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Synthesis and structural characterization of bis(diphenylvinylphosphonio)isophosphindolylium bromide and investigation of the bonding in bis(phosphonio)isophosphindolylium cations

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Summary – Whereas all attempts to prepare α,α'-bis(diphenylvinylphosphonio)-*o*-xylylene di-bromide as a potential precursor to 1.3-bis(diphenylvinylphosphonio)isophosphindolylium bromide, **7**, resulted only in the formation of bicyclic phosphonium salts, the target was directly accessible in a one-pot synthesis starting from α,α'-bis(β-chloroethyldiphenylphosphonio)-*o*-xylylene dibromide. The X-ray crystal structure analysis of **7** suggested the presence of π-electron delocalization within the fused heterocyclic ring system which was confirmed by the results of *ab initio* quantum chemical studies using the parent 1.3 bis(phosphonio)isophosphindolylium cation, **13a**, as a model compound. According to the theoretical analysis, the bonding in **13a** and the 1.3-bis(phosphonio)phospholium cation **14a** is similar to the isophosphindolyl and phospholyl anions, **13/14b**, respectively, and can be described in both cases in terms of a delocalized 10π (6π) electron system. In contrast to the known reactivity of a bis(triphenylphosphonio)isophosphindolylium cation, reaction of **7** with HBF_4 proceeded *via* protonation at the C rather than the P atom to yield a bicyclic trisphosphonium salt as the final product.

bis(phosphonio)isophosphindolylium cation / crystal structure / *ab initio* calculations

Introduction

The syntheses of benzoheterophospholium cations of type **1** [1] have given new impulses to the chemistry of cationic phosphorus π-systems. It has been established in structural, spectroscopic, and theoretical studies [1] that these novel compounds may be described as "heteronaphthalenic" π-systems where a two-coordinate phosphorus is stabilized within a delocalized 10π-electron system similar to that in naphthalene. Recently, Schmidpeter *et al* reported the synthesis of the bis(triphenylphosphonio) isophosphindolyl cation **2** (R = Ph) [2], which contains a two-coordinate phosphorus in a topologically related environment. Under accentuation of an ylidic structure of the exocyclic P-C bonds, **2** is also isolobal to the cations **1**. Considering further the isolobal relationship between a phosphonio group and a hydrogen, a similar relation between **2** and the benzophospholyl anion **3** may be established. Regarding these connections, the question arises if a similar "heteronaphthalenic" character as for **1** (and certainly for **3**) can be verified for **2**. An answer to this problem would be of particular interest, since concise theoretical studies of the electronic structures of "Arduengo's carbenes" **4** [3] indicate that in this case π-electron delocalization is practically absent. Since a similar isolobal relationship as for **1-3** can be formulated between **4** and the monocyclic heterophospholylium cations **5** and **6**, it is not *a priori* clear whether **2** and **6**, respectively, should be regarded as π-delocalized "heteroaromatics" or not.

In connection with our investigations into the coordination chemistry of **2** [4], we were interested in the synthesis of functionalized bis(phosphonio)isophosphindolyl cations in order to create a basis for systematic studies of the coordination properties of this interesting ligand system. Regarding the known reactivity of vinylphosphonium salts with respect to further functionalization of the double bond [5], we thought that the vinyl-substituted cation **7** (see scheme 2) should constitute a valuable synthon, which might make further functional derivatives accessible. In this work, the synthesis, structural characterization, and acidolysis of **7** will be reported. In addition to the experimental investigations, structure and bonding in the bis(phosphonio)isophosphindolylium and the related bis(phosphonio)phospholylium cations will be discussed on the basis of results of *ab initio* quantum chemical studies.

Results and Discussion

Synthesis of 7

By analogy with the known synthesis of **2**[Br] [2], the target molecule **7** should be accessible via condensation

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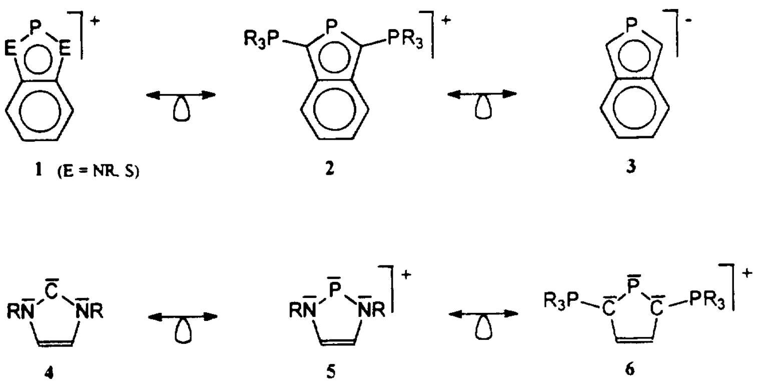
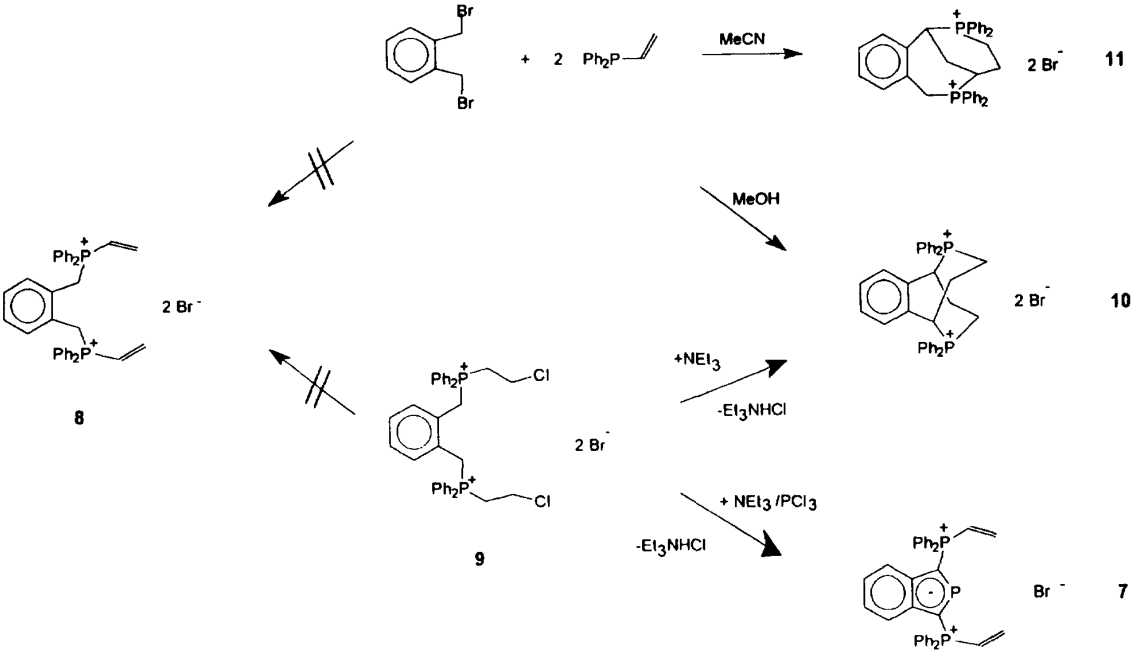


Scheme 1



Scheme 2

of the corresponding vinyl-substituted bis-phosphonium salt **8** with PCl_3 in the presence of triethylamine (scheme 2). Following standard routes for the formation of vinylphosphonium salts [5], we pursued two different strategies to the synthesis of the precursor **8**, viz quaternization of diphenylvinylphosphine with α,α'-dibromo-*o*-xylene, and alternatively, dehydrohalogenation of the bis-β-chloroethyl-substituted phosphonium salt **9**, which is easily prepared from α,α'-dibromo-*o*-xylene and two equivalents of β-chloroethyl-diphenylphosphine. We think it is worth mentioning that both reactions afforded not the expected product **8**, but rather the bicyclic phosphonium salts **10** and **11** (scheme 2). Furthermore, the reaction of diphenylvinylphosphine with α,α'-dibromo-*o*-xylene showed a remarkable solvent dependence, yielding the symmetric product **10** when the reaction was conducted in MeOH, while in MeCN **11** was formed as the major product (> 90%). **10** was the only detectable (^{31}P NMR spectroscopy) reaction product obtained by treatment of **9** with NEt_3.

