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Intramolecular Phosphine−Phosphine Donor−Acceptor Complexes

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The reaction of 5-diphenoxyphosphanyl-6-diisopropylphosphinoacenaphthene **12** with chlorotrimethylsilane unexpectedly gave a phosphonium-phosphine compound **13**, containing the structural motif of four phosphorus atoms connected in a chain. To explain the mechanism of this complex transformation, a proposed intermediate 5-dichlorophosphino-6-diisopropylphosphinoacenaphthene **14** was synthesized by an alternative method. The two (formally) phosphine environments in **14** form an intramolecular donor−acceptor (phosphonium-phosphoranide) complex, stable at room temperature in the solid state and as a solution in certain solvents. A ^{31}P NMR mechanistic study showed that, despite the presence of a rigid acenaphthene backbone, **14** is unstable in the presence of nucleophiles and disproportionates into **13** and other phosphorus containing products. Both **13** and **14** have been crystallographically characterized.

Introduction

In organophosphorus compounds, phosphorus exists in many oxidation states and bonding environments. Some of these are known as Lewis donors, while others show characteristics of Lewis acceptors. Phosphines PR_3 are considered prototypical donors because of the presence of the lone pair which is readily accepted by a transition metal atom (having a vacant orbital); such complexes have found a wide range of applications especially in catalysis.[1] The acceptors are not limited to metals only, for example trivalent heavier group 15 halides EX_3 (E = arsenic, antimony, and bismuth, X = halogen) accept electrons from the phosphines.[2]

The textbook examples of electrophilic phosphorus environment are phosphorus(V) halogenides; neutral six-coordinate species such as **1** are easily prepared by direct reaction of these Lewis acidic molecules with various lone pair donors (Scheme 1).[3] Somewhat more surprisingly, some phosphorus environments containing lone pairs can also act as acceptors. Although usually not prepared by a direct reaction of a "donor" and "acceptor", triphosphenium cations **2**[4−7] and phosphinophosphonium cations **3**[8−10] (Scheme 1) can formally be considered donor−acceptor complexes with low coordinate phosphorus acting as an acceptor. Other interesting examples are double phosphine adducts of phosphenium ion **4** and **5**, which contain ten-electron phosphoranide environments.[11,12]

The familiar $\sigma^3\lambda^3$ (phosphine, R_3P) environment can also act as an electron pair acceptor under certain circumstances. In the presence of highly electronegative substituents R, the central atom becomes sufficiently Lewis acidic to accept anionic nucleophiles (Scheme 2, route a) and form stable phosphoranide environment. Other synthetic routes for phosphoranides involve oxidation of phosphides with halogens or interhalogens (Scheme 2, route b) and deprotonation of phosphoranes with a P−H bond (Scheme 2, route c).[13,14,4]

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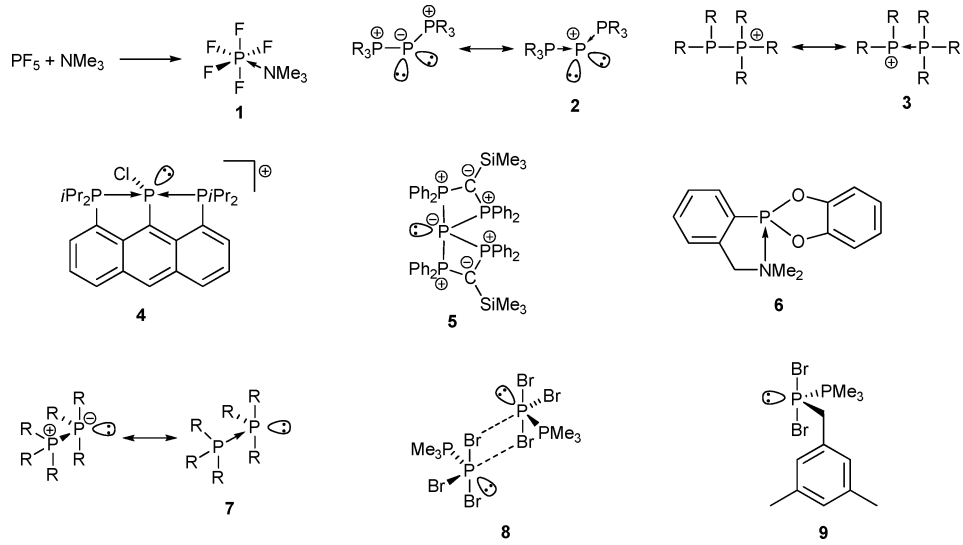
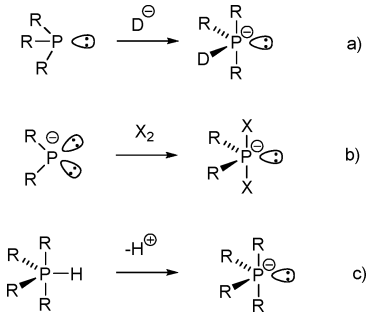
Scheme 1



Scheme 2



The nucleophilicity of electroneutral donors is usually inferior to those which are anionic, which makes synthesis of stable phosphoranides by addition of an electroneutral donor to a phosphine (acceptor) more difficult. Indeed, mainly NMR data showed that aryloxy bearing tricoordinated $\sigma^3\lambda^3$ phosphorus functionalities in **6** displayed "extended (intramolecular) coordination" when positioned in the proximity of dialkylamino groups; however these N→P interactions were rather long.[15,16]

