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Phosphorus Heterocycles

1,1- and 1,4-Addition Reactions with 3a,6a-Diaza-1,4-diphosphapentalene Containing Two-Coordinate and Formally Divalent Phosphorus

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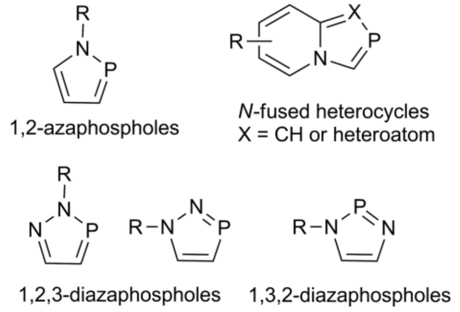
Abstract: 3a,6a-Diaza-1,4-diphosphapentalene (DDP) reacts with halocarbons to give addition products to one or both phosphorus atoms depending on the substrate. Chlorotriphenylmethane affords a 1,4-addition product, which slowly decomposes in solution to form the Ph_3C radical and the chloro-DDP coupling product with a P–P bond. Benzyl chloride is added to one phosphorus atom to form hypervalent (trivalent, four-coordinate) phosphorus with a N···P distance (nonvalent interaction) of 2.191(2) Å. A workup of the latter with $GeCl_2$ results in a complex salt containing the $GeCl_3^-$ anion and cation with covalent N–P bonding.

Introduction

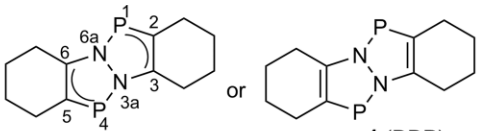
Azaphospholes bearing σ^2,λ^3-phosphorus and σ^3,λ^3-nitrogen atoms have been the subject of a number of articles and reviews.[1–3] The spectroscopic and computational studies[3] of azaphospholes have revealed their aromatic character. The two-coordinate phosphorus and three-coordinate nitrogen atoms contribute one and two π electrons, respectively, to the aromatic sextet.



On the one hand, most of the azaphospholes are as stable and unreactive as the classical aromatic five-membered heterocycles and exhibit electrophilic C–H substitution reactions.[2a]

On the other hand, the enhanced reactivity of the P=C and N=P bonds in such ring systems is a fact that is documented by various types of 1,2-addition and, in particular, [3+2] and [4+2] cycloaddition reactions.[2a,4]

Previously we have reported the annulated heterophosphole (**1**) of a novel type, based on a planar hydrazine block containing two-coordinate and formally divalent phosphorus atoms.[5]



1 (DDP)

This compound may also be assigned to the class of heteropentalene derivatives.[6,7] The curious feature of 3a,6a-diaza-1,4-diphosphapentalene (DDP, **1**) is its unusual chemical structure, which is impossible to depict by classical Lewis schemes. Using the terms “hypovalent phosphorus” or “formally divalent phosphorus” we aim to show the essential differences in the chemical properties between **1** and usual diazaphospholes.

DDP should be a biradical, judging from the structural formula.

However, the singlet state of this molecule proved to be 40 kcal mol^{-1} more favorable than the triplet one.[5] The coordinating activity of compound **1** is much higher than that known for azaphospholes. This is because of the new type of complexation, where the lone pair at the phosphorus atom is not involved in the coordination. Instead, the 10π-electron system provides two electrons for the formation of the P→M coordination bond, as we have shown from examples of Sn^{II}, Ge^{II}, and Hg^{II} complexes.[5,8]

Recently we have found that **1** reacts with hexachlorodisilane at –30 °C to give the 1,1-addition product resulting from the splitting of the Si–Si bond.[9]

Herein we report on addition reactions of halocarbons (Ph_3CCl and $PhCH_2Cl$) to **1**, which may provide 1,1- or 1,4-addition products, allowing the phosphorus atoms to remain in the trivalent state.

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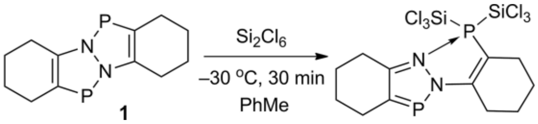
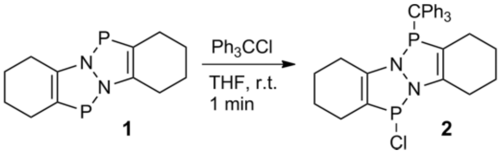


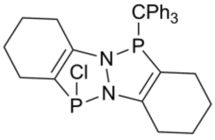
Results and Discussion

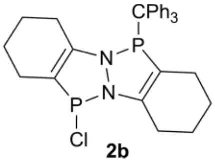
It is known that azaphospholes do not interact with halocarbons while tertiary phosphines give quaternary phosphonium salts. Unlike usual phosphines, we did not observe the formation of quaternary phosphonium salts with DDP when an excess of halocarbon was used. Chlorotriphenylmethane reacts smoothly with DDP in a THF solution to give a 1,4-addition product.