The constitution of **10** and **11** was established by analytical and spectroscopic data. In both cases, the ^{31}P NMR chemical shifts are compatible with a phosphonium structure (**10** : A_2-spectrum, $\delta^{31}P = 16.5$ ppm, **11** : AX-spectrum, $\delta^{31}P = 13.9$, 15.6 ppm, $J = 3.5$ Hz). The conversion of the vinyl groups is immediately evident from the ^1H and ^{13}C NMR spectra, which display sets of resonances attributable to aliphatic CH_2- and CH-groups, respectively, in the place of the expected olefinic resonance signals. Assignment of all aliphatic and benzylic resonances, as well as the determination of the connectivities, was achieved from a set of $^1H,^1H$, $^1H,^{31}P$, and $^1H,^{13}C$ COSY spectra and allowed to derive unequivocally the constitution of the bicyclic ring system. The observed number and multiplicity of ^1H and ^{13}C signals for the fused aromatic ring is consistent with the different molecular symmetries. Due to the presence of two asymmetric carbons in the skeletons of both **10** and **11**, the two C_6H_5 substituents on each phosphorus are diastereotopic, and a total of two (**10**) or four (**11**) sets of resonance signals are found. The diastereoselective formation of a single stereoisomer in both cases is consistent with studies of molecular models which demonstrate that the observed diastereomers exhibit the least conformational strain within the bicyclic ring system. A further remarkable feature of **10**, **11** are the different kinetic acidities of the protons in β-positions to the phosphorus centers which lead to substantial differences in the outcome of H/D exchange reactions with deuterated solvents; whereas solutions of **10** in methanol-d_4 exhibited quantitative deuteriolysis of all β-protons, only the benzylic protons were exchanged for **11**. Furthermore, upon dissolution of **11** in a 90:10 mixture of dmso-d_6/methanol-d_4, specific deuteration of one of the two protons in the unique benzylic CH_2-moiety was observed.

The conversion of **9** into **10** constitutes another example of the well-known cyclization of phosphonium salts via intramolecular C-alkylation of the anionic position in an ylide intermediate [5] which is formed via base-induced deprotonation of the starting material. In an analogous way, the observed formation of **10** and **11** during the quaternization of vinyldiphenylphosphine can be accounted for by a Michael-type addition of an ylide intermediate to the vinylic double bond, assuming that excess phosphine plays the role of the base during the ylide formation. Reactions of vinylphosphines with benzyl halides, which proceed via loss of the olefinic functionality, have been described earlier [6], even though a different constitution than in our case was ascribed to the reaction products. The solvent-dependent change in regioselectivity could point to solvent participation during the reaction; indeed the reversible addition of alcohols to the electron-deficient double bond in vinyl-phosphonium salts is known [5, 7]. The different stereochemistry of the reaction products **10** and **11**, as well as their different behavior in H/D exchange reactions with solvent molecules, indicate that the CH-acidity in these compounds (and in the supposed intermediates) may be subtly dependent on conformational and stereochemical differences; however, no further explanation of this phenomenon was attempted.

Failing at the explicit synthesis of the vinylphosphonium salt **8**, we investigated the prospect of a direct synthesis of the target molecule **7** from **9**, carrying out the dehydrohalogenation and ring closure steps as a one-pot reaction (scheme 2). Treatment of **9** with PCl_3 in the presence of NEt_3 under conditions similar to the synthesis of **2**[Br] [2] indeed yielded reaction mixtures whose ^{31}P and ^1H NMR spectra indicated the presence of the desired product **7**, together with varying amounts (20-50%) of the dehydrohalogenation product, **10**. Improvement of selectivity as well as reproducibility of the reaction was feasible by careful optimization of the reaction conditions, and pure **7** was finally isolated after employing a workup procedure similar to that reported for **2**[Br] [2].

The constitution of **7** was proven by analytical and spectroscopic investigations. The appearance of the ^{31}P NMR spectrum (A_2X-pattern, $\delta = 238.9$ (A), 12.2 ppm (X_2), $J = 92.8$ Hz) and the observation of the ^{13}C NMR signal of the C1/C3 ring carbons as a characteristic multiplet centered at $\delta = 108.0$ closely resemble the data reported for **2** [2]. The presence of the peripheral vinyl groups was unequivocally derived from the ^1H and ^{13}C NMR-spectra. ^1H and ^{13}C NMR parameters of the remaining atoms in the aromatic fragments exhibit no peculiarities and are in close agreement with those of **2**.

Structural Characterization of 7

Single crystals of **7** that were suitable for X-ray diffractometry were obtained by slow crystallization from ethanolic solution. Similar to the corresponding bis(triphenylphosphonio)isophosphindolylium carbonylmetallate **2**[$CpW(CO)_3^-$] (R = Ph, **12**) [4], solid **7** consists of discrete cations (see fig 1) and bromide anions. Furthermore, the structure contains one solvent molecule (EtOH) per unit cell. The observed short distance between the alcohol oxygen and the bromide anion (304 pm) suggests the presence of a O..H..Br hydrogen bridge, even though the hydrogen atom was not localized during the structure refinement. The ring atoms P1, C1-C8 and the adjacent phosphorus atoms P2 and P3 in the cation show a nearly coplanar arrangement (mean deviation from the least-square plane 1.6 pm; maximum distance 4.1 pm for P2). The sum of valence angles is 360° for all ring carbon atoms. The lengths of the phosphorus carbon bonds originating from C1 and C8 are equal within experimental error (P1-C1 174.0(7), P2-C1 173.5(8) P1-C8 172.3(8), P3-C8 175.2(8) pm), but the average of the endocyclic bonds is slightly shorter than that of the exocyclic ones. The C1-C2 (143.4(10) pm) and C7-C8 distances (143.4(11) pm)

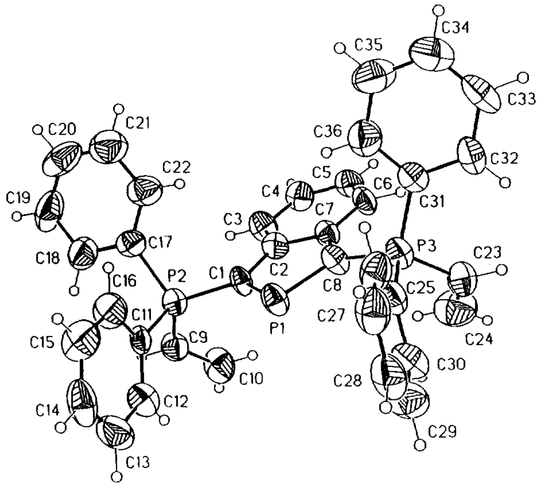


Fig 1. Drawing of the cation of crystalline **7** at a probability level of 50%. Important bond distances (pm) and angles (°) : P1-C1 174.0(7), P1-C8 172.3(8), P2-C1 173.5(8), P3-C8 175.2(8), C1-C2 143.4(11), C2-C3 141.3(11), C2-C7 140.6(11), C3-C4 138.5(13), C4-C5 139.3(12), C5-C6 135.7(11), C6-C7 142.0(11), C7-C8 143.4(10), C1-P1-C8 91.0(4).

are longer than the C-C bonds in the six-membered ring (135.7-142.0 pm, average 139.6 pm). Both phosphonio substituents are arranged in a conformation where one of the two P-C (phenyl) bonds is oriented nearly parallel to the ring plane and points into the direction of the two-coordinate phosphorus, P1. The corresponding phenyl moieties are roughly perpendicular to the ring plane and form a "pocket" around the two-coordinate phosphorus atom. The distance between the centers of the two opposite phenyl groups is 669 pm and is thus of equal size as in the cation of **12** (676 pm) where an essentially similar arrangement of the triphenylphosphonio substituents is observed. Both vinyl groups stand on the same side of the fused ring system, with the terminal C-atoms pointing towards each other. The C-C distances correspond to typical double bonds (C23-C24 1.293(15), C9-C10 131.2(13) pm).