According to HSAB,[17] the phosphine→phosphine adducts **7** should be more stable than amine→phosphine adducts (such as **6**). Reactions of electron rich phosphines as (electroneutral) donors with electron poor phosphines (acceptors) have historically received some attention. The first report on such phosphonium-phosphoranide DA complexes was published in 1958, with vapor pressure measurements indicating formation of $(Me_3P)\cdot PCl_3$ and $2(Me_3P)\cdot PCl_3$.[18] A systematic study of a number of reactions of tri-*n*-alkylphosphines with chlorophosphines showed that at room temperature, tri-*n*-alkylphosphines generally abstract chlorine from mono-, di- and trichlorophosphines to give the corresponding tri-*n*-alkyldichlorophosphoranes and phosphorus (polymeric), oligophosphines and tetraalkyldiphosphines, respectively. In some cases, formation of the DA phosphine-phosphine adduct was observed initially by ^{1}H NMR, but further transformation to chlorine abstraction products was easily achieved by heating. Thus, triethylphosphine with phenyldichlorophosphine afforded adduct $Et_3P\cdot PhPCl_2$ at −20 °C, which decomposed to Et_3PCl_2 and $(PhP)_n$ oligomer at room temperature.[19] Relative stability of adducts $R_3P\cdot PX_3$ with regards to the oxidative coupling reaction was established for several substituents R and halides X. The adduct becomes less stable as the bulk of the alkyl groups R of the trialkylphosphine increases, while with regard to the nature of the halide X the stability of the adduct decreased in the order I > Br > Cl > F.[20] The first ^{31}P NMR evidence of the formation of the phosphine-phosphine complexes was reported in the dissertation of Lochschmidt,[21] where the formation of both 1:1 and 1:2 adducts ($PMe_3\cdot PCl_3$ and $(PMe_3)_2\cdot PCl_3$) was observed. To date, structural data are available only for phosphonium-phosphoranide adducts **8** and **9**.[22] Adduct **8** forms a loosely bound dimeric structure, in which one bromine atom acts as a bridging atom and the acceptor phosphorus atom has pseudo-octahedral geometry (with one site occupied by a lone pair). Replacement of one bromine atom in the acceptor (PBr_3) with substituted benzyl (in **9**) resulted in a change of acceptor phosphorus atom geometry to pseudo-tbp. In both **8** and **9**, the P−P bond lengths are well within the range for a single covalent P−P bond, while some P−Br bonds are lengthened to intermediate between covalent and ionic.[22]

We have a long-term interest in chemistry of peri-substituted (i.e., 1,8-disubstituted) naphthalenes and related molecular frameworks. The special geometry in these

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systems forces the two substituents to a close proximity, making the attractive interaction (i.e., bond) between them highly favorable as it releases the steric strain, concomitant with deformation of organic backbone in nonbonding (repulsive) interaction. Since no intramolecular phosphonium-phosphoranide complex has been reported to date, we decided to utilize the forced close interaction, induced by peri-substitution, in stabilizing this uncommon bonding situation. Here we report the synthesis and structure of a first room temperature stable intramolecular phosphonium-phosphoranide complex, along with the unexpected structure of its decomposition product.

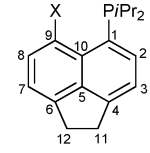
Experimental Section

General Procedures. All experiments were carried out in standard Schlenk glassware or in a glovebox with strict exclusion of air and moisture, using nitrogen or argon atmosphere. Solvents were dried on an MBraun solvent purification system and stored over molecular sieves prior to use. 5,6-Dibromoacenaphthene **10** was prepared according to the published procedure.[23] All the new compounds were fully characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR, including measurement of $^1H\{^{31}P\}$, ^{31}P (^1H coupled), H−H DQF COSY, H−P HSQC, and H−C HSQC experiments. Measurements were performed at 25 °C unless otherwise indicated; 85% H_3PO_4 was used as external standard in ^{31}P, TMS as internal in ^1H and ^{13}C NMR.

5-Bromo-6-diisopropylphosphinoacenaphthene 11. To **10** (8.0 g, 21.79 mmol) dissolved in thf (100 mL) and cooled to −78 °C, *n*BuLi (13.6 mL of 1.6 M solution in hexanes, 21.79 mmol) was added dropwise. After 2 h stirring at −78 °C, chlorodiisopropylphosphine (3.5 mL, 13.62 mmol) dissolved in thf (10 mL) was added dropwise, the reaction mixture was then allowed to warm to room temperature and was stirred overnight. The solvent was replaced with diethyl ether, and the mixture was washed with water (10 mL). The organic phase was then separated and dried using magnesium sulfate. Solvent evaporation gave **11** as a yellow solid in 80% yield (mp. 83−86 °C); elemental analysis (%) calculated for $C_{18}H_{22}BrP$: C 61.90, H 6.36; found: C 62.49, H 6.67; ^1H NMR (300.1 MHz, $CDCl_3$, for atom numbering see Scheme 3): δ 7.67 (d, $^3J_{HH}$ = 7.4 Hz, 1H, H8), 7.59 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 2.4 Hz, 1H, H2), 7.20 (d, $^3J_{HH}$ = 7.4 Hz, 1H, H7), 6.98 (dt, $^3J_{HH}$ = 7.3 Hz, 1H, H3), 3.28−3.23 (m, 2H, H12), 3.20−3.15 (m, 2H, H11), 2.14 (d of septets, $^3J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 1.8 Hz, 2H, CH), 1.10 (dd, $^3J_{HH}$ = 6.9, $^3J_{HP}$ = 12.7 Hz, 6H, 2 × CH_3), 0.98 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 13.4 Hz, 6H, 2 × CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 148.3 (s, q), 147.4 (s, q), 142.0 (d, J_{CP} = 4.3 Hz, q), 135.7 (s, C2), 135.3 (s, C8), 134.4 (d, J_{CP} = 18.9 Hz, q), 130.6 (d, $^1J_{CP}$ = 34.3 Hz, C1), 120.7 (s, C3), 120.0 (s, C7), 30.8 (s, CH_2), 30.1 (s, CH_2), 26.0 (d, $^1J_{CP}$ = 17.9 Hz, 2 × CH), 21.0 (d, $^2J_{CP}$ = 15.7, 2 × CH_3), 19.7 (d, $^2J_{CP}$ = 16.5, 2 × CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): −2.2 (s); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −0.5 to −1.4 (m, $^3J_{PH}$ = 13 Hz); MS (ES+): 371.0 ($M + Na^+$); HRMS for $C_{18}H_{22}BrPNa^+$ calculated: 371.0540; found: 371.0540.

