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Synthesis and structures of non-cyclic and cyclic mono- and bisphosphonium salts derived from 1,8-bis(diphenylphosphino) naphthalene

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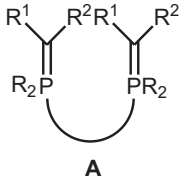
ABSTRACT

A monoalkylated 1,8-bis(diphenylphosphino)naphthalene (dppn) was prepared by treating diphosphine with 1,8-bis(bromomethyl)naphthalene. Unprecedented cyclizations of monophosphonium salts in polar solvents, such as DMF or acetonitrile were elucidated. The mechanistic pathway of the cyclization reaction was postulated and X-ray crystal structure analyses of the resulting 2,2-diphenyl-2,3-dihydro-1*H*-2-phosphoniaphenalene bromide was performed. 1,8-Bis(diphenylphosphino)naphthalene and α,α′-dibromo-*o*-xylene afforded—despite unfavorable steric strain—the first dialkylation product of 1,8-bis(phosphino)naphthalene, namely corresponding cyclic bisphosphonium salt. The use of acetonitrile as the solvent was the key for this synthesis. The bromide anions were exchanged in metathesis reaction with hexafluorophosphate anions and the new compound was fully characterized including single crystal X-ray diffraction. The large distance between phosphorus atoms of 3.974 Å clearly demonstrate a strong proximity effect in this hindered bisphosphonium salt.

1. Introduction

Bidentate phosphorus ylides are important reagents in coordination chemistry and their utility in synthetic chemistry has been well documented.[1,2] While the coordination chemistry of carbodiphosphoranes ($R_3P{=}C{=}PR_3$) is already a fairly well developed area,[2] information about chelating bis-ylides **A** is limited to only few examples.[3] These ylides with various substituents should exhibit specific coordination behavior toward certain metal centers.



A

In the naphthalene molecule the 1- and 8-positions are said to be *peri* to each other. The close proximity of the substituents at these positions has been responsible for the appearance of several unique properties of *peri*-substituted naphthalenes.[4] Such 'proximity effects' enable coordination of the bidentate ligand to a bridging metal center,[5] but make it difficult to quaternize both phosphorus atoms.[6–9] In some cases, unfavorable steric strain operating in the mono- or diadduct can be relieved by formation of products with a bridging geometry.[8,9] In view of the geometry of naphthalene, hydrogen atoms located at these positions are in much closer proximity (2.5 Å) than those located at the *ortho*-positions (3.1 Å). Therefore, vicinal diphosphoniums derived from the *o*-bis(diphenylphosphino)benzene (*o*-dppb) have been successfully synthesized (Fig. 1).[10] The 2,2′-bis(diethylphosphino)-1,1′-biphenyl offers possibilities for the synthesis of quaternary derivatives of

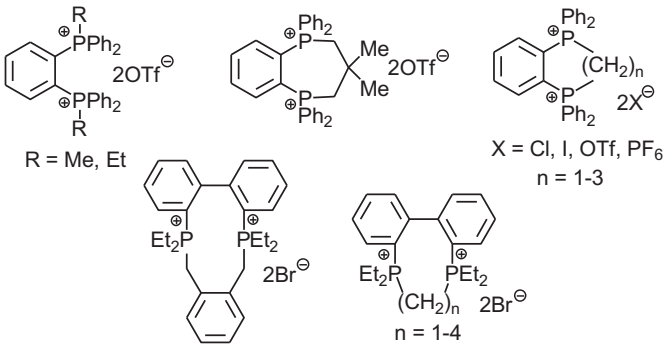


Fig. 1. Bisphosphonium salts of *o*-dppb and 2,2′-bis(diethylphosphino)-1,1′-biphenyl.

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heterocyclic phosphorus compounds, from which free cyclic phosphines might be obtained by thermal decomposition (Fig. 1).[11]

Previous attempts at two-fold quaternization of 1,8 bis(dimethylphosphino)naphthalene (dmpn) and 1,8-bis(diphenylphosphino) naphthalene (dppn) (**1**) using MeI, BnBr or TfMe failed because of unfavorable steric strain and only products of monoalkylation have been observed.[7,9] On the other hand, excess of strong Brønsted acids, such as concd H_2SO_4, tetrafluoroboric acid or trifluoromethanesulfonic acid afforded the symmetrically diprotonated species as confirmed by ^{31}P NMR spectroscopy.[7] Herein we report our attempts at the synthesis of cyclic phosphonium salts—potential reagents for synthesis of the corresponding type **A** bis-ylides, through quaternization of the two phosphorus atoms of dppn with 1,4- and 1,5-dihalo derivatives, such as α,α′-dibromo-*o*-xylene and 1,8-bis(bromomethyl)naphthalene. These compounds or their chloro derivatives react readily with reactive phosphorus compounds giving cyclic monophosphonium salts **2** and **3**·**X** (Fig. 2).[12] The use of such dihalogens should facilitate the bis-alkylation by linking and bridging two terminal phosphonium groups.