All measured bond lengths in the ring system of the cation of **7** agree with those of the triphenylphosphonio-substituted cation in **12** [4] within experimental error, demonstrating that the bonding situation in both cases is practically identical. Comparable bond distances as for the exocyclic P-C bonds are also found in stabilized phosphonium ylides of the type $R_3P^{(+)}$-C(R)=C(R')-X^- (173-176 pm) [8], while the endocyclic P-C bonds range between single and double bond distances found in heterophospholes [9]. The lengths of the bonds connecting C1/C2 with the six-membered ring are shorter than a standard single bond (C(sp^2)-C(sp^2) 148 pm [10]), but may be compared to the C3-C3a bond distances of indoles (143.4 ± 1.9 pm [10]). Altogether, the structural parameters of **7** display similar features as observed for the hetero-benzophospholium cations **1** [1], suggesting that the electronic structure may be likewise described in terms of a heteronaphthalenic 10π-electron system.

Theoretical studies

In order to gain further insight into the electronic structure of the bis(phosphonio)isophosphindolyl system, we investigated the bis(phosphonio)-substituted isophosphindolyl (**13a**), phospholyl (**14a**), and phosphaallyl cations (**15/16a**) together with the corresponding hydrogen-substituted anions, **13b-16b** (see fig 2), respectively, by *ab initio* quantum chemical methods. On the ground of experimental evidence for the absence of ion pairing between bis(phosphonio)isophosphindolyl cations and the corresponding anions both in solution and solid state [2, 4], all theoretical investigations were confined to the bare ions. It must be borne in mind, however, that phospholyl anions frequently exist as π-complexes with the corresponding cations in condensed phases [11], and the results of this study cannot be expected to give a realistic description of the properties of these species.

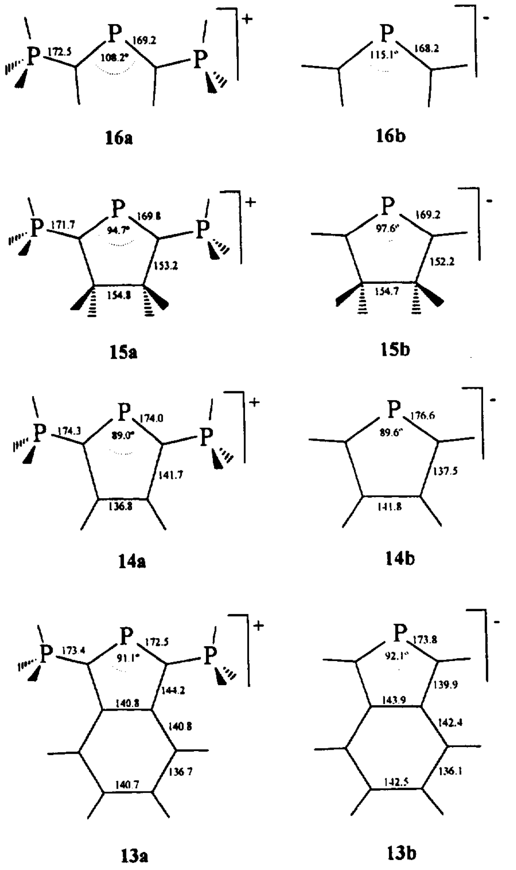


Fig 2. Schematic drawing of the *ab initio* HF/6-31 g* optimized geometries of **13-16** with important bond distances (pm) and angles (°). With the exception of **15**, all ions exhibit planar rings and C_{2v} symmetry. **15a/b** have C_2 symmetry and a twisted five-membered ring.

Theoretical equilibrium geometries of **13-16** were obtained by full geometry optimization at an *ab initio* HF/6-31g* level of theory, within the constraints of C_{2v} (**13, 14**) and C_2 symmetry (**15**), respectively. Subsequent frequency calculations confirmed that all optimized structures correspond to real minima with no negative frequencies. The resulting equilibrium geometries are given in figure 2, the calculated total energies and zero-point vibrational energies in table I. Further included in table I are energies resulting from HF/6-31 + g*//HF/6-31g* and MP2/6-31g*//HF/6-31g* calculations, respectively. Although the use of these more sophisticated theoretical models yields lower energies, closer inspection of the results indicates that no significant changes in the description of the electronic structure occur. A comparison of the calculated geometry of

Table I. *ab initio* calculated energies of **13-16** (in au)[a,b].

	HF/6-31g*	HF/6-31+g*	MP2/6-31g*	Zero-point energy[c]
13a	−1330.6473	−1330.6555	−1331.9806	0.1635
13b	−647.1484	−647.1713	−648.2871	0.1198
14a	−1177.9909	−1177.9971	−1178.8175	0.1129
14b	−494.4877	−494.5090	−495.1161	0.0694
15a	−1178.9973	−1179.1401	−1179.9648	0.1380
15b	−495.5795	−495.6042	−496.2217	0.0919
16a	−1102.2353	−1102.2388	−1102.7976	0.0981
16b	−418.6855	−418.7118	−419.0559	0.0518

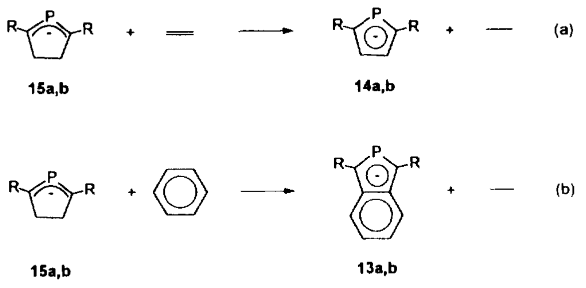
[a] HF/6-31g* optimized geometry used in all cases.

[b] See *Experimental section* for explanation of basis sets.

[c] Based on HF/6-31g* calculated frequencies.

13a with the experimentally determined bonding parameters in the cations of **7** and **12** shows that the agreement between the experimental and theoretical geometries is satisfactory.

When the calculated geometries of **13** and **14** are compared with those of **15** and **16** clear evidence for a significant perturbation of the phosphaallylic fragments by the adjacent organic π-system can be seen in both the anions and cations. Thus, while the P-C_α bonds in the phospholyl anion **14b** (176.6 pm) are considerably longer than their counterparts in **15/16b** (169±1 pm), the adjacent C_α-C_β bond lengths are contracted (137.5 pm (**14b**) vs 152.2 pm (**15b**)) and are shorter than the lateral C_β-$C_{\beta'}$ distance of 141.8 pm. The decrease of the phosphorus valence angle (**14b** : 89.6°, **15b** : 97.6°, **16b** : 115.1°) is mainly attributable to the geometric constraints arising from incorporation of the phosphorus into the five-membered ring, as well as the shorter P-C_α bond distances in **14b**. The P-C_α bond length in the benzophospholyl ion, **13b**, lies almost half way between those of **14b** and **15b**. The C_α-C_β bonds are longer than in **14b**, but significantly shorter than the C_α-C_β single bond in **15b**. The anellated C_β-$C_{\beta'}$ bond is still longer than the C_α-C_β bonds, although the differences are less pronounced than in **14b**. The peripheral bonds in the six-membered ring show a significant alteration; the mean value of the six bonds in the benzene moiety (140.6 pm) is longer than the calculated (HF/6-31g*) bond distance in benzene (138.6 pm).