5-Diphenoxyphosphanyl-6-diisopropylphosphinoacenaphthene 12. To **11** (1.22 g, 3.50mmol), dissolved in thf (50 mL), *n*BuLi (1.4 mL of 2.5 M solution in hexanes, 3.50 mmol) was added dropwise at −78 °C, and the reaction mixture was stirred at this temperature for additional 2 h. Triphenylphosphite (0.91 mL, 3.496 mmol) was added at −78 °C, and the reaction mixture was stirred at this temperature for additional 4 h, and then at room temperature overnight. The solvent was replaced with hexane, and the precipitate was filtered off. The crystallization from hexane afforded **12** as yellow solid in 70% yield (mp. 102−104 °C); ^1H NMR (300.1 MHz, $CDCl_3$, for atom numbering see Scheme 3): δ 8.42 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 3.4 Hz, 1H, H2 or H8), 7.62 (dd, $^3J_{HH}$ = 7.1 $^3J_{HP}$ = 3.5 Hz, 1H, H2 or H8), 7.35 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H3 or H7), 7.33 (d, $^3J_{HH}$ = 7.1 Hz, 1H, H3 or H7), 7.21−7.14 (m, 4H, *m*-CH in OPh), 7.07−7.05 (m, 4H, *o*-CH in OPh), 6.95−6.91 (m, $^3J_{HH}$ = 7.3 Hz, 2H, *p*-CH in OPh), 3.35 (s, 4H, 2 × CH_2), 2.14−2.02 (m, 2H, 2 × CH in *i*Pr), 0.90 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, 2 × CH_3), 0.77 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 12.3 Hz, 6H, 2 × CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): 156.6 (d, $^2J_{CP}$ = 10.8 Hz, C−O), 150.7 (s, q), 149.3 (s, q), 140.2 (d, J_{CP} = 14.2 Hz, q), 134.7 (s, C2), 134.6 (s, q), 133.5 (d, $^2J_{CP}$ = 7.8 Hz, C8), 129.6 (s, *m*-C in OPh), 129.3 (d, J_{CP} = 10.9 Hz, q), 129.0 (d, J_{CP} = 10.7 Hz, q), 122.7 (s, *p*-C in OPh), 120.1 (s, C3 or C7), 119.9 (s, C3 or C7), 119.7 (s, *o*-C in OPh), 30.8 (s, CH_2), 30.5 (s, CH_2), 26.2 (dd, $^5J_{CP}$ = 8.3 Hz, $^1J_{CP}$ = 14.9 Hz, 2 × CH in *i*Pr), 20.1 (m, CH_3), 19.9 (m, CH_3); $^{31}P\{^1H\}$ NMR (109.4 MHz, $CDCl_3$): 132.8 (d), −9.1 (d), $^1J_{PP}$ = 199.5 Hz; MS (EI+): 486.1 (M^+), 393.1 (M-OPh), 154 ($C_{12}H_{10}$).

Scheme 3. NMR Numbering Scheme



11 X = Br
12 X = $P(OPh)_2$

Dimer 13. To **10** (1.062 g, 3.40 mmol), dissolved in thf (30 mL), was added *n*BuLi (1.4 mL of 2.5 M solution in hexanes, 3.50 mmol) dropwise at −78 °C, and the reaction mixture was stirred for 2 h at −78 °C. $ClP(iPr)_2$ (0.57 mL, 3.40 mmol), dissolved in 10 mL of thf was added at −78 °C, and the reaction mixture was left to heat up to room temperature and stirred overnight. The solvent was replaced with diethylether, and lithium chloride was filtered off from the resulting suspension. The volatiles were evaporated in vacuo, then thf (30 mL) was added and the solution was cooled to −78 °C. *n*BuLi (1.4 mL of 2.5 M solution, 3.50 mmol) was added, and the reaction mixture was stirred for 2 h at −78 °C. Then triphenyl phosphite (0.89 mL, 3.40 mmol) was added at once, and the reaction mixture was allowed to warm to r.t. and stirred overnight. $ClSiMe_3$ (1.3 mL, 10.20 mmol) was added at −78 °C, and the reaction mixture was left to heat up to room temperature. The solid product was filtered off and dried in vacuo to yield 0.3 g of **13** as pale yellow solid (cocrystallized with one molecule of phenol). Standing of the filtrate for few days yielded an additional crop of **13** (0.15 g).[24] Overall yield 0.45 g, 41%. Mp 188−192 °C (with decomposition); elemental analysis (%) for $C_{36}H_{44}Cl_2P_4 \cdot C_6H_6O$ calculated: C 65.89, H 6.58; found: C 65.91, H: 6.20; ^1H NMR (300.1 MHz, $CDCl_3$): δ 9.47 (s, 1H, OH), 8.16 (t, $^3J_{HH}$ = 6.0 Hz, 2H), 7.70 (d, $^3J_{HH}$ = 6.0 Hz, 2H), 7.04 (m, 4H, CH in PhOH), 6.90 (d, $^3J_{HH}$ = 6.0 Hz, 2H), 6.69−6.63 (m, 1H, *p*-CH in PhOH), 5.85 (d, $^3J_{HH}$ = 7.30 Hz, 2H), 4.49−4.45 (m, 2H, 2 × CH in *i*Pr), 3.80−3.72 (m, 2H, 2 × CH in *i*Pr), 3.52−3.36 (m, 4H, 2 × CH_2), 1.82−1.29 (m, 12H, 4 × CH_3); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): δ 158.3 (s, C-OH), 154.8 (s, q), 149.4 (s, q), 140.8−140.6 (m, 2 × q), 139.0 (m, 2 × q), 136.0 (s, CH), 134.3−134.2 (m,

