –80 °C) the structure of **2a** is extremely fluctuational in solution. With the CH<sub>3</sub>–P unit as the reference, any con- or disrotatory motion of the two five-membered rings can convert the trigonal bipyramid into a square pyramid (with the methyl group in the apical position). Reversion to the trigonal bipyramid will scramble the P-bound methylene units to make them NMR-equivalent. This *pseudorotation* is very common in the stereochemistry of pentacoordinate phosphorus compounds.<sup>37,39</sup> The activation barrier for the process appears to be extremely low for the phosphorane **2a** in keeping with results for other polyorganophosphoranes with no major mobility restraints.<sup>10,13,40,41</sup> The unknown pentamethylphosphorane can be expected to be equally fluctuational, as already demonstrated for pentamethylarsenic, -antimony, and -bismuth.<sup>7,10,42,43</sup>

## Conclusions

The spiro[4,4]phosphonium salts of the type [(CH<sub>2</sub>)<sub>4</sub>-P(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>X<sup>–</sup> are readily available through a “direct synthesis” from elemental phosphorus and diiodobutane followed by metathesis reactions. In a conformational analysis of the cation structure a set of six possible isomers have been identified which differ in the folding of the two five-membered rings in strain-

free envelop conformations. Owing to symmetrical folding, two pairs of enantiomers have point group C<sub>2</sub> symmetry, while the other pair of enantiomers is devoid of symmetry (point group C<sub>1</sub>, Scheme 3). All four conformers have been detected experimentally in the crystal structures of the iodide (C<sub>2</sub>), picrate (C<sub>1</sub>), and benzoate-hydrate (C<sub>2</sub>) (**1b–d**). This result and solution NMR data suggest very high flexibility of the cations with only minor differences in energy between the conformers.

The configurational details of the structure of the cations with narrow endocyclic and wide exocyclic C–P–C angles are indicative of significant strain, which invites incoming nucleophiles to assist in the expansion of the coordination number at phosphorus from 4 (tetrahedral) to 5 (trigonal-bipyramidal). In the resulting trigonal bipyramid the five-membered rings are able to span axial/equatorial sites which can entertain smaller C–P–C angles more readily.

Based on this observation it is not surprising that the reactions of the phosphonium salts with organolithium reagents indeed lead to a series of stable pentaorganophosphoranes of the type R–P[(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> with R = Me, Et, n-Bu, Vi, and Ph. The yields are satisfactory for R = Me, Et, and n-Bu, but low for R = Vi and Ph.

The crystal structure of the methylphosphorane (**2a**, R = Me, mp –36 °C) shows that the molecule has the expected trigonal-bipyramidal configuration with the methylene chains linking equatorial with axial positions leading to approximate overall C<sub>2</sub> symmetry. The conformation of the bicyclic moiety (CH<sub>2</sub>)<sub>4</sub>P–(CH<sub>2</sub>)<sub>4</sub> in the phosphorane **2a** is thus very similar to that in the precursor phosphonium cations, but the exocyclic C–P–C angles involving the ring C-atoms are smaller than in the phosphonium cations. This change reduces conformational strain and favors phosphorane formation over ylide formation in the reactions of the phosphonium salts with organometallic reagents.<sup>30,36,44,45</sup>

The chemical reactivity of the phosphonium salts **1a–e** and the phosphoranes **2a–e** is the subject of current investigations extending previous studies.<sup>30,36,44,45</sup>

## Experimental Section

**General.** All reactions were carried out routinely in an atmosphere of dry nitrogen. Standard equipment was used throughout. All chemicals used as starting materials were commercially available, except for EtLi and ViLi which were prepared according to the literature.<sup>46,47</sup>

**5-Phosphonia-spiro[4.4]-nonane Salts. (a) Triiodide 1a:** Reference 36. NMR (CDCl<sub>3</sub>) <sup>31</sup>P{<sup>1</sup>H} +73.9 (s). MS (FAB) *m/z* 143 (100%), M<sup>+</sup>. For analytical data see ref 36.

**(b) Iodide 1b:** Reference 36. New NMR data (CDCl<sub>3</sub>, 25 °C) <sup>31</sup>P{<sup>1</sup>H} +72.1 (s). <sup>13</sup>C{<sup>1</sup>H} 26.3 (d, *J* = 5.7 Hz), 24.0 (d, *J* = 46.2 Hz). <sup>1</sup>H 2.70 (d, *J* = 10.4 Hz, 8H), 2.19 (d, *J* = 18.1 Hz, 8H).

