Naphthalene-1,8-diyl Bis(Halogenophosphanes): Novel Syntheses and Structures of Useful Synthetic Building Blocks

Petr Kilian, Alexandra M. Z. Slawin, and J. Derek Woollins*[a]

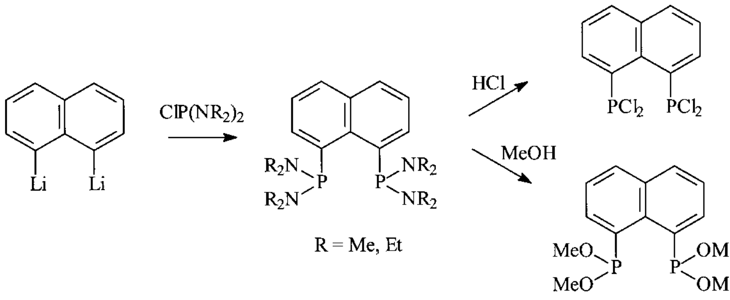
Abstract: A series of new bay region disphospha-functionalised naphthalenes is reported. The reduction of ylidic phosphonium phosphoride $NapP_2Cl_6$ (**1**) (Nap = naphthalene-1,8-diyl) with $MeOPCl_2$ gives the important synthon $Nap(PCl_2)_2$ (**2**) in nearly quantitative yield. Reaction of **1** with magnesium metal affords $(NapP_2)_n$ (**3**), which reacts with Br_2 and I_2, yielding $Nap(PBr_2)_2$ (**4**) and $Nap(PI)_2$ (**5**), respectively. X-ray structure determinations reveal a twisted geometry of the naphthalene ring in sterically strained **2** and **4**, whilst the presence of a P–P bond in **5** results in the release of the steric strain and generation of the planar $NapP_2$ moiety. Although the tetrahedral P environments are severely distorted the $\sigma^3P-\sigma^3P$ bonding in **5** represents a new type of P–P bonding environment in 1,8-diphosphanaphthalenes. Compounds **1**, **4** and **5** each represent the highest coordination, achievable by direct halogenation. The new compounds **2**–**5** were fully characterised by NMR, IR, and Raman spectroscopy, mass spectrometry, and elemental analysis.

Keywords: halogens · neighboring-group effects · phosphorus · strained molecules

Introduction

Naphthalene-based systems have received much attention as the simplest polycyclic aromatic hydrocarbons that allow substitution in a bay region (positions 1 and 8 of the naphthalene ring). If no bonding interaction between the two substituents is present, substantial steric strain is introduced. This strain can be released in various ways, for example by protonation—this phenomena found its use in the area of proton sponges.[1] Another feature of bay-substituted naphthalenes—bidenticity combined with rigid C_3 backbone—has found use in the design of ligands for catalysis.[2]

In the case of 1,8-diphospha substitution, the synthetic approach is simplified by the relative inertness of the P–C bond, which allows a huge variety of interesting main group as well as organometallic chemistry to be performed on phosphorus functionalities. A concise summary of work done by Schmutzler et al. in the area of 1,8-diphosphinonaphthalenes was published recently.[3] However, the area partially suffers from lack of readily obtainable, versatile starting materials, because the principles known from classical organophosphorus chemistry are not always applicable here. Only some of the derivatives with anticipated high synthetic potential have been reported to date, namely $Nap(PCl_2)_2$,[4] $Nap[P(OMe)_2]_2$[5] and $Nap[P(NR_2)_2]_2$ (R = Me, Et)[4, 6] (Nap = naphthalene-1,8-diyl, Scheme 1). Attempts to prepare $Nap(PH_2)_2$ were repeatedly unsuccessful.[5] A detailed study of the reaction mechanism for the formation of the most desirable synthon $Nap(PCl_2)_2$ from $Nap[P(NR_2)_2]_2$ was published recently, in which the low overall yields obtained by this route were explained.[6]



Scheme 1. Routes to basic synthons in 1,8-diphosphanaphthalene chemistry using 1,8-dilithionaphthalene as starting compound.

All of the above-named synthons were prepared by using 1,8-dilithionaphthalene as a key precursor. The only other known method for introducing two phosphorus functionalities

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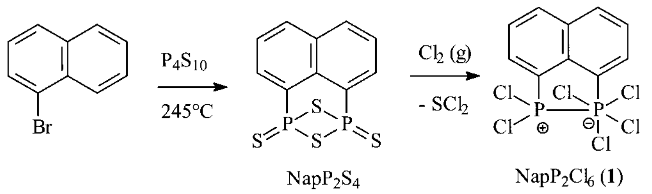
into positions 1 and 8 of a naphthalene ring selectively was reported by us; the high-temperature reaction of 1-bromonaphthalene and P_4S_{10} yields $NapP_2S_4$ (Scheme 2).[7] We have



Scheme 2. Route to $NapP_2Cl_6$ (**1**) via $NapP_2S_4$.

used $NapP_2S_4$ to generate a range of new heterocycles;[7, 8] however, the situation described above motivated us to develop $NapP_2S_4$ transformations towards more versatile synthons than $NapP_2S_4$ itself. To fulfill this objective, we have recently discovered a relatively simple preparation of $NapP_2Cl_6$ (**1**) by chlorination of $NapP_2S_4$ (Scheme 2).[9] The high synthetic potential of compound **1** will be demonstrated herein.