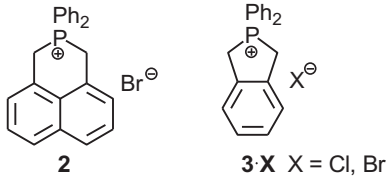
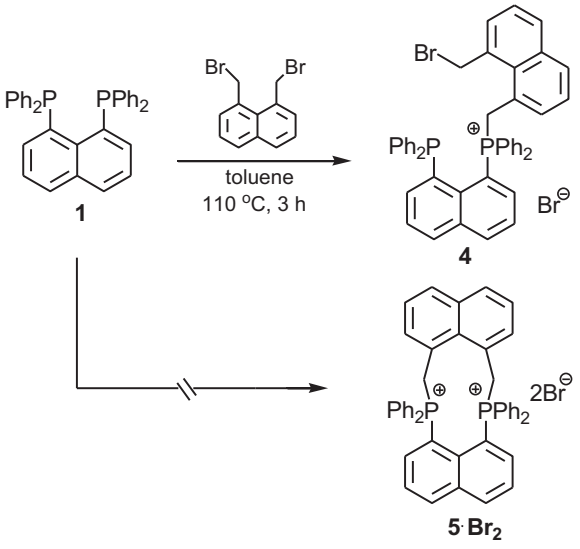


Fig. 2. The cyclic monophosphonium salts derived from 1,8-bis(bromomethyl)naphthalene, α,α′-dichloro-*o*-xylene and α,α′-dibromo-*o*-xylene.

2. Results and discussion

1,8-Bis(diphenylphosphino)naphthalene (**1**) was treated with 1 equiv of 1,8-bis(bromomethyl)naphthalene in boiling toluene. After 3 h the reaction led to monoadduct **4** in 62% yield and did not afford the cyclic diphosphonium salt **5**·**Br$_2$**, even after prolonged heating (Scheme 1).



Scheme 1. Synthesis of (8-bromomethylnaphthalen-1-ylmethyl)-(8-diphenylphosphanylnaphthalen-1-yl)diphenylphosphonium bromide (**4**).

The structure of the product **4** has been studied by NMR spectroscopy, mass spectrometry and elemental analysis. In the ^{31}P NMR spectrum, two characteristic AB-patterns were observed. The spectrum displays sharp doublets at −14.6 ppm for the PPh_2 and 16.7 ppm (J_{PP}=36 Hz) for the phosphonium group. Moreover, broad signals at −13.1 ppm and 19.7 ppm were observed. The J_{PP} value is larger than normal $^4J_{PP}$ values (up to 10 Hz) and indicates a considerable through-space coupling associated with the close proximity of the phosphorus atoms.[8,9] The latter signals are assigned probably to the other conformers, as has been proved for benzyl-(8-diphenylphosphanylnaphthalen-1-yl)diphenylphosphonium bromide.[7]

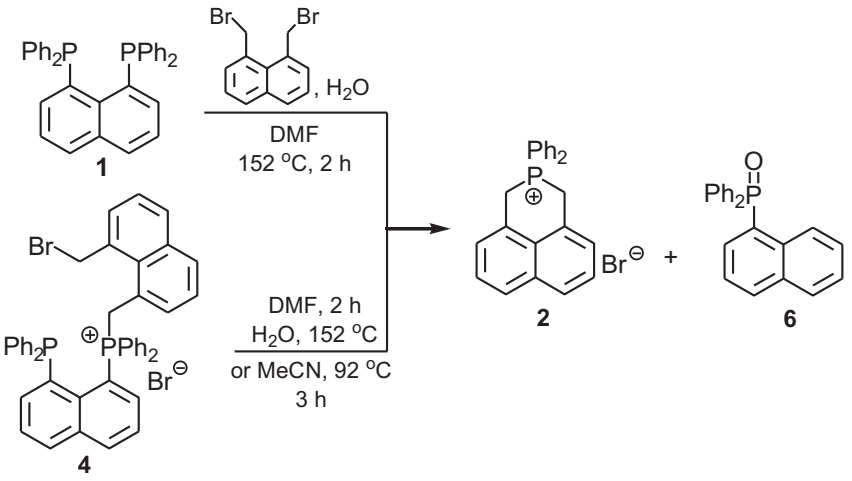
Due to the fact that prolongation of the reaction time in boiling toluene did not produce the desired salt we decided to raise the temperature of this reaction and apply DMF as a solvent. Treatment of **1** with 1,8-bis(bromomethyl)naphthalene in DMF at 152 °C for 2 h resulted in the formation of a white precipitate (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of a crude mixture exhibited two singlets at 6.0 ppm and 29.0 ppm, which suggested cleavage of the P–C_{Nph} bond. The products were separated, purified and characterized initially by FAB mass spectrometry and NMR spectroscopy. These spectra confirmed the structures of cyclic phosphonium salt **2** and phosphine oxide **6** formed in a 1:1 ratio.