13a-15a: R = PH_3^+

13b-15b: R = H

Scheme 3

Formal attachment of two positively charged phosphonio substituents at the C_α positions of a phospholene anion (**15b**) leads to elongation of the adjacent P-C_α (169.8 pm) and C_α-C_β bonds (153.2 pm) in **15a**, which can be explained with a bond weakening effect associated with inductive electron withdrawal by the substituents. The lateral C_β-$C_{\beta'}$ bond is nearly unchanged. The exocyclic P-C_α bonds in **15a** (171.7 pm) are shorter as in **16a**, but remain longer than the endocyclic ones. As in the case of the phospholyl anion **14b**, the presence of an additional π-bond in the five-membered ring leads to elongation of both endocyclic and exocyclic P-C_α bond distances in **14a** as compared to the allylic derivative **15a**, although the variation is less pronounced than for **14b/15b**. In contrast to the anion, the lateral C_β-$C_{\beta'}$ bond in the cation is shorter than the adjacent C_α-C_β bonds. Comparison of the geometry of **14a** with the benzoanellated **13a** shows the same pattern as was observed for the corresponding anions. Thus, both the endocyclic and exocyclic P-C distances are between those of the corresponding phospholene (**15a**) and phospholyl derivatives (**14a**). The contraction of the adjacent C_α-C_β bonds compared with **15a** is less pronounced than in the case of the anions, and the anellation of a benzene unit produces lengthening of the C_β-$C_{\beta'}$ bond (140.8 pm vs 136.8 pm in **14a**). The bond alteration in the six-membered ring is less pronounced as in **13b**.

Further insight into the electronic structure of the heterocycles **13** and **14** is gained from the analysis of the SCF electron density. For a comparison of the electronic structures of **13-16**, it is convenient to describe the π-system of a phospholyl anion in terms of a formal interaction of the three π-orbitals of a 2-phosphaallyl-fragment (**16a**) with an olefinic double bond (see fig 3). Such a view gives insight into the mutual charge transfer between both fragments upon forming a cyclic array. Of the two occupied levels in the phosphaallylic fragment, the $2B_1$ orbital is considerably lower in en-

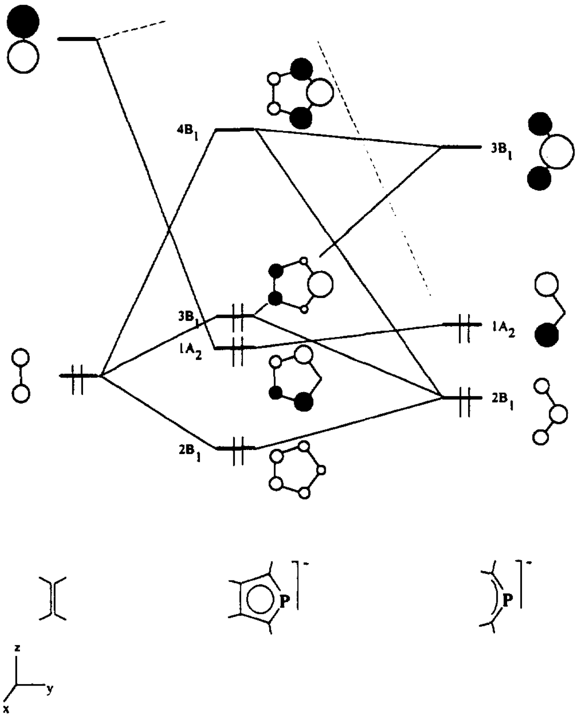


Fig 3. Correlation diagram showing schematically the π-orbital interaction between ethylene (left) and 2-phosphaallyl (right) fragments to form a phospholyl-anion (middle). All fragments are in a standard orientation. The radius of the circles is proportional to the coefficients of the valence p_x atomic orbitals to the corresponding molecular orbitals as obtained from a Mulliken population analysis of the HF/6-31g* electron density. Solid (empty) circles denote positive (negative) signs of individual coefficients. The highest energy MO of the phospholyl anion is not shown.

ergy than the $1A_2$ level, which is the HOMO. Mixing of the latter with the antibonding C-C orbital results in stabilization of the bonding $1A_2$ level in **14a**. Interaction of the two phosphaallyl B_1 orbitals with the C-C bonding orbital gives rise to three molecular orbitals, two of which are higher in energy than the occupied A_2 orbital. Since six π-electrons are present, the HOMO now becomes the $2B_1$ orbital. The delocalization of all π-orbitals over the five ring atoms as well as the analysis of the π-contributions to the Mulliken overlap population justify a description of **14b** as a "heteroaromatic" 6π-electron system, in agreement with the results of previous theoretical analyses of the phospholyl anion [12]. In contrast to **16b**, whose HOMO has a nodal plane through the phosphorus atom, the largest lobe in the HOMO is now placed at the two coordinate phosphorus atom. In terms of a valence bond (VB) description, this enhances the contribution of a resonance structure which exhibits two electron pairs at the phosphorus atom ("phosphido" type structure; this view is essentially supported by an NBO analysis [13] of the SCF electron density) and should result in an increased nucleophilicity of the two-coordinate phosphorus.

In the same manner, the π-electron system of the benzophospholyl anion **13b** can be described in terms of interaction of a phosphaallylic with a benzene fragment. As compared to **14b**, the π-overlap populations are somewhat larger in the P-C_α and smaller in the C_α-C_β bonds, indicating a lower degree of mixing between the two fragments. Nonetheless, the calculated data support a description in analogy to **14b** as a "heteronaphthalenic" 10π-system whose highest occupied levels appear as two very closely spaced orbitals of B_1 and A_2 symmetry (see fig 4).

For the bis(phosphonio)-substituted cations **13a** and **14a**, both Mulliken and natural population analyses [13] reveal that the overlap populations between the π-orbitals at C_α and PH_3-fragment orbitals of appropriate symmetry are small. As in the case of **13/14b**, the π-electron system is thus essentially confined to the ring atoms. Apart from a reversed order of the highest two highest occupied orbitals and an overall drop in orbital energies, which is easily attributable to the increased total charge, the structure of the π-orbitals is at a first glance very similar to the anions **13/14b**. Upon closer inspection, however, the influence of the PH_3-substituents shows up in decreased gross atomic populations for the remaining PC_4H_2- and PC_8H_4- fragments in **14a** (sum of Mulliken charges -0.61) and **13a** (-0.56) as compared to **14b** (-0.79) and **13b** (-0.76), respectively. This formal electron deficit results predominantly in weakening of the bonds between the C_α carbons and the neighboring ring atoms, and is more pronounced in **14a**. The values of the Mulliken overlap populations reveal that in both cases π- and σ-contributions to the bonds are likewise affected; however, when only the π-contribution to the bonding is considered, it becomes evident that the overlap population in the C_α-C_β bonds is most reduced ($p\pi(C_\alpha C_\beta)$ 0.044 (**13a**) [0.088 (**14a**)] as compared to 0.134 (**13b**) [0.180 (**14b**)]), while the π-bonding contribution in the endocyclic P-C bonds remains similar ($p\pi(C_\alpha C_\beta)$ 0.119 (**13a**) [0.118 (**14a**)] vs 0.123 (**13b**) [0.106 (**14b**)]). Contrary to the weakening of the C_α-C_β bonds, the π-overlap population in the C_β-$C_{\beta'}$ bonds is increased. This effect can be identified as the main reason for the observed shortening of this bond in **13/14a**, as the corresponding σ-overlap populations exhibit only marginal variations.