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(24) At this moment, few crystals of **14** were mechanically separated from the additional crop based on their different habitus. These crystals were used for X-ray diffraction work.

Table 1. Crystallographic Data for **13**·C_6H_6O·H_2O and **14**·thf

	13·C_6H_6O·H_2O	**14**·thf
chemical formula	$C_{42}H_{52}Cl_2O_2P_4$	$C_{22}H_{30}Cl_2OP_2$
formula weight	783.62	443.30
crystal system	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
a/Å	27.883(6)	8.007(2)
b/Å	11.919(3)	11.328(3)
c/Å	26.114(5)	12.594(4)
α/deg		75.418(19)
β/deg	114.549(8)	85.80(2)
γ/deg		77.593(18)
V/Å^3	7894(3)	1079.6(5)
Z	8	2
D_{calcd}/g cm^{-3}	1.319	1.364
μ/cm^{-1}	0.362	0.459
R1[a]	0.0891	0.0670
wR2[b]	0.1958	0.1841

[a] $I > 2\sigma(I)$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]]$, where $p = [(F_o^2) + 2F_c^2]/3$.

CH), 129.4 (s, CH in PhOH), 122.8 (m, CH), 121.5 (s, CH), 119.0 (CH in PhOH), 116.4 (CH in PhOH), 32.0 (s, CH_2), 31.3 (s, CH_2) 29.1−28.7 (m, CH in *i*Pr), 27.5−26.6 (m, CH in *i*Pr), 21.0 (m, CH_3), 19.9 (m, CH_3), 18.7 (d, $^2J_{CP}$=17.9 Hz, 2 × CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): AA′XX′ spin system δ 65.2 (m), −43.2 (m), $^1J(P^{IV}P^I) = 250$, $^2J(P^{IV}P^I) = 54.5$, $^1J(P^IP^I) = 250$, $^3J(P^{IV}P^{IV}) = -33.0$ Hz.

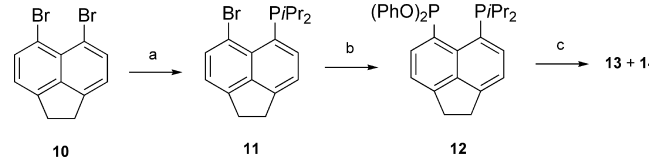
Phosphonium-phosphoranide 14. To **11** (2.00 g, 5.73 mmol), dissolved in diethyl ether (50 mL), was added *n*BuLi (2.30 mL of 2.5 M solution in hexanes, 5.73 mmol) at −78 °C dropwise. When the addition was completed, the formation of pale yellow precipitate was observed. The reaction mixture was stirred for 2 h at −78 °C, then the solution along with the precipitate was cannulated to the solution of phosphorus trichloride (5 mL, 57.3 mmol, excess) in diethyl ether (30 mL) and cooled to −78 °C. The reaction mixture was left to heat up to room temperature and stirred overnight. The white precipitate, consisting of compound **14** and LiCl, was filtered off and dried in vacuo. Contamination with lithium chloride prevented establishing the yield and elemental analysis; IR (Nujol mull) ν_{max}/cm^{-1} 1608s, 1593s, 1062s, 1032s, 841s, 720s; ^1H NMR (300.1 MHz, $CDCl_3$, for atom numbering see Figure 3): δ 8.59 [m (≈dd), $^3J_{HH}$ = 8.0 Hz, 1H, H8], 8.10 [m (≈dd), $^3J_{HH}$ = 6.9 Hz, 1H, H2], 7.66−7.62 (m, 1H, H7), 7.56−7.53 (m, 1H, H3), 4.13−3.99 (m, 2H, 2 × CH in *i*Pr), 3.51 (m, 4H, 2 × CH_2), 1.60−1.42 (m, 12H, 4 × CH_3); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): δ 154.1 (d, J_{CP} = 2.6 Hz, q), 151.0 (s, q), 140.2 (d, J_{CP} = 4.9 Hz, q), 139.0 (d, J_{CP} = 12.8 Hz, q), 136.7 (s, C8), 133.5 (dd, $^2J_{CP}$ = 32.7 Hz, $^3J_{CP}$ = 8.7 Hz, C2), 122.3 (m, C2 and C8), 114.1 (s, q), 113.5 (s, q), 31.5 (s, CH_2), 31.2 (s, CH_2), 27.0 (dd, $^1J_{CP}$ = 29.1 Hz, $^2J_{CP}$ = 4.1 Hz, CH), 18.9 (m, 2 × CH_3), 18.3 (m, 2 × CH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 68.8 (d, R-PCl_2), 40.4 (d, R-P*i*Pr_2), $^1J_{PP}$ = 363 Hz.