The availability of X-ray structural data plays an essential role in assessing steric strain and allows critical insight into the bonding in the *peri*-substituted naphthalenes. Therefore, even though the phosphonium salt **2**[12] was previously synthesized and its NMR spectra were also described we decided to characterize it by X-ray diffraction. Colorless crystals of **2** were obtained by crystallization from MeOH/toluene (5:1) and the molecular structure was determined by X-ray analysis (Fig. 3). In the molecular structure of **2** the six-membered heterocyclic ring is found to be in a slightly distorted sofa conformation with the phosphorus atom deviation of 0.869 Å from the C1C2C3C4C5 plane. All the carbon atoms of this ring are almost coplanar with the naphthalene (C1 and C5 carbon atoms deviation 0.096 Å and 0.017 Å). The bridging of the carbon atoms of the C–P–C system by naphthalene lead to straining of the C1PC5 angle, therefore the phosphorus center adopts a tetrahedral geometry with C1P1C5 angle 101.3° substantially narrower than the normal tetrahedral angle. This one, as well as distances P1C5 (1.772 Å) and P1C1 (1.768 Å) in the ring, are smaller than those of the cyclic phosphonium salt with a chair conformation of heterocyclic ring (103.9°, 1.797 Å and 1.794 Å, respectively).[14]

The reaction in boiling acetonitrile at 92 °C for 3 h also leads to the conversion of **4** into **2** and **6**, but probably because of a low boiling point of the solvent the reaction is slower and it does not occur until the end.

Subsequently, the alkylation of **1** with another bis-halide, such as α,α′-dibromo-*o*-xylene in different solvents was also examined (Scheme 3). In this case, depending on the conditions used, the reaction leads to various products. In a polar solvent as DMF the cyclic phosphonium salt **3**·**Br**,[12,13] analogous to the salt **2**, was formed. However, a completely different result was obtained when acetonitrile has been used in place of DMF. Surprisingly, instead of the cyclic monophosphonium salt **3**·**Br**, the bis-alkylation product **5**·**Br$_2$** was obtained as a white solid after 5 h heating in boiling acetonitrile. Metathesis of the salt **5**·**Br$_2$** with an excess of KPF_6 in methanol gave the corresponding hexafluorophosphate **5**·**[PF$_6$]$_2$**. The reaction in toluene at different temperatures leads to the formation of a mixture of both monoalkylation **7** and dialkylation **5**·**Br$_2$** products. Unfortunately, all attempts to isolate the compounds **7** in a pure form from the reaction mixture were unsuccessful.

Compound **5**·**[PF$_6$]$_2$** crystallizes from acetone/hexane mixture in a tetragonal system, space group $I(-4)2d$ (Fig. 4). The asymmetric unit contains a half of the dication moiety, a half of the first PF_6^- ion, a half of the second PF_6^- ion, and a quarter of the acetone molecule, that lies at the special position and has positional disorder (see Experimental section). The presence of an acetone molecule in the crystal has been experimentally confirmed by ^1H NMR spectroscopy (one singlet from CH_3 groups at 2.13 ppm).



Scheme 2. Conversion of **1** and **4** into cyclic monophosphonium salt **2** and phosphine oxide **6** using 1,8-bis(bromomethyl)naphthalene.

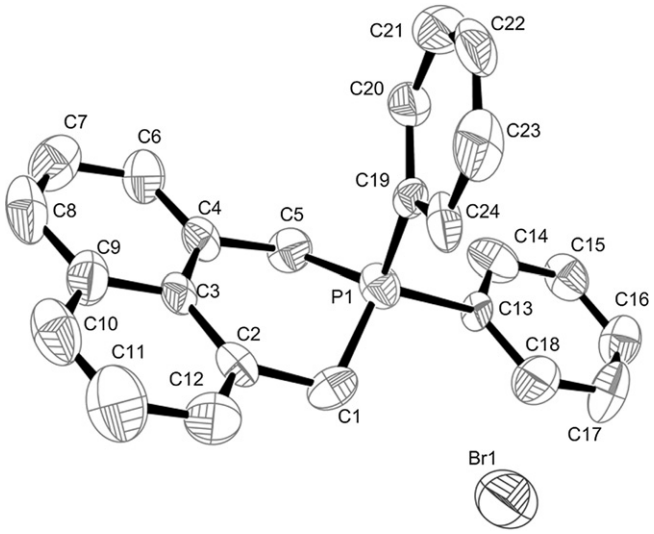
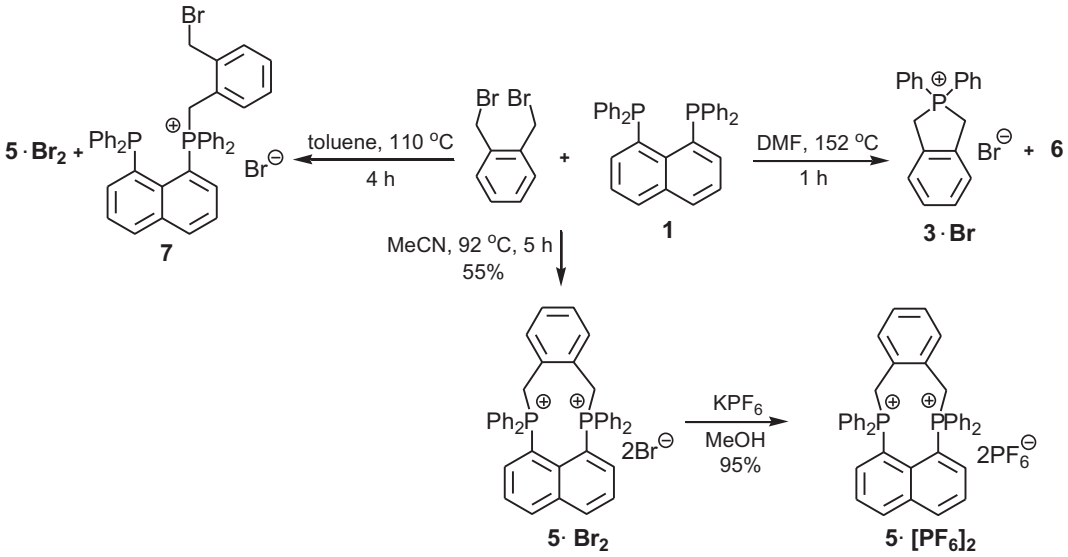