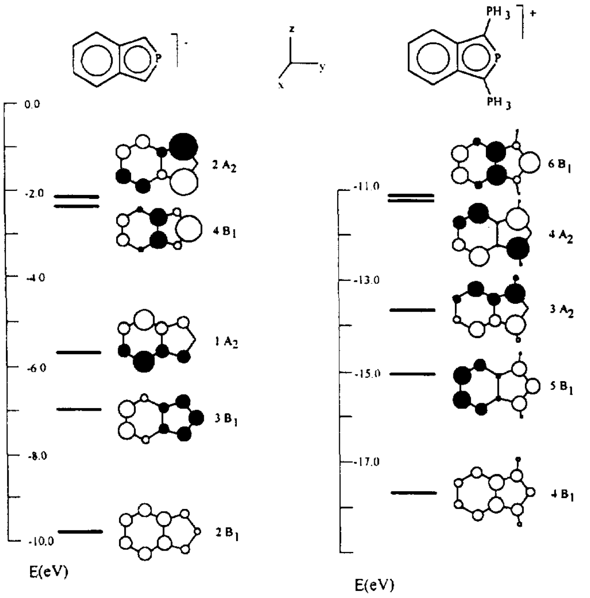


Fig 4. Schematic drawing of the occupied π-orbitals in the isophosphindolyl-anion, **13a** (left) and the bis(phosphonio) isophosphindolylium cation, **13a** (right). The radius of the circles is proportional to the coefficients of the valence p_x atomic orbitals to the corresponding molecular orbitals as obtained from a Mulliken population analysis of the HF/6-31g* electron density. Solid (empty) circles denote positive (negative) signs of individual coefficients. The contributions from the s-orbitals on the out-of-plane hydrogen atoms in the PH_3-groups of **13a** are omitted for clarity; their coefficients are of similar magnitude than those of the atomic orbitals centered at the adjacent phosphorus atoms.

Inspection of individual gross atomic populations further reveals that the negative charge densities at the C_α carbons ($q(C_\alpha)$ -0.60 (**13a**), -0.57 (**14a**)) are significantly larger than in the corresponding anions ($q(C_\alpha)$ -0.50 (**13b**), -0.42 (**14b**)). At the same time, the adjacent exocyclic phosphorus atoms have positive charges ($q(P)$ $+$ 0.62 (**13a**), $+0.63$ (**14a**)). Together with the above-mentioned small contribution of PH_3-centered orbitals to the π-system, which can be traced to mixing with orbitals of predomintantly PH-antibonding character ("negative hyperconjugation"), this bond polarity can be considered as a typical feature of an ylidic bond [14]. However, as both the charge separation and the extent of the hyperconjugative orbital interactions are considerably lower than in the bis(phosphonio)phosphaallyl derivatives **15/16a**, this "ylidic" character is apparently not very pronounced.

The results obtained from the Mulliken population analysis of the π-electron distribution can be summarized by stating that π-electron delocalization between the phosphaallylic and olefinic (aromatic) fragments is still important for a concise description of the electronic structure of the heterocyclic cations **13a** and **14a**, even if the extent of interaction between both fragments is less than in the corresponding anions, **13/14b**.

Furthermore, the ylidic character of the exocyclic P-C bond is reduced with respect to the phosphaallylic systems **15/16a**. Comparison of the electronic structures of **14a** and its benzoanellated congener, **13a**, indicate that both effects appear more significant for the former, thus suggesting that the two phenomena are closely related. This view is entirely consistent with the results of a NBO analysis, which show that the dominant resonance structures feature $C_\alpha C_\beta$ single bonds for the phosphonio substituted cations and double bonds for the anions. Analysis of the second-order perturbation energies between individual orbitals suggests that PH-antibonding orbitals generally provide rather little stabilization of P-C π-bonding orbitals, corresponding to a low degree of ylidic character, and that these effects are less important in **14a** than in **13a**.

In order to assess the energetic contribution of the π-electron delocalization in the studied phospholyl and benzophospholyl ions, we computed the energies of the homodesmic reactions (a) and (b) shown in scheme 3. In our opinion, this approach should be preferable to the commonly used analysis of bond separation energies, since no concise description of the compounds under study in terms of a single localized Lewis-structure is possible. All the energies given in table II were obtained with the HF/6-31g* optimized geometries and include corrections for zero-point vibrational energies based on calculated HF/6-31g* frequencies. The HF/6-31+g*//HF/6-31g* reaction energies are generally slightly less exothermic than HF/6-31+g* energies, while notably more exothermic energy values are obtained at the MP2/6-31g*//HF/6-31g* level. In any case, comparison of the individual data displays entirely the same trend on all three levels of theory. Thus, the formation of a phospholyl anion by interaction of a phosphaallylic and a double bond fragment yields a stabilization of some 60 kcal/mol, while this value is reduced by approximately 30 kcal/mol in the case of the bis(phosphonio)-substituted derivative. A slightly lower stabilization energy is obtained for the interaction of the phosphaallyl anion with a benzene moiety, which we attribute to the price that has to be paid for the perturbation of the aromatic π-system in the C_6H_6 moiety. Again, a reduction in energy by some 30 kcal/mol is found for the phosphonio-substituted cation. The computed HF/6-31g*-stabilization energy for the phospholyl anion is of comparable magnitude as the bond separation energy for benzene on the same level of theory (64 kcal/mol), indicating that π-electron delocalization affords similar stablilization in both cases. The comparison of the homodesmic reaction energies further supports the conclusion drawn on ground of the geometries and population analyses that π-electron delocalization still adds significantly to the stability of the phosphonio-substituted cations **13a** and **14a**, even if the gain in energy is lower than that found for the corresponding phospholyl anions, **13/14b**.

Reaction of 7 *with* HBF_4

Reaction of **2** with strong acids was reported to occur via P-protonation to yield an interesting novel dication featuring a cyclic bis(methylene)phosphorane unit [2]. In order to establish whether formal replacement of two phenyl groups by vinyl moieties leads to a modification of this reaction scheme, we studied the corresponding reaction of **7**. We found that, in contrast to **2**, treatment of a CH_2Cl_2 solution of **7** with one equivalent of etheral HBF_4 afforded a mixture of unreacted starting material together with a new product, whose ^{31}P NMR spectrum exhibits an AMX-instead of an AX_2-type splitting expected for a P-protonated product, **16** (scheme 4). Complete conversion of **7** into the new product was observed upon addition of three equivalents of the acid. Monitoring the whole reaction by ^{31}P NMR spectroscopy gave no evidence for any intermediates. The pure product was isolated by crystallization from the crude reaction mixture and its constitution was determined from analytical and spectroscopic investigations.

A P-protonation was immediately excluded on the basis of the coupled ^{31}P NMR spectrum, which showed the absence of a $^1J_{PH}$ coupling. The ^1H and ^{13}C NMR spectra allowed to deduce the presence of one vinyl-group as well as an aliphatic CH_2-CH_2 group per molecule. Furthermore, two resonances attributable to different isolated CH-moieties could be identified. The connectivity between the individual fragments was unequivocally derived from a consistent set of $^1H,^1H$, $^1H,^{13}C$-, and $^1H,^{31}P$ COSY spectra and led to formulation of the product as the tricyclic trication, **17**. Despite the presence of three chiral centers, we observed only a single diastereomer. Even if the NMR data allowed no statement on the relative conformation on the stereochemically active atoms, we believe on the basis of ring strain argumentes that the two five-membered rings are *cis*-connected. A possible explanation for the formation of **17** can be given based on the assumption that protonation of **7** occurs at the ring carbons rather than at the two-coordinate phosphorus, leading to an intermediate bis(phosphonium) species, **18** (scheme 4). The reaction would then be completed by addition of a further equivalent of the acid to one of the vinyl-moieties and subsequent quaternization of the ring phosphorus atom.

Table II. Calculated energies (in kcal/mol) of the homodesmic reactions shown in scheme 3^{a,b,c}.

