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# New mode of sterically imposed phosphorus hypercoordination

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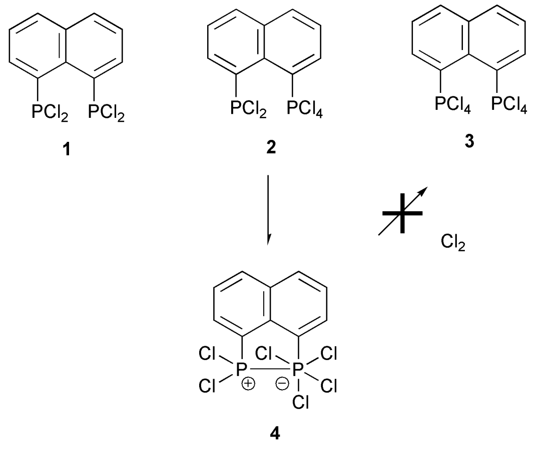
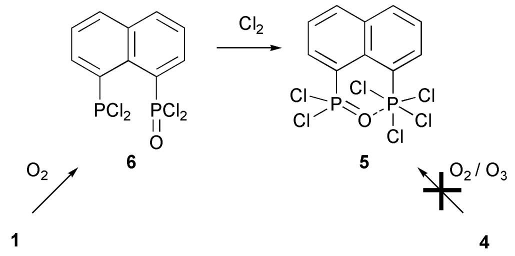
**The sterically imposed electronic interaction in Nap(POCl$_2$)(PCl$_4$) (Nap = naphthalene-1,8-diyl) results in hypercoordination of the P atom by the O donor in the bridging position between the two peri-substituents.**

The extent of steric strain in peri-diphospha substituted naphthalenes is only partially driven by the number and size of substituents attached to phosphorus atoms, and further factors such as P$\cdots$P interaction or bridging are also important. Both the non-bonding (repulsive) and bridged interaction of peri-substituents leads generally to an encumbered geometry.

The repulsive interaction in the series of chlorinated derivatives of 1,8-di-P,P-naphthalenes is expected in bisphosphane Nap(PCl$_2$)$_2$ **1**, phosphano-phosphorane Nap(PCl$_2$)(PCl$_4$) **2** and bisphosphorane Nap(PCl$_4$)$_2$ **3** (Scheme 1). Interestingly, whilst **1** shows the expected repulsive P$\cdots$P interaction,[1] **2** collapses its steric strain to form structure **4**, which was found in both solid state and in solution.[2] Formation of bisphosphorane **3** was not observed even if **2** was exposed to excess of Cl$_2$ gas, and thus remains hypothetical.[2] These results may indicate that a change of structure from repulsion to bonding occurs between **1** and **2**, and that further oxidation of P$^{III}$ in **2** might not be possible for steric reasons. Here we report the preparation, structural and spectroscopic characterisation of phosphoryl-phosphorane **5**, the hypercoordinate peri-substituted diphosphanaphthalene with the same number of P connectivities as **4**, exhibiting a different mode of partial relaxation of steric strain. Compound **5** is the formal product of oxidation of P$^{III}$ to P$^{V}$ in **4**.



**Scheme 1**



**Scheme 2**

As direct oxidation of **4** using O$_2$ or O$_3$ did not prove to be possible,[3] an alternative strategy to obtain **5** was used (Scheme 2). The oxidation of bisphosphane **1** by O$_2$ afforded phosphoryl-phosphane **6**,[4] which after chlorination and recrystallization gave **5** in the form of extremely moisture sensitive pale yellow prisms.[5]

Crystallographic analysis[6] of **5** (Fig. 1 and 2) reveals a twisted geometry of the naphthalene backbone, with atoms P(1) and P(9) displaced above and below the naphthalene least-squares plane (0.50 and 0.48 Å). Also the positive value of splay angle[7] 9.3° and the relatively long P$\cdots$P distance 3.023(1) Å (in **1** a P$\cdots$P distance 2.81 Å was found) indicates substantial strain

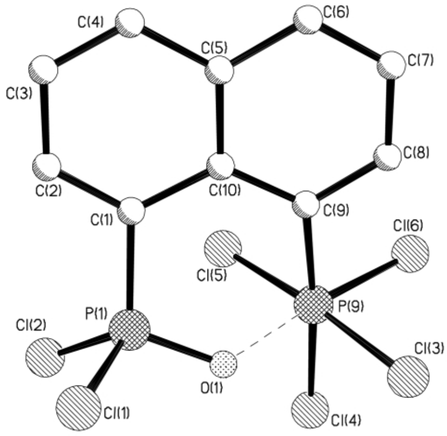


**Fig. 1** Molecular Structure of **5**. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.505(2), P(9)–O(1) 1.841(2), P(1)–Cl(1) 1.9783(9), P(2)–Cl(2) 1.9733(9), P(9)–Cl(3) 2.1320(9), P(9)–Cl(4) 2.1513(9), P(9)–Cl(5) 2.1754(9), P(9)–Cl(6) 2.1385(9), P(1)–C(1) 1.750(2), P(9)C(9) 1.883(2), P(1)–O(1)–P(9) 129.0(1), Cl(1)–P(1)–Cl(2) 102.79(4), Cl(1)–P(1)–O(1) 106.10(7), Cl(2)–P(1)–O(1) 113.63(7), Cl(3)–P(9)–Cl(5) 175.36(4), Cl(6)–P(9)–O(1) 173.33(6), Cl(4)–P(9)–C(9) 174.96(8), C(9)–P(9)–Cl(6) 95.29(8).