X-ray Crystallography. Table 1 lists details of data collections and refinements. Intensities were corrected for Lorentz-polarization and for absorption. All data were collected at 93(2) K using Mo Kα radiation (λ = 0.71073 Å) from a high brilliance Rigaku MM007 generator. Data were collected using a Rigaku Mercury ccd detector with ω and φ scans. The structures were solved by direct methods. The positions of the hydrogen atoms were idealized. Refinements were done by full-matrix least-squares based on F^2 using SHELXTL.

Results and Discussion

We synthesized 5-diphenoxyphosphanyl-6-diisopropylphosphinoacenaphthene **12** by sequential addition of phosphorus onto the aromatic ring, using metal-halogen exchange and P−C coupling reactions, first with chlorodiisopropylphosphine and then with triphenylphosphite (Scheme 4).[25]

Scheme 4. Synthesis of Compound **11**–**14**[a]



[a] (a) *n*BuLi, thf, −78 °C, then $ClPiPr_2$, −78 °C to room temp.; (b) *n*BuLi, thf, −78 °C, then $P(OPh)_3$, −78 °C to room temp.; (c) $ClSiMe_3$, thf, −78 °C to room temp.

Step *a* in the reaction sequence (Scheme 4) proceeded very cleanly as judged by ^{31}P NMR. After extraction **11** was obtained in good yield, and the purity was sufficient for its preparatory use in step *b*.

The ^{31}P NMR spectrum of the crude reaction mixture after the addition of triphenylphosphite to the lithiated compound **11** (step *b* in Scheme 4) showed that **12** was formed cleanly (2 × d, δ_P 133.8 and −9.1 ppm, with large magnitude of through space coupling constant J_{PP} = 199 Hz). A small amount of pure **12** for characterization was obtained by crystallization from hexane; the bulk of **12** was used for the next step without further purification. Since one of the byproducts of the coupling reaction was lithium phenolate, we followed the general quenching procedure, adding chlorotrimethyl silane to the crude reaction mixture. This was intended to transform LiOPh quantitatively into easily separable and less reactive products, Me_3SiOPh and LiCl. To our surprise, addition of Me_3SiCl (at −78 °C) led to the formation of a large amount of a pale yellow precipitate in the reaction mixture. The precipitate **13** was filtered off and dried in vacuo. Its $^{31}P\{^1H\}$ NMR spectrum consisted of a second order AA′XX′ spin system (Figure 1) with two sets of multiplets at δ_P 65.2 and −43.2, corresponding to terminal and inner phosphorus atoms in a catenated P_4 chain structure of **13**. Despite the presence of two stereogenic centers in the dication (σ^3 P atoms), no separate signals assignable to other diastereomeric form were observed in ^{31}P NMR spectra. Diastereotopic *i*Pr groups were anisochronous in both ^1H and ^{13}C NMR.

Compound **13** was crystallized from dichloromethane with one molecule of phenol. Furthermore, a cocrystallized molecule of water was present in two locations of occupancies 75 and 25% (water was introduced with the solvent used for crystallization). The dication is formed by two acenaphthene units joined head to head with the charge being balanced by two chloride anions (Figure 2, Tables 1 and 2). The phosphorus atoms form a zigzag chain; the configurations of the two enantiomers contained in the racemate crystal structure are *R*,*R* (shown in Figure 2) and *S*,*S*. The two acenaphthene units including the peri-phosphorus atoms are very close to planar with dihedral angles P(1)−C(1)−C(9)−P(9) 0.1(3)° and P(21)−C(21)−C(29)−P(29) 6.0(2)°. The P−P and P−C distances are as expected and are comparable with those in a related dication **15**.[7] The geometry around the

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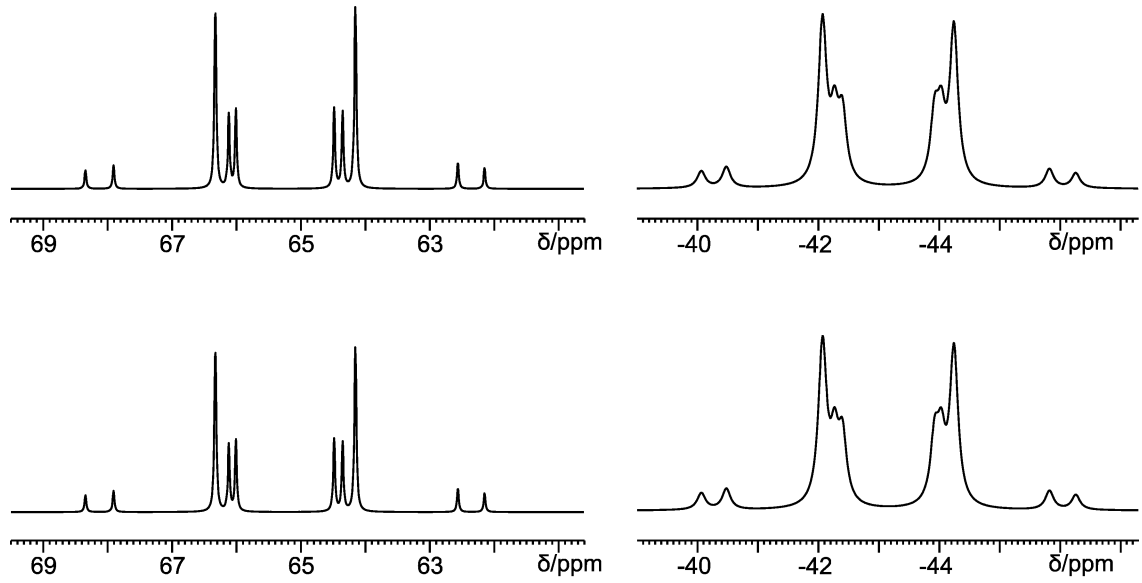