**(c) Picrate 1c:** Reference 36. NMR (CDCl<sub>3</sub>, 25 °C) <sup>31</sup>P{<sup>1</sup>H} +72.3 (s). <sup>13</sup>C{<sup>1</sup>H} 26.6 (d, *J* = 5.2 Hz), 23.6 (d, *J* = 46.7 Hz), 178.8 and 126.3 (picrate). <sup>1</sup>H 2.11 (d, *J* = 20.0 Hz, 8H), 2.49 (d, *J* = 10.0 Hz, 8H), 8.71 (s, 2H (picrate)).

**(d) Benzoate 1d:** The iodide **1b** (0.30 g, 1.1 mmol) is treated with silver benzoate (0.25 g, 1.1 mmol) in methanol (50 mL) at room temperature in the dark for 5 h. The AgI precipitate is removed by filtration. Evaporation of the solvent from the filtrate leaves the product

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**Table 2.** Crystal Data, Data Collection, and Structure Refinement of Compounds **1b–d** and **2a**

	$[(\text{CH}_2)_4\text{P}(\text{CH}_2)_4]^+ \text{I}^-$ ( <b>1b</b> )	$[(\text{CH}_2)_4\text{P}(\text{CH}_2)_4]^+ [\text{picrate}]^-$ ( <b>1c</b> )	$[(\text{CH}_2)_4\text{P}(\text{CH}_2)_4]^+ [\text{benzoate}]^- \times$ $\text{H}_2\text{O}$ ( <b>1d</b> )	$\text{MeP}[(\text{CH}_2)_4]_2$ ( <b>2a</b> )
crystal data				
formula	$\text{C}_8\text{H}_{16}\text{IP}$	$\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_7\text{P}$	$\text{C}_{15}\text{H}_{23}\text{O}_3\text{P}$	$\text{C}_9\text{H}_{19}\text{P}$
$M_r$	270.08	371.28	282.30	156.21
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
$a$ (Å)	6.9167(4)	7.1279(2)	8.8855(1)	11.711(1)
$b$ (Å)	12.8234(7)	11.5556(2)	10.3734(2)	6.814(1)
$c$ (Å)	12.2391(9)	20.0157(5)	16.0944(3)	12.003(2)
$\alpha$ (deg)	90	90	90	90
$\beta$ (deg)	104.080(2)	97.342(1)	96.104(1)	102.06(1)
$\gamma$ (deg)	90	90	90	90
$V$ (Å <sup>3</sup> )	1052.9(1)	1635.2(1)	1475.1(1)	936.8(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.704	1.508	1.271	1.122
$Z$	4	4	4	4
$F(000)$	528	776	608	352
$\mu(\text{Mo K}\alpha)$ (cm <sup>-1</sup> )	31.31	2.12	1.88	2.24
data collection				
$T$ (°C)	−110	−130	−130	−120
no. of measd reflns	7605	46920	75515	4404
no. of unique reflns	2202 [ $R_{\text{int}} = 0.045$ ]	3609 [ $R_{\text{int}} = 0.067$ ]	4602 [ $R_{\text{int}} = 0.042$ ]	2029 [ $R_{\text{int}} = 0.1449$ ]
absorption correction	DELABS	none	none	none
$T_{\text{min}}/T_{\text{max}}$	0.593/0.877			
refinement				
no. of refined parameters	91	226	264	167
final $R$ values [ $I \geq 2\sigma(I)$ ]				
$R1$	0.0588	0.0445	0.0469	0.0492
$wR2^a$ $a/b$	0.1159 0.0228/6.96	0.1062 0.0449/1.27	0.1225 0.0655/0.70	0.0947 0.0128/0.155
(shift/error) <sub>max</sub>	<0.001	<0.001	<0.001	<0.001
$\rho_{\text{fin}}$ (max/min) (eÅ <sup>-3</sup> )	1.227/−1.306	0.479/−0.366	0.315/−0.608	0.720/−0.481

$$^a wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3.$$

as a white powder: 0.29 g, 98% yield. Single crystals of the monohydrate are obtained from wet chloroform without exclusion of atmospheric moisture. NMR ( $\text{D}_2\text{O}$ , 25 °C)  $^31\text{P}\{^1\text{H}\}$  +71.7 (s).  $^{13}\text{C}\{^1\text{H}\}$  175.1 (s)  $\text{CO}_2$ , 135.9, 131.5, 128.9, and 128.4 (all s, for C ipso, para, ortho, and meta, respectively), 25.3 (d,  $J = 5.7$  Hz), 22.5 (d,  $J = 46.2$  Hz).  $^1\text{H}$  7.90–7.43 (m, 5H, benzoate), 2.33 (d,  $J = 7.2$  Hz, 8H), 2.03 (d,  $J = 18.3$  Hz, 8H).