Results and Discusssion

$Nap(PCl_2)_2$

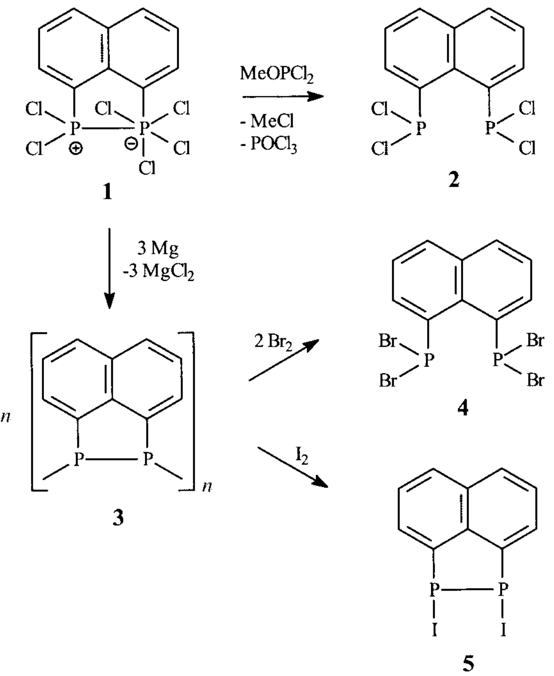
A new synthetic pathway to 1,8-bis(dichlorophosphino)naphthalene **2** was designed because of its importance as a versatile synthetic intermediate for 1,8-diphosphanaphthalenes. The reaction of **1** with a slight excess of methyldichlorophosphite ($MeOPCl_2$) in refluxing toluene gives bis(dichlorophosphane) **2** in nearly quantitative yield (Scheme 3). Starting from the well-established intermediate $NapP_2S_4$ the overall yield after purification steps was 49 %.

Tetrachlorophosphoranes $RPCl_4$ are transformed into dichlorophosphanes $RPCl_2$ by various reducing agents such as Hg, Zn, and other metals. Nevertheless, $MeOPCl_2$ seems to be the reagent of choice; firstly, the by-products of the reaction ($POCl_3$ and MeCl) are both volatile and thus are easily removed by evaporation in vacuo at room temperature; and secondly, the reaction is not critically sensitive to a molar ratio of reactants (excess of $MeOPCl_2$ does not further react with **2**).

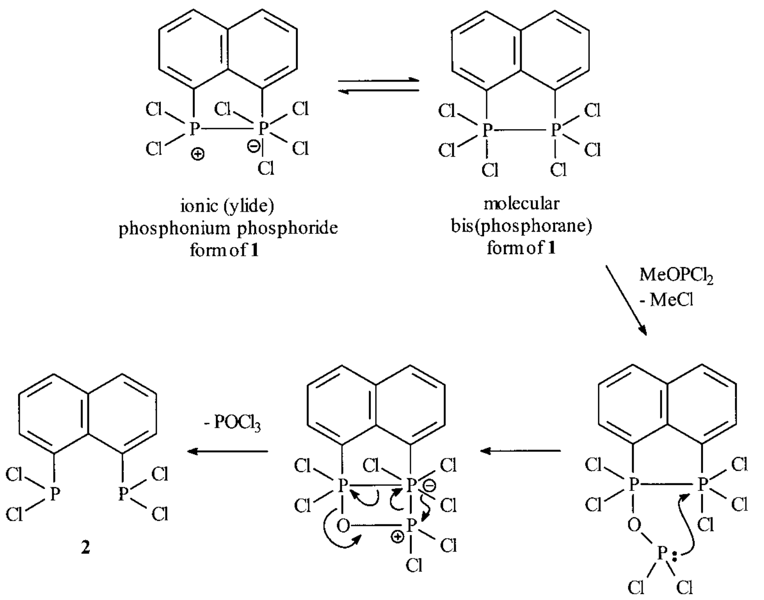
We have shown[9] that two equilibrium forms of **1** exist in solution at normal and elevated temperature; both isomers contain a P–P bond in their structure (Scheme 4).

A plausible mechanism for the reaction of **1** with $MeOPCl_2$ involves nucleophilic attack of the molecular bis(phosphorane) by $MeOPCl_2$, followed by consecutive elimination of MeCl and $POCl_3$ (Scheme 4). The bonding situation in the bis(phosphorane) structure of **1** suggests that the reaction with another equivalent of reducing agent ($MeOPCl_2$) might proceed with back formation of the P–P bond to give the diphosphino product $Nap(PCl)_2$ whose structure is analogous to that of $Nap(PI)_2$ (**5**, vide infra); however, ^{31}P NMR spectroscopy of the reaction mixture after prolonged heating of **1** with two equivalents of $MeOPCl_2$ in toluene did not show the presence of any other phosphorus-containing product than **2**.

The purity of **2**, after sublimation in vacuo, was assessed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, and its identity was



Scheme 3. Routes to new synthons from $NapP_2Cl_6$ (**1**).



Scheme 4. Equilibrium forms of **1** in solution, and plausible reaction scheme for reaction of **1** with $MeOPCl_2$.

reconfirmed by X-ray structure determination (vide infra). ^{31}P and ^{1}H NMR and MS spectra of a sample of **2** prepared by another route were reported elsewhere,[4] we report the ^{13}C NMR data here.

$(NapP_2)_n$

The reaction of organodichlorophosphanes $RPCl_2$ with magnesium metal affords cyclic oligomers of the general formula $(RP)_n$. In the case of R = aryl, n usually reaches 4–6.[10] Oligomeric $(RP)_n$ reacts with sodium or potassium metal to afford highly reactive metallated species $M(PPh)_nM$ (M = Na, K),[11] no such species were reported on reaction with magnesium.

Treatment of 1,2-phenylenebis(diiodophosphane) with two equivalents of magnesium in THF affords a white microcrystalline material, which was insoluble in common organic solvents. It was characterised by mass spectrometry, ^{31}P-CP-MAS spectrometry, and by microanalysis. Based predominately on the highest mass peak found in the EI-MS spectrum, which corresponds to $(C_6H_4P_2)_5$, a bicyclic pentameric structure was suggested for this product.[12] On the other hand, catalytic dehydrocoupling of $1,2\text{-}C_6H_4(PH_2)_2$ affords the octamer $(C_6H_4P_2)_8$, which contains a P_{16} macrocycle, as shown by X-ray structure analysis[13]—although the asymmetric unit in the crystal consists of two pairs of dimers, its simplest structural formula can be written as in Figure 1.