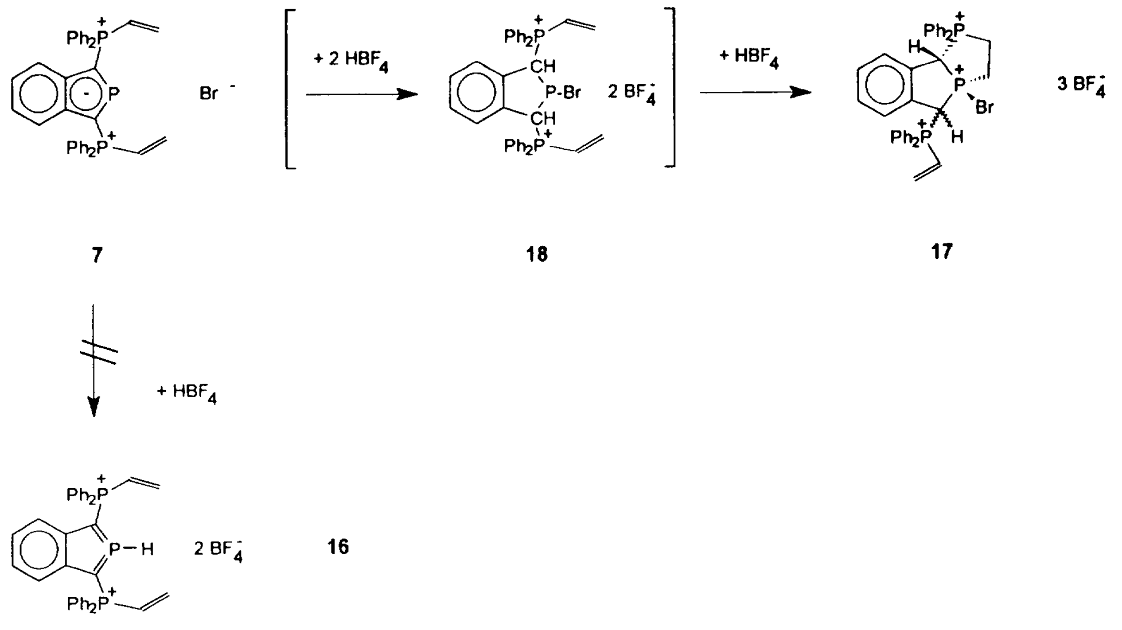
	HF/6-31g*	HF/6-31+g*	MP2/6-31g*
Reaction (a), R = H	−64.5	−60.2	−64.1
Reaction (a), R = PH_3^+	−33.1	−31.9	−39.6
Reaction (b), R = H	−59.4	−53.7	−64.9
Reaction (b), R = PH_3^+	−25.1	−23.4	−35.3

^{a,b} See footnotes on table I.

^{c} Including correction for zero-point vibrational energies.

Conclusions

We have shown that the synthesis of the vinyl functionalized bis(phosphonio)isophosphindolylium cation **7** was easily accomplished via a modification of the



Scheme 4

reported synthetic procedure. The structural investigation of **7** by X-ray diffractometry, in connection with a theoretical analysis of the π-bonding in the bis(phosphonio)phospholyl and bis(phosphonio)benzophospholyl cations, gave evidence that the bonding situation bears close similarities to phospholyl and benzophospholyl anions, respectively. Both the cations and the anions can be regarded as essentially isolobal delocalized π-systems, even if the degree of delocalization in the cations is visibly reduced by the influence of the phosphonio substituents. Nonetheless, the bis(phosphonio)benzophospholyl cation in **7** may be regarded as a further example of a "heteronaphthalenic" π-electron system similar to other heterobenzophospholium cations. The C-protonation observed in the reaction of **7** with HBF_4 establishes an alternative reaction channel to the known reactivity of the triphenylphosphonio-substituted cation of **2** [2].

Experimental section

All manipulations were performed with strict exclusion of moisture under an inert Argon atmosphere. Solvents were dried according to standard procedures and were distilled before use. β-Chloroethyldiphenylphosphine [15] and diphenylvinylphosphine [16] were prepared according to literature procedures. α,α'-Bis(β-chloroethyldiphenylphosphonio)-*o*-xylene dibromide, **9**, was prepared in analogy to a standard procedure [15] from reaction of α,α'-dibromo-*o*-xylene with excess β-chloroethyldiphenylphosphine in MeCN. The crude product which separated from the reaction mixture was used without further purification. NMR spectra were recorded on a Bruker AMX 300 spectrometer (^{1}H : 300.13 MHz, exernal standard Me_4Si; ^{13}C : 75.46 MHz, external standard Me_4Si; ^{31}P : 121.5 MHz, external standard 85% H_3PO_4). A positive sign of δ denotes a shift to lower field. All couplings are given as absolute values in Hz. ^{1}H and ^{13}C NMR signals originating from the C_6H_5 moieties are denoted as *p*-C_6H_5, C^{ipso}, etc. The assignment of signals in the ^{1}H- and ^{13}C NMR spectra of **10**, **11** and **17** is based on the results of ^{1}H,^{1}H, ^{1}H,^{31}P, and ^{1}H,^{13}C shift correlated 2D spectra, all of which were obtained with standard techniques under ^{1}H detection. Microanalyses were obtained with a Heraeus CHNO-Rapid instrument. *Ab-initio* quantum chemical studies were performed with the Gaussian92/DFT package [17]. The 6-31g* basis set denotes a standard 6-31g basis augmented by one set of six *d*-polarization functions on all non-hydrogen atoms. The 6-31+g* basis set further contains one set of diffuse (*sp*)-functions. Further details to the calculations are given in the text.

1.3-Bis[diphenyl(vinyl)phosphonio]isophosphindol-2-ure bromide 7

6.00 g (7.9 mmol) of the bisphosphonium salt **9** were suspended in a mixture of 0.80 mL (8.5 mmol) of phosphorus tribromide and 50 mL CH_2Cl_2. To the boiling mixture, 25 mL NEt_3, which had been previously heated to 40°C, was rapidly added, and the resulting brown mixture was further refluxed for 1 h. After cooling to ambient temperature, volatiles were removed *in vacuo*. The residue was dissolved in 50 mL CH_2Cl_2 and once more evacuated to dryness to remove residual NEt_3. The remaining solids were again dissolved in 100 mL CH_2Cl_2 and rapidly extracted with 30 mL degassed water. The organic layer was then separated and dried over $MgSO_4$. The filtered solution was concentrated to 15 mL and 100 mL THF was added. The resulting suspension was stirred for 30 min and then filtered. Evaporation of the solution to dryness afforded crude **7** as an orange powder of 95-98% purity (determined by NMR spectroscopic assay). Recrystallization of the crude product from a toluene/ethanol (9:1) mixture gave 4.2 g (78% yield) of pale-yellow crystals of the composition **7***EtOH, mp > 250°C (dec).

^{1}H NMR ($CDCl_3$) : δ = 7.55-7.83 (m, 20 H, C_6H_5); 7.25 (ddd, 2H, $^{3}J_{HH}$ = 12.3, 17.2 Hz, $^{2}J_{PH}$ = 14.3 Hz, P-C*H*=CH_2); 7.15 (m, 2H, 5-H/6-H); 6.98 (m, 2H, 4-H/7-H); 6.85 (dd, $^{3}J_{HH}$ = 12.3 Hz, $^{2}J_{PH}$ = 52 Hz, 2H) and 6.15 (dd, $^{3}J_{HH}$ = 17.2 Hz, $^{2}J_{PH}$ = 24.0 Hz), P-CH=CH_2.

$^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CH_2Cl_2}$) : $\delta = 238.9$ (t, $^{2}J_{\mathrm{PP}} = 92.8$ Hz); 12.2 (d, $^{2}J_{\mathrm{PP}} = 92.8$ Hz).