**5-Organyl-5-phosphaspiro[4.4]nonanes 2.** (a) **Methylphosphorane 2a:** The compound is prepared from the chloride **1e** (1.5 g, 8.1 mmol) and 10 mmol of MeLi in anhydrous diethyl ether as described in refs 29 and 30. The product is purified by distillation: 0.59 g, 43% yield. Mp −36 °C. Single crystals are grown by slow cooling of the melt. NMR ( $\text{CDCl}_3$ , 25 °C)  $^31\text{P}\{^1\text{H}\}$  −89.3 (s).  $^{13}\text{C}\{^1\text{H}\}$  33.1 (d,  $J = 41.0$  Hz,  $\text{CH}_2$ ), 22.6 (d,  $J = 8.8$  Hz,  $\text{CH}_2$ ), 19.7 (d,  $J = 66.6$  Hz,  $\text{CH}_3$ ).  $^1\text{H}$  1.44 (d,  $J = 9.7$  Hz, 3H,  $\text{CH}_3$ ), 1.35 (dt,  $J = 16.0$  Hz, 8H,  $\text{CH}_2$ ), 0.97 (dt,  $J = 6.6$  Hz, 8H,  $\text{CH}_2$ ). The spectrum in  $\text{CD}_2\text{Cl}_2$  is largely unchanged in the temperature range +25 to −95 °C.

(b) **Ethylphosphorane, 2b:** The chloride **1e** (2.75 g, 15.4 mmol) is dispersed in anhydrous diethyl ether (50 mL) and treated with EtLi (0.77 g, 21.0 mmol) dissolved in 50 mL of diethyl ether at −50 °C with stirring. The reaction mixture is allowed to warm to room temperature and stirring is continued for 2 h. The mixture is filtered and the product isolated from the filtrate by distillation: 0.48 g, 15.7% yield. Bp 60 °C (0.9 mbar). NMR ( $\text{C}_6\text{D}_6$ , 25 °C)  $^31\text{P}\{^1\text{H}\}$  −81.2 (s).  $^{13}\text{C}\{^1\text{H}\}$  31.3 (d,  $J = 40.8$  Hz,  $\text{CH}_2$ ), 29.1 (d,  $J = 69.9$  Hz,  $\text{CH}_2\text{Me}$ ), 23.6 (d,  $J = 8.4$  Hz,  $\text{CH}_2$ ), 9.0 (d,  $J = 5.4$  Hz, Me).  $^1\text{H}$  1.50 (dq,  $J = 7.9$  Hz, 2H,  $\text{CH}_2\text{Me}$ ), 1.36 (dt,  $J = 15.4$  Hz, 8H,  $\text{CH}_2$ ), 1.15 (dt,  $J = 7.8$  and 18.3 Hz, 3H), 0.97 (dt,  $J = 6.2$  Hz, 8H,  $\text{CH}_2$ ). MS (EI)  $m/z$  172 [ $\text{M}]^+$ , 143 [ $\text{P}(\text{CH}_2)_8]^+$ , 116 [ $\text{EtP}(\text{CH}_2)_4]^+$ . Calcd for  $\text{C}_{10}\text{H}_{21}\text{P}$  (172.25): C, 69.73; H, 12.29; P, 17.98. Found: C, 69.70; H, 12.62; P, 17.27.

(c) **n-Butylphosphorane 2c:** The chloride **1e** (0.25 g, 1.4 mmol) is dispersed in anhydrous diethyl ether (7 mL) and treated with 1 mL of a 1.7 M solution of n-BuLi (1.7 mmol) in hexane, dissolved in 7 mL of diethyl ether at −50 °C. After the addition is completed the reaction

mixture is allowed to warm to room temperature and stirred for another 2 h. The reaction mixture is quenched with 5 mL of degassed water and extracted with 3 × 5 mL of diethyl ether. The organic phase is dried with  $\text{MgSO}_4$  and filtered. On evaporation of the solvent a colorless oil remains: 0.14 g, 49% yield. NMR ( $\text{C}_6\text{D}_6$ , 25 °C)  $^31\text{P}\{^1\text{H}\}$  −84.3 (s).  $^{13}\text{C}\{^1\text{H}\}$  36.6 (d,  $J = 68.4$  Hz, C1), 27.1 (d,  $J = 4.6$  Hz, C2), 25.1 (d,  $J = 16.1$  Hz, C3), 14.0 (s, C4 (of n-Bu)), 31.6 (d,  $J = 40.7$  Hz,  $\text{CH}_2$ ), 23.7 (d,  $J = 7.7$  Hz,  $\text{CH}_2$ ).  $^1\text{H}$  1.39 (ddt,  $J = 15.0$  Hz, 8H,  $\text{CH}_2$ ), 1.00 (dt,  $J = 6.3$  Hz, 8H,  $\text{CH}_2$ ), 1.19–1.31 (m, 6H,  $(\text{CH}_2)_3(\text{n-Bu})$ ), 0.88 (t,  $J = 7.4$  Hz, 3H, Me). MS (EI)  $m/z$  200 [ $\text{M}]^+$ , 171 [ $\text{n-BuP}(\text{CH}_2)_4]^+$ , 102 [ $\text{MeP}(\text{CH}_2)_4]^+$ .