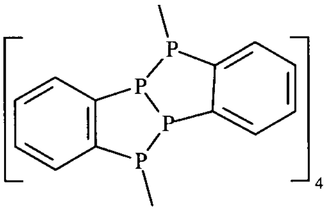


Figure 1. Structural formula of the product obtained from the catalytic dehydrocoupling of $1,2\text{-}(PH_2)_2C_6H_4$.

Despite the importance of oligomeric cyclo-organophosphanes suggested by their rich chemistry, no report has been published on the preparation of the derivative with a naphthalene-1,8-diyl backbone as the organic group. Thus, we used the reduction with magnesium metal for its preparation. The reaction of **1** with three equivalents of magnesium in THF proceeds in two steps. The first step involving formation of $Nap(PCl_2)_2$ is exothermic and external cooling was necessary, whilst the formation of a yellow precipitate of $(NapP_2)_n$ (**3**), in the second step, was substantially slower. After several days no unreacted Mg was present in the stirred suspension, and the precipitated product **3** was separated by filtration (Scheme 3). Compound **3** is stable towards water, but not indefinitely stable to air; a change in colour to pale yellow occurs after several days exposure. The insolubility of **3** in all common organic solvents complicated its purification and prevented its characterisation by solution NMR spectroscopy and the use of advanced soft ionisation techniques for measurement of mass spectra.

The $^{31}P\{^{1}H\}$ CP-MAS spectrum of **3** consists of one broad and slightly asymmetric signal ($\delta(^{31}P) = -21.8$ ppm) with low-intensity spinning side bands. The low intensity in the side bands suggests that the phosphorus environment has a relatively high degree of symmetry, the intense and broad cross polarisation signal suggests relative rigidity of **3** in the solid state, but little long-range order.

EI mass spectra of different batches of **1** (sampled neat) were not always consistent and many unexpected peaks were present; however, an intense peak at m/z 188 (monomeric unit $C_{10}H_6P_2$) was usually found. Poor ionisation of high-molecular-weight oligomeric material and the resulting relative amplification of impurity signals explains this inconsistency of spectra. Use of laser desorption ionisation in combination with a time-of-flight (TOF) analyser resulted in a highest peak at m/z 1128, corresponding to the hexamer $(C_{10}H_6P_2)_6$; the signals corresponding to the pentamer and the tetramer were also observed.

In contrast to the mass spectra, IR spectra from various preparations were very consistent; no intense absorptions were found in the region of $\nu_{P\text{-}Cl}$ (400–600 cm^{-1}). Similarly C and H content found by microanalyses in various batches of **3** was quite consistent, though similar to $(C_6H_4P_2)_5$[12] the values for C were usually 2–4% lower than the theoretical values.

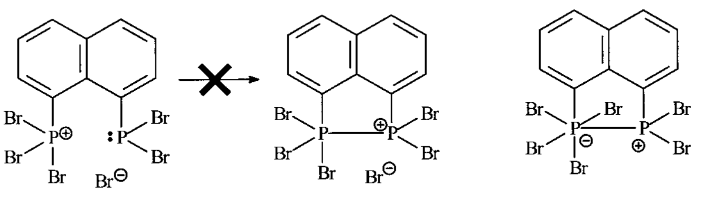
From the spectroscopic and analytical data for **3** shown above, together with the observed high melting point (above 320 °C), the degree of oligomerisation or structure of **3** (linear/branched chain or cyclic) cannot be determined. Nevertheless, the identification of the products of subsequent reactions of **3** with Br_2 and I_2 (vide infra) unambiguously proves conservation of the $NapP_2$ moiety in **3**, which is likely to be its monomeric unit. Further, the MS studies show that the probable minimum degree of oligomerisation is $(NapP_2)_6$.

$Nap(PBr_2)_2$

Many features of the chemistry of dibromoorganophosphanes $RPBr_2$ are similar to that of $RPCl_2$. Bromine reacts readily with $(PPh)_n$ as well as $PhPBr_2$ giving phosphorane $PhPBr_4$, which adopts a PBr_5-like ionic structure $PhPBr_3^+Br^-$ in solution (25% oleum) as well as in the solid state.[14] Encouraged by the unusual bonding observed in $NapP_2Cl_6$ (**1**),[9] we studied the reaction of **3** with bromine (see Scheme 3), anticipating that a product of analogous composition ($NapP_2Br_6$) might be prepared, though possibly showing a different structure.

To test this hypothesis, we attempted the reaction of **3** with three equivalents of Br_2 in 1,2-dichloroethane at elevated temperature. The ^{31}P NMR spectrum of the mixture after reaction showed a major singlet at $\delta(^{31}P) = 119$ ppm, indicating that bromination proceeded only to bis(dibromophosphane) $Nap(PBr_2)_2$ (**4**) (Scheme 3); no high field signals assignable to penta- or hexacoordinate phosphorus or tribromophosphonium ion were observed ($\delta(^{31}P) = 23$ ppm for $PhPBr_3^+Br^-$ [14, 15]). The conversion to **4** was nearly quantitative according to $^{31}P\{^{1}H\}$ NMR spectroscopy, though it was only isolated in a moderate yield in the form of orange crystals. A minor signal for PBr_3 at $\delta(^{31}P) = 229$ ppm was observed in the mixture after the reaction, indicating that the P–C bond was partially cleaved under the conditions used.

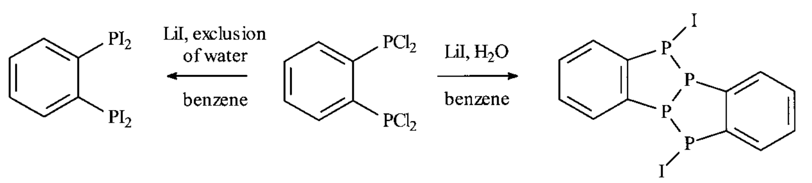
Such low reactivity towards the addition of bromine to organodibromophosphane is unusual, considering that there are at least two reasonable structures with the composition $NapP_2Br_6$ available, namely ionic **A** and ylide **B** (Figure 2).