Figure 1. Simulated (top) and experimental (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of **13** at 121.5 MHz. For NMR parameters see experimental part, line broadening (20 Hz) was used to simulate fluxional character of the low frequency half-spectrum.

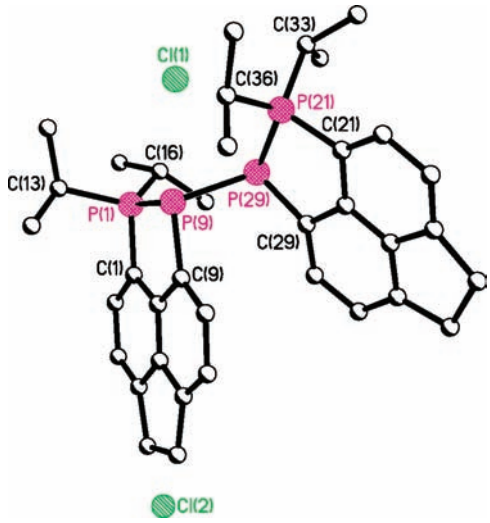


Figure 2. Structure of **13** in the crystal. Cocrystallized molecule of phenol, solvated water and hydrogen atoms are omitted for clarity.

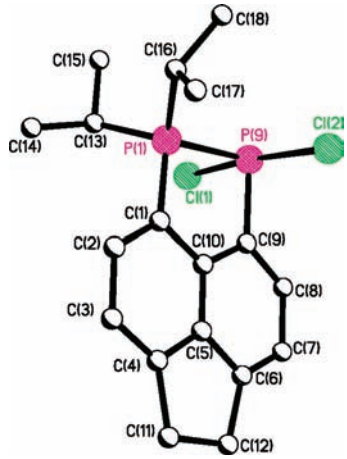
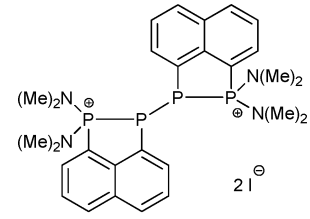
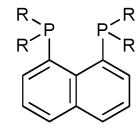


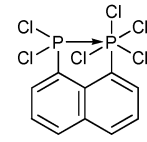
Figure 3. Structure of **14** in the crystal. Hydrogen atoms and solvated molecule of thf are omitted for clarity.

phosphorus atoms is tetrahedral, although the angular distortions are rather pronounced because of the rigid nature of the organic backbone [i.e., angle C(9)−P(9)−P(1) is 90.89(18)°]. We have been unable to grow better quality crystals of **13** obtained by an alternative synthetic route (and thus not containing phenol, see below).



15





16 R = Cl
19 R = iPr

17

Standing of the filtrate after isolation of the first crop of **13** (at the end of the reaction sequence shown in Scheme 4) afforded several crystals of a different habit, which were isolated and identified by X-ray diffraction as a thf solvate of **14** (Table 1 and 2 and Figure 3). Its P*i*Pr$_2$ and PCl$_2$ functionalities form an intramolecular DA bond [(P(1)−P(9) distance 2.2570(14) Å], which results in rehybridization of its phosphorus atoms to what is best described as tetrahedral (donor) and pseudo-tbp (acceptor) configuration, respectively. The chlorine atoms occupy axial positions in the pseudo-tbp coordinated phosphorus atom, with Cl(1)−P(9)−Cl(2) angle of 175.48(5)°. The equatorial positions in the tbp are occupied by P(1) and C(9) atoms and a lone pair, with a P(1)−P(9)−C(9) angle of 89.28(11)°. This rather large

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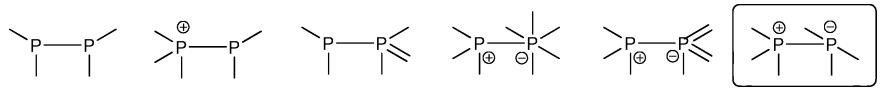
Scheme 5. Attractive P−P peri-Interactions Reported to Date[a]



[a] The motif on the right was observed for the first time in **14**.