(d) **Vinylphosphorane 2d:** The chloride **1e** (1.0 g, 5.6 mmol) is dispersed in anhydrous diethyl ether (100 mL) and treated with ViLi (0.20 g, 6.0 mmol) in 100 mL of diethyl ether at −50 °C. The reaction mixture is allowed to warm to room temperature, stirred for another 2 h, and filtered, and the product is isolated from the filtrate by distillation as a colorless liquid: 0.93 g, 33% yield. Bp 53.5 °C (0.9 mbar). NMR ( $\text{C}_6\text{D}_6$ , RT)  $^31\text{P}\{^1\text{H}\}$  −79 (s).  $^{13}\text{C}\{^1\text{H}\}$  140.8 (d,  $J = 81.5$  Hz, =CH), 121.6 (s, = $\text{CH}_2$ ), 32.3 (d,  $J = 41.5$  Hz,  $\text{CH}_2$ ), 22.4 (d,  $J = 9.2$  Hz,  $\text{CH}_2$ ).  $^1\text{H}$  6.2 (ddd,  $J = 12.5$ , 18.7, and 21.6 Hz, 1 H, =CH), 5.5 (ddd,  $J = 1.5$  and 18.9 Hz, 1 H, = $\text{CH}_2$ ), 5.5 (ddd,  $J = 1.5$ , 12.5, and 39.6 Hz, 1 H, = $\text{CH}_2$ ), 1.4 (dt,  $J = 16.0$  Hz, 8 H,  $\text{CH}_2$ ), 1.1 (dt,  $J = 5.9$  Hz, 8 H,  $\text{CH}_2$ ). MS (EI)  $m/z$  170 [ $\text{M}]^+$ , 114 [ $\text{ViP}(\text{CH}_2)_4]^+$ , 88 [ $\text{HP}(\text{CH}_2)_4]^+$ .

(e) **Phenylphosphorane 2e:** The chloride **1e** (0.50 g, 2.8 mmol) is dispersed in anhydrous diethyl ether (15 mL) and treated with 1.8 mL of a 1.8 M solution of PhLi (3.2 mmol) in cyclohexane/diethyl ether (70/30) diluted with 15 mL of diethyl ether at −50 °C. After the addition is completed the reaction mixture is allowed to warm to room temperature and stirred for another 2 h. The reaction mixture is quenched with 10 mL of degassed water and extracted with 3 × 10 mL of diethyl ether. The organic phase is dried with  $\text{MgSO}_4$  and filtered. On evaporation of the solvent a colorless oil remains: 17 mg, 6.4%. NMR (RT)  $^31\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ) −72.5 (s).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ ) 139.5 (d,  $J = 83.8$  Hz, C1), 127.2 (d, 7.7 Hz, C2/C6), 127.1 (d,  $J = 10.0$  Hz, C3/

C5), 126.5 (s, C4 (of Ph)), 33.2 (d,  $J = 42.0$  Hz, CH<sub>2</sub>), 22.3 (d,  $J = 8.8$  Hz, CH<sub>2</sub>). <sup>1</sup>H (CDCl<sub>3</sub>) 7.36–7.24(m, 5 H, CH (of Ph)), 1.3–1.0 (16 H, CH<sub>2</sub>). MS (EI)  $m/z$  220 [M]<sup>+</sup>, 164 [PhP(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>, 88 [HP-(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>.

**X-ray Crystallography.** Crystals of compound **2a** were obtained by in situ crystallization in a capillary on the diffractometer, whereas specimens of suitable quality and size of compounds **1b–d** were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo K $\alpha$  radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. Hydrogen atoms in compounds **1d** and **2a** were located and refined with isotropic contributions, whereas all hydrogen atoms of compounds **1b** and **1c** were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Further

information on crystal data, data collection, and structure refinement are summarized in Table 2. Important interatomic distances and angles are given in Table 1 and in the corresponding figure captions, respectively. Thermal parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-183987-90.

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**Supporting Information Available:** Tables of crystal data, structure refinement details, atomic coordinates, bond lengths, and angles for **1b–d** and **2a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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