A **A'** **B**

Figure 2. Expected structures of the product of the reaction of **3** with excess of Br_2.

An analogue of the bonding situation **B** (σ^6P^-–σ^4P^+) was found in the solid state and in solution for the chloro-congener **1** (in solution it is in equilibrium with the σ^5P–σ^5P form, see Scheme 4). If we consider the known structures of $PhPX_4$ (X = halogen), the bromide adopts an ionic $PhPBr_3^+Br^-$ structure, whereas the chloride is molecular in both solution and the solid state. Furthermore, the replacement of chlorine by bromine is expected on steric grounds to make an ionic structure **A** more favourable. On the other hand, several derivatives with a bonding situation (σ^4P^+-σ^3P) equivalent to structure **A** were reported recently;[16] however, X-ray investigations showed no signs of strain relief by a dative P–P$^+$ interaction (the situation shown in structure **A'**).



Scheme 5. Halogen exchange reactions of 1,2-$(PCl_2)_2C_6H_4$.

In conclusion, the origin of the reluctance of **4** to increase the P atom(s) coordination number by addition of Br_2 could be the bulkiness of bromine (concomitant with the destabilizing effect of crowding), as well as differences in P–X bond strength compared to the chloro congener **1**.

With respect to the identification of **4** as the major product of the reaction, the reaction was repeated with the correct ratio of reactants (see Experimental Section). Compound **4** is very air/moisture sensitive, and very soluble in organic solvents. It was characterised by X-ray structure analysis, ^{31}P, ^1H and ^{13}C NMR, spectroscopy, FT-Raman spectroscopy, mass spectrometry, and the purity was assessed by microanalysis.

Nap(PI)$_2$

To complement the series of congeners of naphthalene-1,8-diyl bis(dihalogenophosphanes), the oxidative addition of iodine to **3** was studied. Iodides of trivalent phosphorus tend to dimerise leading to the formation of a P–P bond. For example, $PhPI_2$ is readily converted into sparingly soluble diphosphane $(PhPI)_2$ and I_2 even in the presence of such weak nucleophiles as ethers.[17] Addition of iodine to diphosphenes R–P=P–R leaves the P–P bond intact, resulting in diphosphanes R–P(I)–P(I)–R.[18] A tendency to dimerise, though of a different nature, was also observed with 1,2-bis(diiodophosphino)benzene. The intended metathesis reaction of 1,2-$(PCl_2)_2C_6H_4$ with LiI afforded a bicyclic product (1,2-$C_6H_4P_2I)_2$ (Scheme 5).[19] Reexamination of the reaction showed that the bicyclic product is formed in the presence of water, whilst with strict exclusion of water the corresponding bis(diiodophosphane) 1,2-$(PI_2)_2C_6H_4$ was formed in a good yield (Scheme 5).[12] The preference of the formation of the interleaved bicyclic products is a common feature in 1,2-diphosphabenzene chemistry, presumably as a result of the quite large, fixed distance between the phosphorus atoms (ca. 3.0 Å). In fact, no 1,2-diphosphabenzene with a direct P–P bond (bonding P functionalities in position 1 and 2) is known.

Not surprisingly, the reaction of **3** with two equivalents of I_2 gave diiododiphosphane **5** as the major product (Scheme 3). The reaction proceeded very cleanly, only a minor signal of the side product PI_3 ($\delta(^{31}P) = 175$ ppm) was observed by ^{31}P NMR spectroscopy in the mixture after the reaction. No signal suggesting the formation of $Nap(PI_2)_2$, was found.

Substantial steric strain is connected with out-of-plane and in-plane distortions of phosphorus functionalities in 1,8-bis(phosphino)naphthalenes $Nap(PR_2)$. One of the possibilities for its release is the formation of a direct P–P bond through the formation of a C_3P_2 heterocycle. Although it seems a very favorable arrangement (in contrast to the situation in 1,2-diphospha-substituted benzenes), up to now only very few examples containing P–P bonding interactions were described; the interactions involved were σ^3P–σ^4P^+ and σ^4P^+–σ^6P^-.[6, 9] The σ^3P–σ^3P bonding in **5** thus represents a new type of P–P bonding environment in 1,8-diphosphanaphthalenes. The energy gain, connected with the relaxation of the distorted geometry in the hypothetic $Nap(PI_2)_2$ on transformation to the planar $NapP_2$ scaffolding in $Nap(PI)_2$ in **5**, probably plays an important role in its stabilisation. Compound **5** is less air/moisture sensitive than **4**, and it is only sparingly soluble in organic solvents at room temperature. It was characterised by X-ray structure analysis, ^{31}P, ^1H and ^{13}C NMR spectroscopy, FTIR and FT-Raman spectroscopy, mass spectrometry, and its purity was assessed by microanalysis.

Discussion of NMR spectra

As has been noted earlier, the signal at $\delta(^{31}P) = 135.7$ ppm in $Nap(PCl_2)_2$ (**2**) is substantially shifted upfield in comparison with the corresponding signal in $PhPCl_2$. ($\delta(^{31}P) = 160$ ppm). This is readily explained by the mutual shielding of the phosphorus nuclei, arising from the close proximity of the non-bonding electron pairs in **2**.[4] In view of this, the value of

$\delta(^{31}P) = 118.4$ ppm observed in less neighbour-shielded 1,2-$(PCl_2)_2C_6H_4$ seems to be disputable,[20] especially because in the series of $PhPBr_2$ ($\delta(^{31}P) = 152$ ppm), 1,2-$(PBr_2)_2C_6H_4$ ($\delta(^{31}P) = 136.7$ ppm)[21] and $Nap(PBr_2)_2$ (**4**) ($\delta(^{31}P) = 118.9$ ppm) the reasonable trend, following the increasing shielding, was found. In the same manner, a remarkable upfield shift value in $Nap(PI)_2$ (**5**) ($\delta(^{31}P) = 21.3$ ppm) compared to $(PhPI)_2$ ($\delta(^{31}P) = 45.1$ ppm)[17] was observed; the bicyclic 1,2-$(C_6H_4P_2I)_2$ (Scheme 5) was reported to show an AA′BB′ spin system in the ^{31}P NMR spectra, centered at 37.0 ppm.[19]