$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) : $\delta = 144.2$ (m, C-3a/C-7a); 141.7 (s, P-CH=CH$_2$), 143.4 (s, C^{para}); 133.6 (m, C^{ortho}); 130.1 (m, C^{meta}); 121.7 (s) and 121.2 (s), C-4-C-7; 121.8 (dd, $^{1}J_{\mathrm{PC}} = 92.1$ Hz, $^{3}J_{\mathrm{PC}} = 3.0$ Hz, C^{ipso}), 121.6 (dd, $^{1}J_{\mathrm{PC}} = 86.4$ Hz, $^{3}J_{\mathrm{PC}} = 6.8$ Hz, P-CH=CH$_2$); 108.0 (ddd, $^{1}J_{\mathrm{PC}} = 98.2$, 57.0 Hz, $^{3}J_{\mathrm{PC}} = 14.0$ Hz, PCP).

Anal calc (found) for $\mathrm{C_{36}H_{30}BrP_3} \times \mathrm{C_2H_5OH}$: C 66.97% (66.50) H 5.32% (5.48).

9,9,12,12-Tetraphenyl-9,12-diphosphoniatricyclo [6.3.3.0^{2,7}]tetradeca-2,4,6-triene dibromide **10**

(a) 1.60 g (7.55 mmol) Diphenylvinylphosphine and 0.95 g (3.60 mmol) of α,α'-dibromo-*o*-xylene were dissolved in 15 mL MeOH and stirred for 6 h at 35°C. After cooling to ambient temperature and concentration to 5 mL, a colorless precipitate formed which was separated by filtration. Recrystallization from a small amount of MeOH produced 1.63 g (63% yield) of a colorless microcrystalline solid of the composition **10***MeOH, mp > 250°C (dec).

(b) Crude α,α'-Bis(β-chloroethyldiphenylphosphonio)-*o*-xylylene dibromide **9** (100 mg) was dissolved in a mixture of 3 mL $\mathrm{CH_2Cl_2}$ and 0.5 mL $\mathrm{Et_3N}$ and heated to 40°C for 30 min. ^{31}P NMR spectroscopic assay of the mixture revealed a single resonance at δ 16.8 ppm which was identified by addition of an authentic sample.

^{1}H NMR (DMSO-d_6) : $\delta = 8.40$ (m, 4H) and 7.95 (m, 4H), *o*-$\mathrm{C_6H_5}$; 7.85 (m, 4H) and 7.55 (m, 4H), *m*-$\mathrm{C_6H_5}$; 7.82 (m, 2H) and 7.62 (m, 2H), *p*-$\mathrm{C_6H_5}$; 7.55 (m, 2H) and 7.13 (m, 2H), $\mathrm{C_6H_4}$; 6.2 (m, 2H, 2-H/6-H); 4.38 (m, 2H) and 3.92 (m, 2H), 4(4′)-H/8(8′)-H; 2.91 (m, 2H) and 2.85 (m, 2H), 3(3′)-H/7(7′)-H.

$^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR(DMSO-d_6) : $\delta = 16.5$ (s).

$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) : $\delta = 134.2$ (m, C-9/C-10); 133.5 (d, $J_{\mathrm{PC}} = 6.0$ Hz) and 130.0 (s), arom CH of $\mathrm{C_6H_4}$; 135.2 (s) and 134.6 (s), C_{para}; 132.6 (d, $^{2}J_{\mathrm{PC}} = 9.6$ Hz) and 132.0 (d, $^{2}J_{\mathrm{PC}} = 9.6$ Hz), C_{ortho}; 130.4 (d, $^{3}J_{\mathrm{PC}} = 12.3$ Hz) and 130.1 (d, $^{3}J_{\mathrm{PC}} = 12.3$ Hz), C^{meta}; 37.1 (d, $^{1}J_{\mathrm{PC}} = 42.1$ Hz, C-2/C-6); 23.15 (s, C-3/C-7); 16.25 (d, $^{1}J_{\mathrm{PC}} = 47.7$ Hz, C-4/C-8).

Anal calc (found) for $\mathrm{C_{36}H_{34}Br_2P_3} \times \mathrm{CH_3OH}$: C 61.68% (61.00) H 5.32% (5.05).

*2,2,6,6-Tetraphenyl-2,3,4,5,6,7-hexahydro-1*H*-2,6-benzophosphonine-2,6-dium dibromide* **11**

1.60 g (7.55 mmol) Diphenylvinylphosphine and 0.95 g (3.60 mmol) of α,α'-dibromo-*o*-xylene were dissolved in 15 mL MeCN and stirred for 6 h at 35°C. After cooling to ambient temperature and concentration to 5 mL, a colorless precipitate formed, which was separated by filtration. Recrystallization from a small amount of MeCN produced 1.78 g (72% yield) of a colorless microcrystalline solid, mp > 250°C (dec).

^{1}H NMR ($\mathrm{CD_3OD}$/DMSO-d_6 1:1) : $\delta = 8.43$ (m, 2H), 8.23 (m, 2H), 8.15 (m, 2H) and 7.62 (m, 2H), *o*-$\mathrm{C_6H_5}$; 8.05 (m, 2H), 7.95 (m, 2H), 7.88 (m, 2H) and 7.50 (m, 2H), *m*-$\mathrm{C_6H_5}$; 7.85 (m, 1H), 7.75 (m, 1H), 7.70 (m, 1H) and 7.9 (m, 1H), *p*-$\mathrm{C_6H_5}$; 7.9 (m, 1H), 7.39 (m, 1H), 7.28 (m, 1H) and 7.15 (m, 1H), $\mathrm{C_6H_4}$; 5.45 (m, 1H) and 5.25 (m, 1H), 9(9′)-H; 5.05 (m, 1H, 6-H); 4.3 (m, 1H, 2-H); 3.8 (m, 1H) and 3.43 (m, 1H), 4(4′)-H; 3.05 (m, 1H) and 2.80 (m, 1H), 10(10′)-H; 2,6 (m, 2H, 3(3′)-H).

$^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3OD}$/DMSO-d_6 1:1) : $\delta = 15.6$ (d, $J_{\mathrm{PP}} = 3.5$ Hz); 13.9 (d, $J_{\mathrm{PP}} = 3.5$ Hz).

$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3OD}$/DMSO-d_6 1:1, DEPT 135) : $\delta = 137.31$ (dd, $J_{\mathrm{PC}} = 5.0$, 2.0 Hz), 136.85 (d, $J_{\mathrm{PC}} = 3.5$ Hz), 131.83 (d, $J_{\mathrm{PC}} = 3.0$ Hz), 130.87 (dd, $J_{\mathrm{PC}} = 3.1$, 2.1 Hz), arom CH of $\mathrm{C_6H_4}$; 137.25 (d, $^{4}J_{\mathrm{PC}} = 3.1$ Hz), 136.88 (d, $^{4}J_{\mathrm{PC}} = 3.1$ Hz), 136.86 (d, $^{4}J_{\mathrm{PC}} = 3.1$ Hz), 136.64 (d, $^{4}J_{\mathrm{PC}} = 3.0$ Hz), C^{para}; 134.58 (d, $^{2}J_{\mathrm{PC}} = 10.0$ Hz), 134.32 (d, $^{2}J_{\mathrm{PC}} = 9.9$ Hz), 134.28 (d, $^{2}J_{\mathrm{PC}} = 8.8$ Hz), 134.08 (d, $^{2}J_{\mathrm{PC}} = 9.5$ Hz), C^{ortho}; 132.64 (d, $^{3}J_{\mathrm{PC}} = 12.2$ Hz), 132.32 (d, $^{3}J_{\mathrm{PC}} = 12.2$ Hz), 132.19 (d, $^{3}J_{\mathrm{PC}} = 12.0$ Hz), and 131.41 (d, $^{3}J_{\mathrm{PC}} = 13.0$ Hz), C^{meta}; 37.80 (d, $^{1}J_{\mathrm{PC}} = 42.3$ Hz, C-6); 27.40 (t, $J_{\mathrm{PC}} = 2.7$, 2.7 Hz, C-10); 26.72 (d, $^{1}J_{\mathrm{PC}} = 37.03$ Hz, C-9); 26.10 (d, $^{1}J_{\mathrm{PC}} = 55.0$ Hz, C-2); 21.12 (d, $J_{\mathrm{PC}} = 5.1$ Hz, C-3); 15.03 (d, $^{1}J_{\mathrm{PC}} = 46.0$ Hz, C-4).