Fig. 3. Crystal structure of **2**. The displacement ellipsoids are drawn at the 50% probability level and the H atoms are omitted for clarity.

The P···P distance of 3.974 Å is larger than in the parent bisphosphine **1** (3.052 Å) and monophosphonium salt **10** (3.192 Å) (Fig. 5). As in the structures of other 1,8-P,P′-disubstituted naphthalenes the proximity of the two bulky substituents leads to in-plane and out-of-plane displacement of both phosphorus atoms with respect to the naphthalene ring system. The in-plane distortion takes the form of a widening of the bay angles P1–C31–C36 (126.49°) and C31–C36–C31′ (129.60°) while the out-of-plane distortion can be assessed from pseudo-torsion angle P1–C31···C31′–P1′ (60.2°), or from the distance between the phosphorus atoms P1 and P1′, which reside above and below the naphthalene mean plane (1.124 Å). These values distinctly demonstrate an extremely strong repulsive interaction between the phosphorus atoms in this cyclic bisphosphonium salt **5**·$[PF_6]_2$.

2.1. Mechanistic postulations

As a starting point to study of the mechanism of *peri* ring closure, the reaction of **1** with 1,8-bis(bromomethyl)naphthalene in DMF was monitored by ^{31}P NMR spectroscopy. The spectra showed the disappearance of the signal due to diphosphine **1** (δ=−14.0 ppm) and the appearance of two doublets at δ=−14.6 ppm and 16.7 ppm



Scheme 3. Reaction of diphosphine **1** with α,α′-dibromo-*o*-xylene in different solvents.

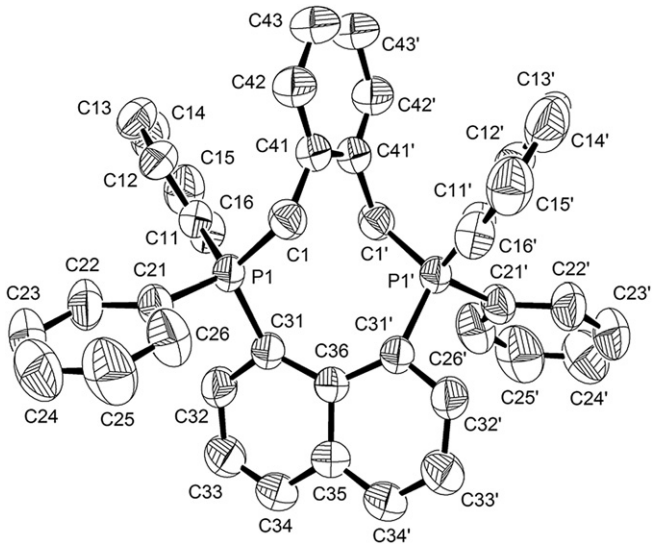


Fig. 4. A view of the structure of **5**·[PF_6]$_2$. The asymmetric unit contains a half of the complete assembly shown in Figure. The symmetry operations that generate the complete assembly are given in Experimental section. The displacement ellipsoids for atoms are drawn at the 50% probability level. The PF_6 anion, H atoms and acetone are omitted for clarity.