^{13}C NMR spectra of various 1,8-bis(diorganophosphino)-naphthalenes and related systems have been widely discussed.[5, 16] Virtual triplets dominate the ^{13}C NMR spectra of these systems. In agreement with that, in the ^{13}C NMR spectra of **2**, **4** and **5**, the signals of tertiary carbon and *ipso*-carbon nuclei appear as virtual triplets, as the result of significant P,P couplings present (through-space ^4J coupling in **2** and **4** and much larger through-bond ^1J coupling in **5**). The small magnitude of the ^1J(P,C) value prevented measurement of the ^1J(P,P) value from ^{13}C satellite subspectra in $^{31}P\{^1H\}$ NMR spectra of **2**, **4** and **5**.

X-ray investigations

The structures of **2**, **4** and **5** in the crystal are shown in Figures 3–5 and Table 1 and 2, and the crystallographic data are summarised in Table 3.

The asymmetric unit in the crystal structure of **2** contains two molecules of very similar geometry; the asymmetric unit in the structure of **4** contains only one molecule. The steric strain introduced by substitution in the bay region is released by out-of-plane and in-plane distortions, concomitant with significant twisting of naphthalene ring in both **2** and **4** (see central torsion angles of the naphthalene ring in Table 2). As usual in 1,8-P,P-naphthalenes, the P atoms lie in opposite directions from the naphthalene least-squares plane. The displacement of P atoms from this plane range from 0.41 to 0.52 Å in **2**, but the out-of-plane distortion is more pronounced in **4**, where this displacement is 0.68 and 0.73 Å. Interestingly, the P1 ··· P9 non-bonding distances in **2** and **4** are comparable (2.80–2.81 Å in **2**, 2.77 Å in **4**); substantially longer P ··· P non-bonding distances (2.93–3.07 Å) were found in 1,8-bis(dialkylphosphino)naphthalenes[22] as well as in 1,8-bis[bis(dialkylaminophosphino)]naphthalenes (3.12 Å).[6]

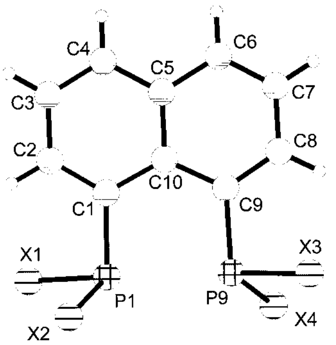


Figure 3. Structure of **2** (X = Cl) and **4** (X = Br) in the crystal. In **2**, the asymmetric unit consists of two molecules with approximately the same geometry.

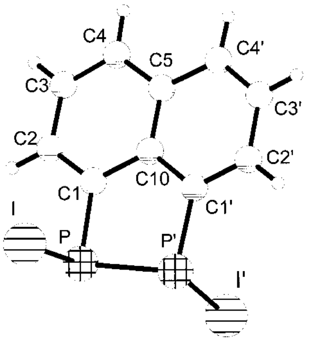


Figure 4. Structure of **5** in the crystal. The asymmetric unit consists of a half of the molecule.

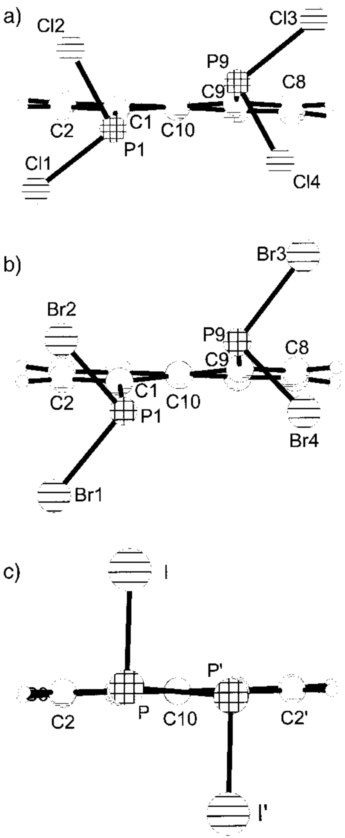


Figure 5. Illustration of the extent of naphthalene ring twisting and out of plane distortions of phosphino groups in a) **2**, b) **4** and c) **5**. Viewed along the naphthalene central C10–C5 bond.

As expected, the differences in geometries of **2** and **4**, which are caused by variation of the bulkiness of their halogeno substituents, are much more significant than those caused by packing effects in the two independent molecules in the asymmetric unit of **2**. Although the out-of-plane distortion somehow complicates the description of the conformation of PX_2 groups in **2** and **4** (idealised conformers are shown in Figure 6), the conformations of PX_2 groups (Figure 5) in **2** and **4** can be regarded as nearly bisecting, with partial (**2**) and slight (**4**) distortion towards eclipsed.

The crystal structure of compound **5** (Figure 4, Table 2) shows that the molecule in the crystal is highly symmetrical,

Table 1. Comparison of selected bonding, non-bonding and displacement distances [Å], angles and dihedral angles [°] in **2** (two independent molecules in asymmetric unit) and **4**.