deviation from the ideal angle of 120° is perhaps best explained by the rigidity of the organic backbone rather than by the repulsion of the lone pair. The P−Cl bond distances in **14** are rather long [P(9)−Cl(1) 2.2745(14) Å, P(9)−Cl(2) 2.4879(15) Å], significantly unequal and elongated as compared to those in PCl_5 (axial bonds 2.12Å) and also in PCl_6^- anion (2.14 Å).[26] Elongation and significant inequality in P-halogen bonds are perhaps general structural features of phosphonium-phosphoranide DA complexes, since similar elongation and inequality of P−Br bonds was observed in **9**.[22] Clearly, the P−Cl bond elongation cannot be accounted for only by existence of a formal negative charge on the phosphorus atom (see P−Cl distance in PCl_6^- anion), and partial ionic character of the bonds is a more likely explanation here. In contrast to elongated P−Cl axial bonds, the equatorial bond lengths are perfectly normal. Thus the P(9)−C(9) bond length of 1.836(3)Å is almost identical with that observed in the related molecule $Nap(PCl_2)_2$ **16** [1.822(3)−1.834(3) Å] where the phosphorus atoms have a tetrahedral configuration.[27]

In **14**, the Aryl-PCl_2 group acts as an acceptor for the lone pair from the electron rich Aryl-$PiPr_2$ group. It is interesting to note, that the same Aryl-PCl_2 group can also act as a donor in a suitable situation, that is, with respect to the much more electrophilic Aryl-PCl_4 environment (in **17**), which in turn rehybridized to octahedral (phosphoride) configuration.[28]

Literature examples of bonding situations in bis(phosphorus) peri-substituted naphthalenes and related systems, where clearly attractive interactions exist,[7,11,28−30] are shown schematically in Scheme 5. The bonding in **14** (shown on right) represents a new entry to the group of compounds with such interactions.

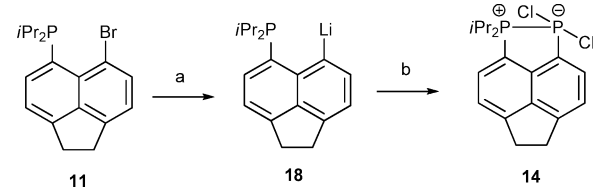
Since **14** is potentially a very useful synthon, it was of interest to develop a rational synthesis. The reaction sequence shown in Scheme 6 was used; however it turned out that the reaction is rather sensitive toward the conditions, and the range of solvents that can be used is limited, since **14** is unstable in some commonly used ones (see below). After extensive reaction optimization the best conversion was achieved with diethylether as a solvent, and when the cold suspension of lithiated intermediate **18** was cannulated to the cooled solution of ten molar excess of PCl_3. Since **14** is not particularly soluble in diethyl ether, it was conveniently isolated (as a mixture with LiCl) by filtration. Such a product contained only very small amount of phosphorus containing impurities, including dicationic compound **13**.

Table 2. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles (deg) for **13** and **14**[a]

	Compound **13**		
P(1)−P(9)	2.2095(19)	P(29)−P(9)	2.222(2)
P(29)−P(21)	2.1968(19)		
P(1)−C(1)	1.758(6)	P(9)−C(9)	1.808(5)
P(29)−C(29)	1.803(5)	P(21)−C(21)	1.780(5)
P(1)−C(16)	1.802(6)	P(21)−C(33)	1.816(5)
P(1)−C(13)	1.814(6)	P(21)−C(36)	1.813(5)
P(1)−P(9)−P(29)	99.69(8)	P(21)−P(29)−P(9)	100.42(8)
C(1)−P(1)−P(9)	97.43(18)	C(9)−P(9)−P(1)	90.89(18)
C(21)−P(21)−P(29)	97.00(18)	C(29)−P(29)−P(21)	91.55(17)
C(1)−P(1)−C(13)	105.7(3)	C(21)−P(21)−C(33)	110.8(2)
C(1)−P(1)−C(16)	110.3(3)	C(21)−P(21)−C(36)	109.0(2)
C(9)−P(9)−P(29)	102.59(18)	C(29)−P(29)−P(9)	104.38(17)
C(9)−P(9)−P(29)−C(29)	32.5(3)		
C(1)−P(1)−P(9)−C(9)	0.1(3)	C(21)−P(21)−P(29)-C(29)	6.8(2)
splay angle around C(10)[b]	−8.3(7)	splay angle around C(30)[c]	−9.1(7)
	Compound **14**		
P(1)−P(9)	2.2570(14)	P(1)−C(1)	1.796(3)
Cl(1)−P(9)	2.2745(14)	P(1)−C(13)	1.836(3)
Cl(2)−P(9)	2.4879(15)	P(1)−C(16)	1.841(4)
P(9)−C(9)	1.836(3)		
C(1)−P(1)−C(13)	109.23(15)	C(9)−P(9)−P(1)	89.28(11)
C(1)−P(1)−C(16)	114.50(17)	C(9)−P(9)−Cl(1)	91.39(12)
C(13)−P(1)−C(16)	105.78(17)	P(1)−P(9)−Cl(1)	93.93(5)
C(1)−P(1)−P(9)	98.14(12)	C(9)−P(9)−Cl(2)	84.68(12)
C(13)−P(1)−P(9)	112.24(12)	P(1)−P(9)−Cl(2)	88.26(5)
C(16)−P(1)−P(9)	116.89(13)	Cl(1)−P(9)−Cl(2)	175.48(5)
C(1)−P(1)−P(9)−C(9)	5.97(16)	splay angle[d]	−7.9(3)

[a] For atom numbering see Figures 2 and 3. [b] Splay angle = P(9)−C(9)−C(10) + C(9)−C(10)−C(1) + C(10)−C(1)+P(1) − 360. [c] Splay angle = P(21)−C(21)−C(30) + C(21)−C(30)−C(29) + C(30)−C(29)−P(29) − 360. [d] Splay angle = P(9)−C(9)−C(10)+C(9)−C(10)−C(1)+C(10)−C(1)−P(1) − 360.