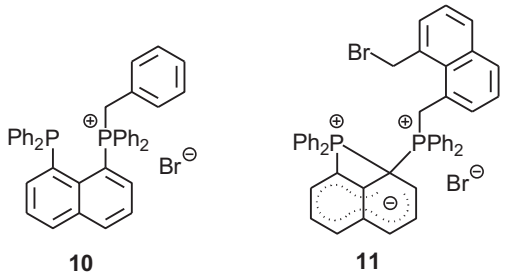
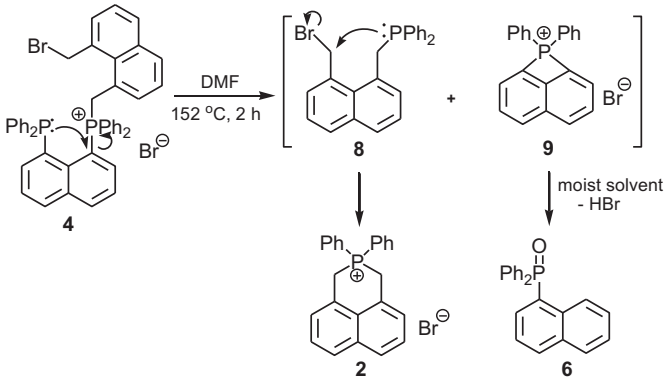


Fig. 5. Monophosphonium salt **10** and intermediate **11**.

with J_{PP}=36 Hz for **4**. After 1 h, besides these doublets two singlets characteristic of the cyclic phosphonium salt **2** (δ_P=6.0 ppm) and phosphine oxide **6** (29 ppm) were observed. Finally, after 2 h two singlets due to the formation of **2** and **6** were only visible in the spectrum. As the characteristic doublets in the ^{31}P NMR spectrum were assigned to monophosphonium salt **4**, we can propose formation of this product as the initial step of this reaction. In fact, heating of **4** in DMF at 152 °C after 2 h also led to formation of **2** and **6** (Scheme 2). On the basis of the literature information[11] and our experimental results, we can suggest two possible pathways for the formation of **2** and **6**, one of them is presented in Scheme 4.



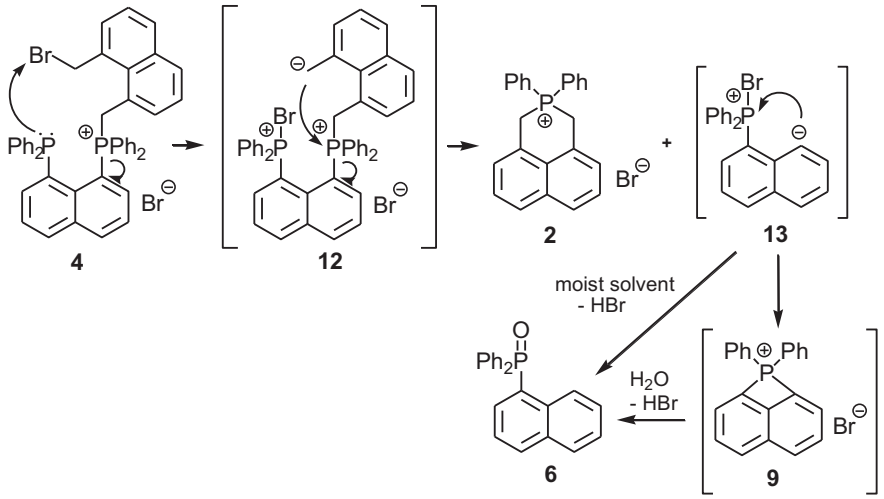
Scheme 4. Proposed stepwise mechanism for the formation of **2** and **6** via intermediate **8** and **9**.

This involves an S_Ni(Ar) displacement for the phosphonium group in the phosphine **4** with the formation of a positively charged four membered cyclic species **9** and phosphine **8**. It is possible that the strained four-membered ring of salt **9** opens in the presence of water giving the phosphine oxide **6** while the monophosphine **8** immediately undergoes an intramolecular quaternization reaction under the reaction conditions giving the six-membered cyclic monophosphonium salt **2**. Inactivity of the halogen group at a nucleophilic displacement stage suggests that monobenzylated 1,8-bis(diphenylphosphino)naphthalene **10** should be a good starting material for the synthesis of salt **9**. Having this in mind, the above mentioned monophosphonium salt **10** was heated for 3 h in boiling DMF, but neither compound **9**, phosphine oxide **6** nor the benzyldiphenylphosphine have been obtained. From this experiment, we can conclude that the formation of a stable six-membered ring presented in Scheme 2 is the driving force of this reaction and leads to **2**. The influence of the solvent nature on the reaction course sometimes provides useful clues regarding the structure of the solvated molecule. Many anions formed during nucleophilic aromatic substitution reactions are expected to be highly polarizable and should strongly interact with polarizable dipolar aprotic solvents like HMPT, DMSO, and DMF.[15] The difference between molecular polarizability values of acetonitrile ($\alpha_{(mol)}$=4.45 Å^3) and DMF ($\alpha_{(mol)}$=7.91 Å^3) suggests an S_Ni(Ar) mechanism and formation of the zwitterionic σ complex **11** (Fig. 5) stabilized by DMF. The dependence of the obtained product on the nature of the solvent is evident for the synthesis of cation **3**·**Br**, but ambiguous for the synthesis of cation **2**, when cyclic monophosphonium salt **2** was formed during reaction in acetonitrile. Presumably, the structure of dihalogens also has an effect on the reaction course. Such thermal decomposition of **4** appears to be a further example of a general S_Ni(Ar) mechanism,[11] although due to the lack of conclusive evidence we cannot exclude an alternative mechanism involving 'electropositive' halogen. Such reactions are known in the literature as *halophilic reactions*.[16] We can assume that non-bonded pair on phosphorus is attacking the antibonding orbital δ^*_{C-Br}, which results in breaking of the C—Br bond and the formation of a benzylic carbanion **12**, which subsequently leads to cyclic phosphonium salt **2** and intermediate **13** (Scheme 5).