Compound	**2** (X = Cl)[a]	**4** (X = Br)
P1–X1	2.0695(9), 2.056(1)	2.2737(9)
P1–X2	2.054(1), 2.073(1)	2.2261(9)
P9–X3	2.079(1), 2.065(1)	2.2551(9)
P9–X4	2.056(1), 2.080(1)	2.2253(9)
P1–C1	1.834(3), 1.822(3)	1.835(3)
P9–C9	1.832(3), 1.832(3)	1.825(3)
C1–C10	1.435(4), 1.437(4)	1.426(4)
C9–C10	1.434(4), 1.438(4)	1.437(4)
P1 ··· P9	2.798(2), 2.811(1)	2.767(1)
C1 ··· C9	2.550(1), 2.553(1)	2.517(1)
out-of-plane displacement of P atoms	0.52 and −0.49, 0.46 and −0.41	0.68 −0.73
X1-P1-X2	99.16(4), 99.26(4)	100.26(3)
X3-P9-X4	99.36(4), 98.33(4)	99.74(4)
C1-P1-X1	100.57(8), 100.72(9)	99.9(1)
C1-P1-X2	101.02(9), 100.14(9)	101.8(1)
C9-P9-X3	100.25(8), 101.36(9)	99.6(1)
C9-P9-X4	101.24(9), 101.09(9)	101.9(1)
bay region angles:		
C10-C1-P1	118.6(2), 119.1(2)	117.0(2)
C10-C9-P9	118.4(2), 119.7(2)	116.6(2)
C1-C10-C9	125.5(2), 125.3(2)	123.0(3)
splay angle[b]	2.5, 4.1	−4.0
dihedral and torsion angles in bay region:		
P1-C1 ··· C9-P9	25.7, 22.4	37.0
P1-C1-C10-C9	15.1(3), 12.9(4)	21.8(4)
P9-C9-C10-C1	14.3(3), 12.9(4)	19.9(4)
central torsion angles of naphthalene ring:		
C4-C5-C10-C9	174.1(2), 175.9(2)	171.7(3)
C6-C5-C10-C1	173.4(2), 174.2(2)	171.1(3)
C4-C5-C10-C1	5.7(4), 5.2(4)	7.9(4)
C6-C5-C10-C9	6.7(4), 4.7(4)	9.4(4)

[a] Values after comma are for second of the two independent molecules, forming asymmetric unit in the structure of **2**. [b] Splay angle = P1-C1-C10 + P9-C9-C10 + C1-C10-C9 − 360.

Table 2. Selected bonding, non-bonding and displacement distances [Å], angles and dihedral angles [°] in **5**. Molecule possess crystallographic twofold axis, the asymmetric unit consists of a half of the molecule.

P–P′	2.218(2)	P–I	2.498(1)
P–C1	1.830(4)	C1–C10	1.423(5)
C1 ··· C1′	2.450(5)		
out-of-plane displacement of P atoms	0.11 and −0.11		
P′-P-I	93.40(6)	C1-P-I	99.0(1)
C1-P-P′	93.5(1)	C1-C10-C1′	118.9(5)
C10-C1-P	116.8(3)		
splay angle[a]	−7.5		
dihedral and torsion angles in bay region:			
P-C1 ··· C1′-P′	5.2	P-C1-C10-C1′	2.9(1)
central torsion angles of naphthalene ring:			
C4-C5-C10-C1′	178.3(3)	C4-C5-C10-C1	1.7(3)

[a] Splay angle = 2 × P-C1-C10 + C1-C10-C1′ − 360.

Table 3. Crystallographic data for **2**, **4** and **5**.

Compound	**2**	**4**	**5**
formula	$C_{10}H_6Cl_4P_2$	$C_{10}H_6Br_4P_2$	$C_{10}H_6I_2P_2$
crystal habit	pale yellow prism	orange prism	yellow prism
crystal size [mm]	0.18 × 0.1 × 0.1	0.15 × 0.1 × 0.1	0.15 × 0.1 × 0.1
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$	$C2/c$
a [Å]	9.9892(9)	6.776(1)	12.338(4)
b [Å]	11.535(1)	16.813(3)	8.484(2)
c [Å]	12.130(1)	12.187(2)	12.476(4)
α [°]	100.299(2)	90.00	90.00
β [°]	105.287(1)	97.195(2)	114.688(4)
γ [°]	103.376(2)	90.00	90.00
U [Å³]	1268.1(2)	1377.5(4)	1186.6(6)
ρ_{calcd}	1.728	2.448	2.474
no. of reflections:			
measured	6353	5578	2725
independent	3555	1899	804
observed ($I > 2\sigma(I)$)	2915	1691	766
μ [mm⁻¹]	1.152	11.888	5.528
min/max transmission	0.8149/1.0000	0.4195/1.0000	0.7926/1.0000
no. of parameters	290	146	66
R (F^2, all data)	0.0388	0.0357	0.0263
wR (F^2, all data)	0.0708	0.0720	0.0634
max. $\Delta\rho$ [e Å⁻³]	0.56	0.77	0.53

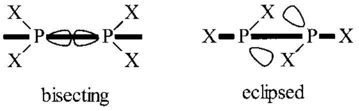


Figure 6. Idealised conformations of 1,8-bis(dihalophosphino)naphthalenes, molecules viewed along the naphthalene plane.

possessing a crystallographic twofold axis, through carbon atoms C5 and C10, thus the asymmetric unit in **5** consists of half of the molecule. The naphthalene ring is essentially planar (mean deviation from planarity 0.02 Å), the P atoms lie 0.11 Å above and below the least-squares plane of the naphthalene ring (dihedral angle P-C1 ··· C1′-P′ is 5.2°), with the five-membered C_3P_2 ring also very close to planarity. The in-plane distortion is concomitant with the difference in *peri*-separation of the carbon atoms (2.450(5) Å) and the P–P distance of 2.218(2) Å; the splay angle (2 × P-C1-C10 + C1-C10-C1 −360°) is negative (−7.5°). The P – P (2.218(2) Å) and P–I (2.498(1) Å) bond lengths are within their usual ranges (2.22 ± 0.05 and 2.48 ± 0.05 Å, respectively); the P–P distance is comparable, though slightly shortened, to that found in the $\mathrm{Nap[PCl][P(NEt2)2]^+}$ ion (2.232(1) Å), which contains a σ^3P–σ^4P$^+$ moiety.[6] The pseudo-tetrahedral geometry (the fourth site being the phosphorus lone pair) at the phosphorus atoms is severely distorted, the C-P-P′ and I-P-P′ angles are 93.5(1) and 93.40(6)°, respectively.