Anal calc (found) for $\mathrm{C_{36}H_{34}Br_2P_3} \times \mathrm{CH_3OH}$: C 61.68% (61.00) H 5.32% (5.05).

*4-Bromo-1,1-diphenyl-5-[diphenyl(vinyl)phosphonio]-2,3,5,9b-tetrahydro-1,3-diphospholio[2,3-*a*]phosphindole tris-tetrafluoroborate* **17**

To a stirred solution of 330 mg (0.47 mmol) of **7** in 5 mL $\mathrm{CH_2Cl_2}$ was added slowly via syringe 34 μL of a 0.1 M solution of $\mathrm{HBF_4}$ in $\mathrm{Et_2O}$. The stirring was continued for further 30 min and the solution kept at 8°C for 12 h. The formed precipitate was filtered off and recrystallized once from $\mathrm{CH_2Cl_2}$ to give 200 mg (60% yield) of a colorless, microcrystalline solid, mp > 250°C (dec).

^{1}H NMR ($\mathrm{CD_3CN}$) : $\delta = 8.05$-7.35 (m, 20H, $\mathrm{C_6H_5}$); 7.3 (m, 1H), 7.15 (m, 1H), 6.95 (m, 1H) and 6.35 (m, 1H), $\mathrm{C_6H_4}$; 6.1 (dd, 1H, $^{2}J_{\mathrm{PH}} = 21.6$, 13.5 Hz, 2-H); 4.8 (t, 1H, $^{2}J_{\mathrm{PH}} = 10.5$, 10.5 Hz, 5-H); 7.40 (ddd, 1H, $^{3}J_{\mathrm{HH}} = 12.6$, 17.4 Hz, $^{2}J_{\mathrm{PH}} = 14.3$ Hz, P-CH=CH$_2$); 6.98 (dd, 1H, $^{3}J_{\mathrm{HH}} = 12.6$ Hz, $^{3}J_{\mathrm{PH}} = 52.0$ Hz) and 6.15 (dd, 1H, $^{3}J_{\mathrm{HH}} = 17.4$ Hz, $^{3}J_{\mathrm{PH}} = 24.0$ Hz), P-CH=CH_2; 3.55 (m, 1H) and 3.37 (m, 1H), 8(8′)-H; 3.08 (m, 1H) and 2.40 (m, 1H), 7(7′)-H.

$^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$) : $\delta = 75.4$ (dd, $J_{\mathrm{PP}} = 50.0$, 8.9 Hz); 38.0 (dd, $J_{\mathrm{PP}} = 50.0$, 5.8 Hz); 19.8 (dd, $J_{\mathrm{PP}} = 8.9$, 5.8 Hz).

$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$) : $\delta = 147$ (s, P-CH=CH$_2$); 136.85 (d, $^{4}J_{\mathrm{PC}} = 3.2$ Hz), 136.55 (d, $^{4}J_{\mathrm{PC}} = 3.1$ Hz), 136.30 (d, $^{4}J_{\mathrm{PC}} = 3.2$ Hz) and 136.10 (d, $^{4}J_{\mathrm{PC}} = 3.1$ Hz), C^{para}; 134.75 (d, $^{2}J_{\mathrm{PC}} = 11.0$ Hz), 134.30 (d, $^{2}J_{\mathrm{PC}} = 9.8$ Hz), 133.95 (d, $^{2}J_{\mathrm{PC}} = 11.7$ Hz), 133.80 (d, $^{2}J_{\mathrm{PC}} = 10.2$ Hz), C^{ortho}; 130.93 (d, $^{3}J_{\mathrm{PC}} = 12.6$ Hz), 130.90 (d, $^{3}J_{\mathrm{PC}} = 13.2$ Hz), 130.35 (d, $^{3}J_{\mathrm{PC}} = 12.9$ Hz), 130.31 (d, $^{3}J_{\mathrm{PC}} = 12.9$ Hz), C^{meta}; 130.8 (s), 130.65 (s), 130.60 (s) and 129.20 (dd, $J_{\mathrm{PC}} = 11.9$, 2.6 Hz), CH in $\mathrm{C_6H_4}$; 130.4 (d, $^{2}J_{\mathrm{PC}} = 3.0$ Hz) and 130.25 (d, $^{2}J_{\mathrm{PC}} = 3.8$ Hz), C-4/C-5; 119.00 (d, $^{1}J_{\mathrm{PC}} = 75.5$ Hz, P-CH=CH$_2$); 115.60 (dd, $J_{\mathrm{PC}} = 87.7$, 4.2 Hz), 115.40 (dd, $J_{\mathrm{PC}} = 88.3$, 1.0 Hz), 115.0 (d, $^{1}J_{\mathrm{PC}} = 81.3$ Hz) and 114.80 (dd, $J_{\mathrm{PC}} = 83.8$, 5.5 Hz), C^{ipso}; 42.2 (dt, $J_{\mathrm{PC}} = 48.7$, 48.7, 3.5 Hz, C-2); 36.9 (t, $J_{\mathrm{PC}} = 45.0$, 45.0 Hz, C-5); 25.70 (dd, $J_{\mathrm{PC}} = 64.5$, 2.0 Hz, C-8); 17.35 (d, $^{1}J_{\mathrm{PC}} = 57.1$ Hz, C-7).

Anal calc (found) for $\mathrm{C_{36}H_{33}BBrF_4P_3} \times \mathrm{CH_3OH}$: C 59.59% (60.23) H 4.55% (4.83).

Crystal structure analysis of **7** EtOH : orange plates, $[\mathrm{C_{36}H_{30}P_3}][\mathrm{Br}] \times$ EtOH, M = 681.5, crystal dimensions 0.15 × 0.35 × 0.38 mm, orthorhombic, space group *Pbca* (No 61) : $a = 2\,002.6(1)$ pm, $b = 1\,731.0(1)$ pm, $c = 2\,037.2(2)$ pm, $V = 7\,062(1) \cdot 10^{6}$ pm^{3}, $Z = 8$, $\rho_{\mathrm{ber}} = 1.28$ Mg m^{-3}, F(000) = 2 816, μ(Cu-Kα) = 3.11 mm^{-1}; 5 236 Symmetry independent reflections between $4 \leqslant 2\theta \leqslant 120°$ were collected (ω-scans) on a

Enraf-Nonius CAD4 diffractometer. Of these, 3 011 reflections with $F > 3.0\sigma(F)$ were used for the solution (direct methods, SHELXTL-Plus) and refinement (full matrix least squares on F, 376 parameters, $R = 0.073$, $Rw = 0.088$, $w^{-1} = \sigma^2(F) + 0.0010\ F^2$) of the structure. An empirical absorption correction with the program DIFABS [18] was applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms with a riding model and common isotropic U. With the exception of the OH hydrogen of the solvent, all hydrogens were localized by difference Fourier analysis. The remaining residual electron density was $+1.00/-0.60 \times 10^{-6}$ e^-/pm in the region of the solvent molecule.

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LA23 7BQ UK, as supplementary publication N° = SUP 30379 and is available on request from the Document Supply Centre.

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