Probably, carbanion **13** in the presence of traces of water gives stable phosphine oxide **6** or is transformed into the unstable four-membered cyclic product **9**.[17] However, the latter intermediate was not detected when the reactions were monitored by ^{31}P NMR spectroscopy.

3. Conclusions

In conclusion, we have successfully performed the first alkylation reaction of 1,8-bis(phosphino)naphthalene on both phosphorus atoms by reacting this bisphosphine with α,α′-dibromo-*o*-xylene in acetonitrile. We have shown that the reaction of 1,8-bis(bromomethyl)naphthalene or α,α′-dibromo-*o*-xylene with dppn in toluene proceeds through conventional alkylation reaction giving the monoalkylation product or a mixture of mono- and dialkylation products. Unprecedented conversion of these mono-salts into the corresponding cyclic products **2**, **3**·**Br** and oxide **6** with P—C bond cleavage in DMF takes place. Their formation was the subject of mechanistic studies and two possible mechanisms have been proposed. We can assume that reaction conditions and particularly the type of solvent, its polarizability as well as the structure of the dihalides are predominant factors affecting the reaction course. The structures of the products **2** and **5**·[PF_6]$_2$ have been confirmed by X-ray crystallographic analysis and strong repulsive $P^+\cdots P^+$ interactions in **5**·[PF_6]$_2$ are expressed by the large value of the *peri*-distance of 3.974 Å. Our current efforts are focused



Scheme 5. Proposed stepwise mechanism for the formation of **2** and **6** via intermediate **12**.

now on further application of the diphosphonium salt **5·[PF$_6$]$_2$** for the synthesis of the corresponding stabilized mono- and bis-ylides.

4. Experimental

4.1. General information

All reactions and manipulations were carried out an atmosphere of argon using standard Schlenk and vacuum-line techniques. The solvents were dried, distilled under argon, and degassed before use. 1,8-Bis(diphenylphosphino)naphthalene (**1**) was prepared by literature methods.[18] All commercial reactant were purchased from Sigma–Aldrich. IR spectra were measured on an Ati Mattson Infinity FTIR 60. MS-FAB spectra were registered on a Finnigan MAT 95 spectrometer. The melting points were measured using a PHMK Boetius (VEB Analytik Dresden) apparatus.

*4.1.1. (8-Bromomethylnaphthalen-1-ylmethyl)-(8-diphenylphosphanylnaphthalen-1-yl)diphenylphosphonium bromide (**4**).* To a suspension of 1,8-bis(diphenylphosphino)naphthalene **1** (0.210 g, 0.423 mmol) in toluene (8 mL) was added solution of 1,8-bis(bromomethyl)naphthalene (0.133 g, 0.423 mmol) in toluene (3 mL). The mixture was stirred at 110 °C for 3 h and then the precipitate was separated and washed with toluene (3×2 mL); yield 0.213 g (62%) of yellowish powder, mp 185–186 °C. ^{1}H NMR (200 MHz, MeOD): δ 8.85–5.80 (m, 32H, CH$_{arom}$), 4.55–4.10 (m, 4H, 2× CH$_2$). ^{31}P{^{1}H} NMR (81 MHz, MeOD): δ 19.7 (br m, P(IV), A2-part), 16.7 (d, *J* 36.0 Hz, P(IV), A1-part), −13.1 (br m, P(III), B2-part), −14.6 (d, *J* 36.0 Hz, P(III), B1-part). ^{13}C NMR (50 MHz, MeOD): δ 143.7, 140.4, 134.9, 134.5 (s, C$_{arom}$), 133.1, 133.0 (d, *J* 8.3 Hz), 130.9, 129.9 (s, C$_{arom}$), 129.5 (d, *J* 5.5 Hz, C$_{arom}$), 129.3, 126.3, 126.0, 115.1 (s, C$_{arom}$), 36.3 (s, BrCH$_2$), 30.2 (d, *J* 45.2 Hz, PCH$_2$). IR (KBr, cm^{-1}): 1437, 1268, 1107, 826, 771, 731, 695. FAB-MS 731 [M−Br$^-$]. Anal. Calcd for C$_{46}$H$_{36}$Br$_2$P$_2$ (810.56): C, 68.16; H, 4.48. Found: C, 68.06; H, 4.53.