Conclusion

Non-mixed halogeno derivatives of 1,8-P,P-naphthalenes demonstrate that the coordination number of the phosphorus atoms decreases with increasing bulkiness of the halogen atoms. The maximum coordinated species known for each halogen are $NapP_2Cl_6$ (**1**), $Nap(PBr_2)_2$ (**4**) and $Nap(PI)_2$ (**5**); they do not react further with Cl_2, Br_2 and I_2, respectively. The route to $Nap(PCl_2)_2$ described here represents a new synthetic pathway for this synthetically very important compound. It consists of three steps from commercially available materials 1-bromonaphthalene and P_4S_{10}. Routes to new synthons $(NapP_2)_n$, $Nap(PBr_2)_2$ and $Nap(PI)_2$ are also described, the synthetic potential of which is clearly evident. Some 'space limitations' of *peri*-substitution using the NapLi$_2$ synthon were reported, with regard to the possibility to crowd very bulky (e.g. two *t*Bu or two N(*i*Pr$_2$) groups on both P atoms in 1,8-diphosphanaphthalenes.[6] The derivatives described here can serve as useful starting materials for the preparation of these highly strained molecules, as well as for a range of other interesting main-group and organometallic derivatives.

Experimental Section

All experiments were carried out in standard Schlenk glassware with exclusion of air and moisture. Solvents were dried, purified, and stored according to common procedures.[23] NapP$_2$S$_4$ was prepared from 1-bromonaphthalene and P$_4$S$_{10}$,[7] NaP$_2$Cl$_6$ (**1**) was prepared by chlorination of NapP$_2$S$_4$.[9] All other reagents were obtained commercially. In vacuo refers to a pressure of ≈13 Pa. Solution NMR: Bruker Avance 300 and Jeol GSX 270; 85% H$_3$PO$_4$ was used as an external standard in ^{31}P, TMS as internal in ^{1}H and ^{13}C NMR. All measurements were performed at 25 °C. Assignments of ^{13}C and ^{1}H NMR spectra were made with the help of ^{1}H{^{31}P}, H-H COSY, H-C HMBC, HSQC and H-P HMQC experiments, vt denotes virtual triplet. The ^{31}P{^{1}H} CP-MAS spectra were obtained on Varian Unity Inova spectrometer, University of Durham. Raman and IR: Perkin-Elmer System 2000; MS: VG Autospec, electron energy 70eV; Bruker Ultraflex MALDI-TOF, was used for measurement of oligomerisation degree of **3**.

Nap(PCl$_2$)$_2$ (2): NapP$_2$Cl$_6$ (**1**) (1.70 g, 4.24 mmol) and MeOPCl$_2$ (0.5 mL, 5.29 mmol) were heated under reflux in toluene (15 mL) for 3 h. The resulting solution was evaporated in vacuo to yield pure, pale yellow crystalline **1** (1.30 g, 93%). Its purity was assessed by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy. Less pure **1** can be used as the starting material, the resulting product (impure **2**) can be purified by sublimation in vacuo at 140–150 °C, which gave **2** only slightly contaminated by the cosublimed product of partial oxidation Nap(POCl$_2$)(PCl$_2$) (assessed by ^{31}P and ^{1}H NMR spetroscopy). ^{1}H and ^{31}P NMR data obtained were in agreement with those published earlier.[4] ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, for numbering of atoms see Figure 3): $\delta = 135.7$ (vt, ^{1}J(C,P) + ^{3}J(C,P) = 73.5 Hz; C1 and C9), 135.0 (vt, ^{2}J(C,P) + ^{4}J(C,P) = 2.49 Hz; C2 and C8), 133.1 (vt, ^{4}J(C,P) + ^{4}J(C,P) = 1.94 Hz; C4 and C6), 132.6 (t, ^{2}J(C,P) = 36.8 Hz; C10), 131.1 (t, ^{3}J(C,P) = 7.19 Hz; C5), 125.7 ppm (s; C3 and C7).

(NapP$_2$)$_n$ (3): Magnesium turnings (0.61g, 25.1 mmol) were added to an externally cooled (0 °C), stirred suspension of NapP$_2$Cl$_6$ (**1**) (3.30g, 8.23 mmol) in THF (40 mL). After the first few minutes of exothermic reaction (formation of Nap(PCl$_2$)$_2$), the mixture was left to heat up to ambient temperature and was stirred for three days. After this period no unreacted Mg was observed in the resulting suspension, the solid was filtered off, washed with degassed water (2 × 10 mL), and THF (10 mL), and dried in vacuo. Compound 3 was obtained as a yellow, very mobile powder (1.27 g; 82%). M.p. above 320°. Microanalysis showed that the C content was lower than that calculted for C$_{10}$H$_6$P$_2$ (60.2 versus 63.8%). IR: $\tilde{\nu} = 3046$m ($\nu_{\text{Ar-H}}$), 1551m, 1485s, 1209m, 812vs, 768vs cm^{-1}; Raman (sealed capillary): $\tilde{\nu} = 3054$m ($\nu_{\text{Ar-H}}$), 1554vs, 1379vs, 881s, 560m, 505m, 486m, 463m, 416s ($\nu_{\text{P-P}}$) cm^{-1}; ^{31}P{^{1}H} CP-MAS (121.4 MHz): broad, slightly asymmetric signal ($\delta(^{31}\text{P}) = -21.8$ ppm) with low-intensity spinning side bands. The insolubility prevented examination by solution NMR spectroscopy; for EI-MS data see text; MALDI-TOF MS (positive-mode, no matrix, *m/z*): 1128 [(C$_{10}$H$_6$P$_2$)$_6$], 1066 [(C$_{10}$H$_6$P$_2$)$_6$ – 2P], 940 [(C$_{10}$H$_6$P$_2$)$_5$], 878 [(C$_{10}$H$_6$P$_2$)$_5$ – 2P, base peak], 752 [(C$_{10}$H$_6$P$_2$)$_4$].