Scheme 6. Rational Synthesis of Compound **14**[a]



[a] (a) *n*BuLi, diethylether, −78°C; (b) PCl_3, diethylether, −78 °C to r.t.

The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **14** consists of two doublets at δ_P 68.8 (phosphonium) and 40.4 ppm (phosphoranide), with $^1J_{PP}$ = 364 Hz, which is in good agreement with the literature data for related compound **8**.[22] Increased shielding of the acceptor phosphorus atom with respect to that in compound **16** (which shows a repulsive interaction of the two PCl_2 groups) is clearly illustrated by the low-frequency shift of the dichlorophosphino group in **14** (δ_P 68.8) vs that in **16** (δ_P 135.7).[31] On the same note, deshielding of the donor phosphorus atom results in high-

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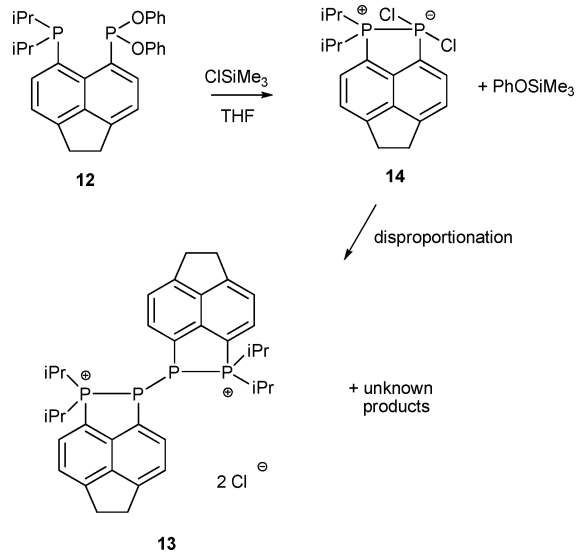
Scheme 7

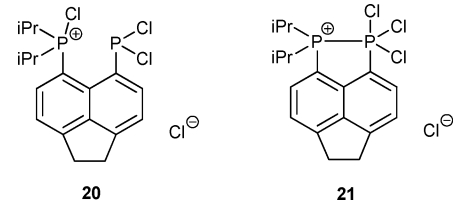


frequency shift of the diisopropylphosphino group in **14** (δ_P 40.4) versus that in **19** (δ_P −4.79, the interaction between the two P*i*Pr$_2$ groups in **19** is repulsive).[32] Interestingly, the NMR chemical shift of the phosphonium environment of **14** is rather solvent dependent, for example, in thf the 11 ppm low-frequency shift was observed (δ_P 29.2 and 68.7, $^1J_{PP}$ = 378 Hz in thf) with respect to values obtained with $CDCl_3$ solution.

Crystallographic identification of **14** as an intermediate in the transformation of **12** to **13** prompts us to suggest a plausible reaction mechanism as shown in Scheme 7.

In the first step of this mechanism, **14** is formed by stepwise substitution of the phenoxy groups of **12** by chloride. **14** is however unstable in the presence of thf and lithium phenoxide (present as byproduct of the preparation of **12**) and disproportionates into **13** and other phosphorus containing products. Formation of **13** from **14** involves a redox step, one equivalent of "Cl_2" is transferred to the other (unknown) byproduct on transformation of 2 equiv of **14** into 1 equiv of **13**. Because the dialkylphosphino group is a better nucleophile than the dichlorophosphino group, we expected **20** rather than **21** to be the co-product of the disproportionation (Scheme 8). Indeed, trialkylphosphines has been shown to be sufficiently strong reducing agents in similar reactions. Thus, tetraalkyl bisphosphine rather than

Scheme 8



PX_3 (X = Cl, Br) acted as a reducing agent in the reactions of bis(1,3-dialkylphosphino)propanes and similar substrates with PX_3 (X = Cl or Br).[6] In the same fashion, Et_3P acted as chlorine abstractor in the reaction of Et_3P with $PhPCl_2$ (the final products were Et_3PCl_2 and $(PhP)_n$ oligomers).[19]

To gain further insight into the nature of the disproportionation step we have performed several NMR-scale reactions, in which we took a solution of **14** (lithium phenolate free, prepared by independent synthesis from PCl_3 and organolithium) in $CDCl_3$ and added a catalytic amount of various nucleophiles. The rate of disproportionation was followed by $^{31}P\{^1H\}$ NMR spectroscopy. The rate of disproportionation of **14** was insignificant in $CDCl_3$ at room temperature, and at 50 °C, only very small amount of products was observed after several weeks by ^{31}P NMR. A substantial increase in the reaction rate was observed when trimethyl phosphine, triphenyl phosphine, as well as trimethylsilyl phenoxide, were added. Addition of trimethylsilyl chloride also accelerated the transformation of **14** to **13**, no signal of starting material **14** was observed after 4 weeks since addition at room temperature. Also other weak nucleophiles such as tetrahydrofuran and 1,4-dioxane increased the rate of disproportionation significantly, so that the full conversion was achieved within 3 days and 2 weeks, respectively. Unfortunately, the disproportionation reactions did not proceed cleanly, and rather complex NMR spectra were observed in these NMR scale experiments. Therefore, we have not been able to identify the co-products of the disproportionation of **14** beyond reasonable doubt.

Acknowledgment. We thank Mrs. S. Williamson and Mrs. C. E. R. Horsburgh for microanalyses and measurement of mass spectra of air sensitive compounds, and EPSRC for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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