*4.1.2. 2,2-Diphenyl-2,3-dihydro-1H-2-phosphoniaphenalene bromide (**2**)[12] and 1-naphthyldiphenylphosphine oxide (**6**).*[19] To a suspension of 1,8-bis(diphenylphosphino)naphthalene **1** (0.180 g, 0.363 mmol) in DMF (5 mL) was added solution of 1,8-bis(bromomethyl)naphthalene (0.114 g, 0.363 mmol) in DMF (2 mL). The mixture was stirred at 152 °C for 2 h and then the precipitate was separated and washed with toluene; yield 0.067 g (44%) of white powder of **2**, mp 258–259 °C. The crystals suitable for X-ray analysis were obtained by crystallization from methanol/toluene (5:1). ^{1}H NMR (200 MHz, DMF-*d*$_7$): δ 8.40–7.54 (m, CH$_{arom}$), 5.36 (d, *J* 15.0 Hz, 2× CH$_2$), ^{31}P{^{1}H} NMR (81 MHz, DMF-*d*$_7$): δ 11.0. ^{13}C NMR (50 MHz, DMF-*d*$_7$): δ 135.5, 133.6, 133.3, 130.9, 130.6, 129.9, 127.0 (s, C$_{arom}$), 126.2 (d, *J* 5.7 Hz, C$_{arom}$), 24.8 (d, *J* 51.3 Hz, CH$_2$). FAB-MS 339 [M−Br$^-$]. The filtrate was concentrated to dryness. The resulting solid residue was extracted with diethyl ether and filtered. The volatiles were evaporated and product **6** was obtained as white powder (0.042 g, 35%), mp 179–180 °C. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 33.5. EI-MS 328 [M].

*4.1.3. Bisphosphonium salt **5·Br$_2$**.* To a suspension of 1,8-bis(diphenylphosphino)naphthalene **1** (0.200 g, 0.403 mmol) in acetonitrile (5 mL) was added solution of α,α′-dibromo-*o*-xylene (0.128 g, 0.484 mmol) in acetonitrile (2 mL). The mixture was stirred at 92 °C for 5 h. The precipitate was separated and washed with acetone; yield 0.168 g (55%) of white powder of **5·Br$_2$**, mp 198–199 °C. ^{1}H NMR (200 MHz, CD$_3$OD): δ 8.92–7.00 (m, 30H, CH$_{arom}$) 5.21 (d, *J* 14.2 Hz, 4H, 2× CH$_2$), ^{31}P{^{1}H} NMR (81 MHz, CD$_3$OD): δ 29.5 (s). ^{13}C NMR (50 MHz, DMSO-*d*$_6$): δ 143.4 (d, *J* 7.2 Hz, C$_{arom}$), 137.8, 133.7, 131.7, 131.7, 129.2, 128.9 (s, C$_{arom}$), 128.3 (d, *J* 13.1), 128.0 (s, C$_{arom}$), 126.7 (d, *J* 12.0), 112.5 (d, *J* 83.3), 29.2 (d, *J* 43.8). IR (KBr, cm^{-1}): 1484, 1436, 1098, 996, 826, 892, 750, 690. FAB-MS 601 [M−2Br$^-$]. Anal. Calcd for C$_{42}$H$_{34}$Br$_2$P$_2$ (760.50): C, 66.33; H, 4.51. Found: C, 66.82; H, 4.58.

*4.1.4. Bisphosphonium salt **5·[PF$_6$]$_2$**.* To a solution of **5·Br$_2$** (0.168 g, 0.221 mmol) in MeOH (1 mL) was added a solution of KPF$_6$ (0.049 g, 0.265 mmol) in MeOH (5 mL). The solution was stirred at room temperature for 2 h and the white precipitate was filtered and washed with MeOH (3 mL); yield 0.187 g (95%) of white powder of **5·[PF$_6$]$_2$**, mp 204–205 °C. The crystals suitable for X-ray analysis were obtained by recrystallization from acetone/hexane (5:1). ^{1}H NMR (200 MHz, CD$_3$OD): δ 8.65–7.00 (m, 30H, CH$_{arom}$), 5.08 (d, *J* 14.2 Hz, 4H, 2× CH$_2$). ^{31}P{^{1}H} NMR (81 MHz, CD$_3$OD): δ 25.6 (s, PPh), −143.4 (septet, *J* 708.2 Hz, PF$_6$). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 144.7 (d, *J* 7.7 Hz, CH$_{arom}$), 139.2 (s, CH$_{arom}$), 136.5, 136.4 (d, *J* 9.1 Hz, C$_{arom}$), 135.0 (s, CH$_{arom}$), 133.2 (br m, C$_{arom}$), 132.9 (s, CH$_{arom}$), 131.3, 131.2 (d, *J* 5.0 Hz, C$_{arom}$), 130.4 (d, *J* 13.8 Hz, CH$_{arom}$), 129.6 (s, C$_{arom}$), 129.4 (s, CH$_{arom}$), 127.9 (d, *J* 13.7 Hz, CH$_{arom}$), 113.3 (d, *J* 84.2 Hz, C$_{arom}$), 30.5 (d, *J* 43.9 Hz, PCH$_2$). ^{19}F{^{1}H} NMR (CD$_3$OD): δ −73.2 (d, *J* 708.2 Hz). IR (KBr, cm^{-1}): 1493, 1440, 1104, 999, 838, 809, 744, 690, 557. FAB-MS 601 [M−2PF$_6^-$]. Anal. Calcd for