Nap(PBr$_2$)$_2$ (4): A suspension of **3** (0.46 g, 2.45 mmol) and bromine (0.30 mL, 5.85 mmol) in 1,2-dichloroethane (10 mL) were heated under reflux for 10 min and the solvent was evaporated in vacuo. The resulting residue was extracted with hot toluene (15 mL), the extract was concentrated to 4 mL and cooled to –20 °C. Precipitated crude **4** was recrystallised from boiling toluene (2 mL) to yield **4** (0.22 g; 18%) as orange crystals, some of which were suitable for X-ray structure analysis. M.p. 156–158 °C; elemental analysis calcd (%) for C$_{10}$H$_6$P$_2$Br$_4$: C 23.7, H 1.2; found C 23.7, H 1.0; Raman (sealed capillary): $\tilde{\nu} = 3069$ and 3038w ($\nu_{\text{Ar-H}}$), 1550m, 1356m, 870m, 378s ($\nu_{\text{P-Br}}$), 351vs ($\nu_{\text{P-Br}}$), 249m, 174m cm^{-1}; NMR (CD$_2$Cl$_2$, for numbering of atoms see Figure 3): ^{31}P{^{1}H} NMR (121.5 MHz): $\delta = 118.9$ ppm (s); ^{1}H NMR (300 MHz): $\delta = 8.72$ (m, 2H, ^{3}J(H,H) = 7.3, ^{4}J(H,H) = 1.2 Hz; H2 and H8), 7.99 (m, 2H, ^{3}J(H,H) = 8.3, ^{4}J(H,H) = 1.1Hz; H4 and H6), 7.68 ppm (m, 2H; H3 and H7); ^{13}C{^{1}H} NMR (75.5 MHz): $\delta = 140.3$ (s, C2 and C8), 135.6 (vt, ^{1}J(C,P) + ^{3}J(C,P) = 79.61 Hz; C1 and C9), 135.0 (vt, ^{4}J(C,P) + ^{4}J(C,P) = 1.9 Hz; C4 and C6), 133.0 (t, ^{3}J(C,P) ≈ 35 Hz; C10), 132.6 (t, ^{2}J(C,P) = 6.8 Hz; C5), 128.0 ppm (s, C3 and C7); MS (EI+): *m/z* 428 [M^+ – Br], 348 [M – 2Br], 267 [M – 3Br], 188 [C$_{10}$H$_6$P$_2$, base peak], 157 [C$_{10}$H$_6$P], 126 [C$_{10}$H$_6$]; MS (CI+, ionizing gas isobutane): *m/z* 405 [C$_{10}$H$_6$P$_2$Br$_2$ + C$_4$H$_9$], 349 [C$_{10}$H$_6$P$_2$Br$_2$ + H], 325 [C$_{10}$H$_6$P$_2$Br + C$_4$H$_9$], 269 [C$_{10}$H$_6$P$_2$Br + H], 245 [C$_{10}$H$_6$P$_2$ + C$_4$H$_9$], 189 [C$_{10}$H$_6$P$_2$ + H].

Nap(PI)$_2$ (5): A suspension of **3** (0.50 g, 2.66 mmol) and iodine (0.68 g, 2.68 mmol) in chlorobenzene (8 mL) was heated to 120 °C for 10 min and the solvent was evaporated in vacuo. The resulting solid residue was washed with hexane (3 × 10 mL) and dichloromethane (10 mL) and recrystallised twice from hot 1,4-dioxane to give **5** (0.59 g; 50%) as a yellow-orange crystalline mateial. M.p. 218–20 °C (decomp); elemental analysis calcd (%) for C$_{10}$H$_6$P$_2$I$_2$: C 27.2, H 1.4; found: C 27.3, H 1.2; IR (KBr tablet): $\tilde{\nu} = 1482$s, 1198s, 880m, 818vs, 767vs, 482s cm^{-1}; Raman (sealed capillary): $\tilde{\nu} = 3055$ and 3038w ($\nu_{\text{Ar-H}}$), 1553m, 1381m, 326vs ($\nu_{\text{P-I}}$), 242m, 178m cm^{-1}; NMR (CD$_2$Cl$_2$, for numbering of atoms see Figure 4): ^{31}P{^{1}H} NMR (121.5 MHz): $\delta = 21.3$ (s) ppm; ^{1}H NMR (300 MHz): $\delta = 8.25$ (m, 2H; H2 and H2′), 7.99 (m, 2H, ^{3}J(H,H) = 8.2 Hz; H4 and H4′), 7.59 (m, 2H; H3 and H3′); ^{13}C{^{1}H} NMR (67.9 MHz, due to low solubility not all quaternary carbons were observed clearly): $\delta = 140.8$ (vt, ^{1}J(C,P) + ^{2}J(C,P) = 58.0 Hz; C1 and C1′), 134.5 (vt; C2 and C2′), 131.4 (s; C4 and C4′), 129.0 (vt; C3 and C3′); MS (EI+): *m/z*: 442 [M^+], 315 [M – I, base peak], 188 [C$_{10}$H$_6$P$_2$], 157 [C$_{10}$H$_6$P], 126 [C$_{10}$H$_6$]; MS (CI+, ionizing gas isobutane): *m/z*: 499 [M + C$_4$H$_9$], 442 [M^+], 315 [M – I], 245 [C$_{10}$H$_6$P$_2$ + C$_4$H$_9$], 231 [C$_{10}$H$_6$P$_2$ + C$_3$H$_7$], 189 [C$_{10}$H$_6$P$_2$ + H, base peak].

Crystal structure analyses

Data for **2**, **4** and **5** were collected at 125 K on a Bruker SMART CCD diffractometer equipped with Oxford Instruments low temperature attachment, using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed on the basis of multiple equivalent reflections (SADABS). All refinements were performed by using SHELXTL (Version 5.10, Bruker AXS, 1997). CCDC-188739 (**2**), CCDC-18870 (**4**) and CCDC-188741 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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