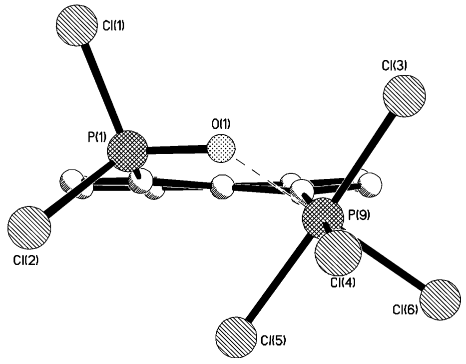


**Fig. 2** Illustration of the extent of naphthalene ring twisting and out-of-plane distortions of peri-substituents in **5**. Viewed along the naphthalene central C(10)–C(5) bond.

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in the molecule, induced by either bridged or repulsive P···P interaction. Indeed, the P···P distance matches well with these found in P–O–P bridged condensed 1,8-bis(phosphonic) naphthalenes (2.89–2.99 Å),[8] and is significantly shorter than that in non-bridged repulsive interacting 1,8-bis(phosphane oxide) naphthalenes (3.38–3.48 Å).[9] Moreover, instead of the (possibly distorted) pseudo-trigonal-bipyramidal P(9) configuration expected for repulsive interaction, the atoms Cl(3)–Cl(6) and C(9) occupy tetrahedral pyramidal positions with the P(9) atom lying at the base of the pyramid, the O(1) atom filling the vacant position in a nearly perfect pseudo-octahedral coordination of P(9). Despite the angular perfection of pseudo-octahedral coordination as well as reasonable value for a P–O–P bridging angle (129.0°) observed, the distance P(9)–O(1) of 1.842(1) Å indicates quite weak interaction (the normal range for a classical $\sigma^6$P–O bond length is 1.65–1.68 Å). However, this is not without precedent, as the recently reported derivatives containing an intramolecularly formed O$\longrightarrow$P dative bond connecting a sulfoxide O donor atom with the then six-co-ordinate P centre show bond lengths of 1.88 Å.[10] The P(1)–O(1) bond length (1.505(2) Å) is just within the range reported for P=O moieties (1.46 ± 0.05 Å), its bond order being ca. 1.7.[11] As expected, the P–Cl distances on the P(1) atom are substantially shorter than those on P(9) (1.97–1.98 *vs*. 2.13–2.17 Å), the latter being comparable to P–Cl distances found in $PCl_6^-$ (2.14 Å).

The above data favour interpretation of the bonding in **5** as a sterically imposed interaction of peri-substituents *via* a bridging O atom, leading to a partial betaine structure. Although the four Cl atoms connected to P(9) greatly enhance its electrophilicity, the P(9) atom probably becomes hypercoordinate also as a result of the forced electronic interaction with the (quite weak) donor of electron density O(1), this interaction being imposed by the stiff organic backbone.

The NMR of **5** shows that the bonding in solution is the same as observed in the crystal. The $^{31}P\{^1H\}$ NMR spectrum of **5** is an AX system with $\delta_{P(1)}$ 63.5, $\delta_{P(9)}$ −182.7 ppm and $^2J$(PP) = 64.0 Hz. The signal of P(1) is significantly deshielded compared to the phosphoryl signal in **6** ($\delta_P$ 44 ppm), although still lying in the range for $RPOCl_2$ (35–65 ppm). The same deshielding effect was observed on coordination of $Ph_3PO$ ($\delta_P$ 29) onto $PCl_5$, yielding betaine $Ph_3P^+$–O–$P^-Cl_5$ ($\delta_{P+}$ 67).[12] The shift of the P(9) signal belongs clearly in the six-co-ordinate region and compares well with the shift observed for $[PhPCl_5]^-$ (−203 ppm).[13] Most importantly, the observed magnitude of $^2J$(PP) is extremely high and indicates significant electronic P–P interaction in **5**.[14] Such a magnitude is much higher than those observed in adducts $R_3P^+OP^-F_5$ (R = Ph and Bu, $^2J$(PP) = 24 and 27 Hz, respectively),[15] containing significantly more electrophilic and nucleophilic P centres, thus having good prerequisites for very strong interaction. We have to conclude, that increased electronic interaction between the P centres in **5** is again a phenomenon imposed by the presence of the rigid organic skeleton in **5**.[16] In contrast to **4**, only very subtle changes of *J*(PP) with temperature (range 213–295K) were observed in the $^{31}P\{^1H\}$ NMR spectrum of **5**. Compound **5** was further characterised by $^1H$ NMR (including H-H DQF COSY experiment), IR, Ra and MS spectroscopy, its purity was assessed by elemental analysis.[17] Very low solubility of **5** did not allow measurement of $^{13}C$ NMR spectra.