$C_{42}H_{34}F_{12}P_4 \cdot 1/2$ acetone (919.69): C, 56.81; H, 4.06. Found: C, 57.21; H, 4.11.

4.2. X-ray crystal structure

Crystallographic measurements of compound **2** were performed at low temperature (180 K) on an Xcalibur Oxford Diffraction diffractometer using graphite-monochromated Mo Kα radiation (λ=0.71073 Å) (Table 1). The final unit cell parameters have been obtained by means of a least-squares refinement. The structure has been solved by direct methods using SIR92[20] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[21] included in the softwares package WinGXversion 1.63.[22] Drawing of molecule was performed with the program ORTEP32[23] with 30% probability displacement ellipsoids for non-hydrogen atoms.

Table 1
Crystal data and experimental details for compounds **2** and **5**·$[\mathbf{PF_6}]_2$

Compound	**2**	**5**·$[\mathbf{PF_6}]_2$
Molecular formula	$C_{24}H_{20}BrP$	$(C_{42}H_{36}P_4F_{12})^*C_3H_6O$
Formula weight	419.28	950.70
Crystallographic system	Monoclinic	Tetragonal
Space group	*P*21/*c*	*I*(−4)2*d*
a [Å]	9.206(2)	20.3806(2)
b [Å]	12.957(3)	20.3806(2)
c [Å]	16.757(4)	20.7970(2)
V [Å^3]	1976.1(8)	8638.4(2)
Z	4	8
D_{calcd} [g/cm^3]	1.409	1.462
T [K]	180(2)	296(2)
F(000)	856	3904
μ[mm^{-1}]	2.166	2.396
Reflections measured	13,018	114,239
Reflections unique (all)	3749	4372
Rint	0.1585	0.0279
Parameters refined	235	300
wR^2	0.1108	0.1391
R_1 (all data)	0.2355	0.0466
Goodness-of-fit	0.825	1.053
Residual density max [e Å^{-3}]	0.614	0.499

Crystallization of the product **5**·$[\mathbf{PF_6}]_2$ from acetone/hexane (5:1) resulted in colorless crystals. The data were collected with Bruker APEX-II CCD diffractometer at room temperature using CuKα radiation.[24] An experimental absorption correction was applied, with transmission min=0.45 and max=0.65.[25] Structure was solved by direct methods with SHELXS-97 and refined with SHELXL-97 using full-matrix least-squares with F^2.[26] The H atoms were found in a difference Fourier map and their geometry was regularized. Then all H atoms were positionally constrained to ride on their parent atoms. The isotropic thermal displacement parameters for all H atoms were refined. All nonhydrogen atoms were refined anisotropically. For all data, the final wR^2 was 0.1391, R_1=0.0466, *S*=1.053, max Δρ=0.50 e Å^{-3} (Table 1).

The COOT and MERCURY programs were used for model building and structure visualization.[27] The asymmetric unit contains a half of the molecule. The following atoms lie on the special positions: naphthalene carbons C35 and C36, phosphorus P2 and fluorides F23 and F24 of the first PF_6^- ion, phosphorus P3 of the second PF_6^- ion, and oxygen O51A with carbon C51A of the acetone moiety. The complete structure (shown in Fig. 4) could be assembled by applying the respective symmetry operations to the following items that are present in the asymmetric unit: (*x*+1, 1.5−*y*, 0.25−*z*: for 1,8-bis(diphenylphosphino)naphthalene moiety), (1−*x*, 1−*y*, *z*: for the first PF_6^- ion with phosphorus atom labeled as P2), (1.5−*x*, *y*, 0.75−*z*: for the second PF_6^- ion with phosphorus atom labeled as P3). The complete coordinates for both conformers of positionally disordered solvent (acetone) molecule could be generated by applying symmetry operation (2−*x*, 1−*y*, *z*) (to generate complete conformer A) and (0.5+*y*, 1.5−*x*, 0.5−*z* and 1.5−*y*, −0.5+*x*, 0.5−*z*) (to generate conformer B).

Crystallographic data for structures **2** and **5**·$[\mathbf{PF_6}]_2$ in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 792140 and 859561. Copies of the data can be obtained, free of charge, from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.11.081. These data include MOL files and InChiKeys of the most important compounds described in this article.

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