In summary, the presence of an electrophilic $PCl_4$ group in sterically encumbered 1,8-diphospha naphthalenes results in its interaction with suitable, even weak, donor, as *e.g.* P in the case of **4**, or O in the case of **5**. In both cases a DA bond formation affords relaxation from more strained repulsive geometry.

## Notes and references

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3 No reaction occurred when the attempted oxidations were performed with excess of $O_2$ (in toluene at 110 °C) or $O_3$ (generated by UV light, at 25 °C).

4 Preparation of **1** was reported by us recently.[1] Phosphoryl-phosphane **6** was prepared by oxidation of **1** with excess of oxygen gas. To this end a solution of **1** in toluene saturated with $O_2$ gas was heated to 80 °C for 2 days, the solvent was evaporated *in vacuo* and the solid residue was sublimed at 140 °C *in vacuo*, which yielded **6** as a colorless solid (64%). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): AX system, $\delta_P$ 44.4 ($P^V$) and 147.0 ($P^{III}$), $^2J$(PP) ≈ 3 Hz. The detailed preparation and full characterization of **6** will be published elsewhere.

5 Compound **6** (0.75 g, 2.17 mmol) in $CH_2Cl_2$ (12 $cm^3$) was chlorinated at 0 °C with mild stream of chlorine gas for 1 min. The precipitated yellow solid was collected by filtration, washed with $CH_2Cl_2$ (4 $cm^3$) and dried *in vacuo*. Recrystallization from boiling 1,2-dichloroethane yielded 0.19 g (21%) of pure **5**.

6 Crystal data for **5**: $C_{10}H_6Cl_6OP_2$, $M$ = 416.79, space group $P2_1/c$, monoclinic, $a$ = 6.958(1), $b$ = 16.895(3), $c$ = 12.498(2) Å, $\beta$ = 90.921(3)°, $U$ = 1469.1(4) $Å^3$, $T$ = 125 K, $Z$ = 4, $\mu$(Mo–K$\alpha$) = 1.372 $mm^{-1}$, 6089 reflections measured, 2062 unique ($R_{int}$ = 0.0283) which were used in all calculations. The final $R$ was 0.0239 for $I > 2\sigma(I)$ and $wR(F^2)$ was 0.0549 for all data. CCDC reference number 203952. See http://www.rsc.org/suppdata/cc/b3/b301601c/ for crystallographic data in CIF or other electronic format.

7 Splay angle = P(1)–C(1)–C(10) + C(1)–C(10)–C(9) + C(10)–C(9)–P(9) −360.

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14 The reports of $^2J$(PP) in the similar systems are very scarce, but from the few examples available it is clear that the value observed in **5** is exceptional.

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16 For comparison, in **6**, lacking through-bond as well as through-space coupling the magnitude of $^4J$(PP) 3.0 Hz was found (ref. 4).

17 Spectroscopic and analytical data for **5**: M.p. 228–232 °C with decomposition (gas evolution); $C_{10}H_6Cl_6OP_2$: calcd. C 28.8, H 1.4; found C 29.1, H 1.2%; $^1H$ NMR (500.1 MHz, $CD_2Cl_2$, 298 K, for numbering of atoms see Fig. 1): $\delta$ = 7.72 [m, 1H, H7], 7.78 (m, 1H, H3), 7.98 (m, 1H, H6), 8.27 [ddd, 1H, $^3J$(HP) = 26.1, $^3J$(HH) = 7.3, $^4J$(HH) = 1.2 Hz, H2], 8.39 (m, 1H, H4), 9.04 [ddd, 1H, $^3J$(HP) = 40.9, $^3J$(HH) = 7.9, $^4J$(HH) = 0.8 Hz, H8]; IR (Nujol mull, $cm^{-1}$): $\nu$ = 1491s, 1448s ($\nu_{P-C}$), 1082vs ($\nu_{P=O\cdots P}$), 470s ($\nu_{P-Cl}$), 453s ($\nu_{P-Cl}$); Ra (sealed capillary, $cm^{-1}$): $\nu$ = 3069m ($\nu_{Ar-H}$), 1553s, 1346vs, 332vs; MS (EI+, sampled neat): *m*/*z* 414 ($M^+$), 379 (M − Cl), 344 (M − 2Cl), 309 (M − 3Cl, base peak), all listed peaks showed correct isotopic pattern; accurate mass measurement on (M − Cl) peak: theoretical mass 378.8331, measured 378.8331.