The ^{31}P NMR spectrum of the reaction mixture reveals two doublets at 125.2 and 75.3 ppm with $^3J_{PP}$ values of 17 Hz demonstrating conjugation between distant phosphorus atoms.

For compound **2**, one can envision two possible positional isomers, represented graphically here as **2a** and **2b**.


2a


2b

However, we saw no evidence for equilibration of **2a** with **2b** by pyramidal inversion of phosphorus on the ^{31}P NMR time scale.

The molecular structure of complex **2** with its atom numbering scheme is shown in Figure 1. Crystal data and some details of the data collection and refinement are given in Table S1 in the Supporting Information.

The solid-state structure reveals the formation of isomer **2a** despite the close arrangement of the chlorine atom with the sterically encumbering Ph3C group. The five-membered rings in **2a** are close to planar, with a deviation of atoms from the mean plane of 0.06 Å. The compound **2a** has a somewhat elongated Cl(1)–P(1) bond [2.290(1) Å]. Crystal packing analysis of **2a** revealed stacking interactions between two molecules with the shortest intermolecular contacts C(2)···H(10B) (2.64 Å). Additionally, short intermolecular contacts were found in the crystal between atoms H···H (2.24 Å) and H···Cl (2.86 Å). All observed contacts are close to the sum of van der Waals radii of the elements[10] (Figure 2).

Geometry optimizations of the isomers **2a** and **2b** were performed using DFT calculations with the method B3LYP and the 6-31+G(d) basis set. The calculations revealed that the isomer **2a** is 1.4 kcal mol^{-1} more stable than **2b**.

The adduct **2a** is quite stable at room temperature in the solid state. However, a solution of **2** undergoes slow transformation (over two weeks) accompanied by the formation of the stable triphenylmethyl radical whose ESR spectrum[11] was detected (Figure S1 in the Supporting Information). A second product was isolated and was shown to be the diphosphine **3**, which we characterized earlier.[5]

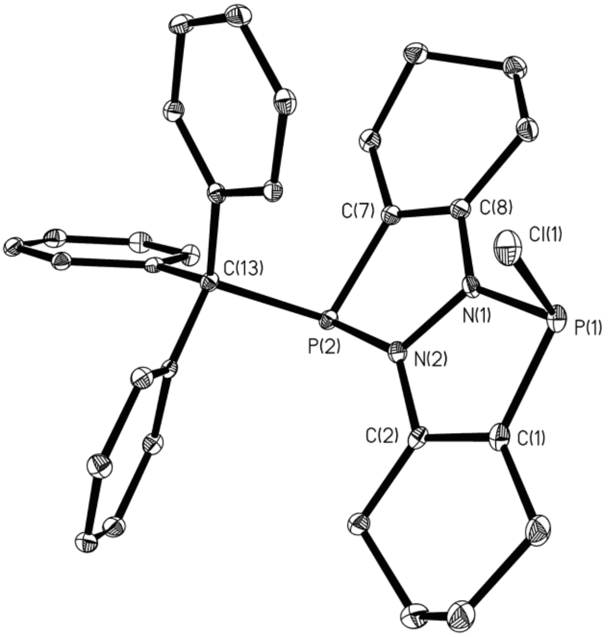


Figure 1. The molecular structure of **2a** together with the atomic numbering system (thermal ellipsoids at the 30 % probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl(1)–P(1) 2.290(1), P(1)–N(1) 1.681(2), P(1)–C(1) 1.776(2), P(2)–N(2) 1.745(2), P(2)–C(7) 1.822(2), N(1)–N(2) 1.423(2), N(1)–C(8) 1.401(2), N(2)–C(2) 1.382(2), C(1)–C(2) 1.363(3), C(7)–C(8) 1.340(3); N(1)–P(1)–C(1) 87.92(9), N(1)–P(1)–Cl(1) 106.32(6), C(1)–P(1)–Cl(1) 101.40(7), N(2)–P(2)–C(7) 88.06(8), N(2)–P(2)–C(13) 106.57(8), C(7)–P(2)–C(13) 102.88(9), C(8)–N(1)–N(2) 110.3(2), C(8)–N(1)–P(1) 133.5(2), N(2)–N(1)–P(1) 116.2(2), N(1)–N(2)–P(2) 113.9(2), C(2)–N(2)–N(1) 108.3(2), C(2)–N(2)–P(2) 135.5(2).

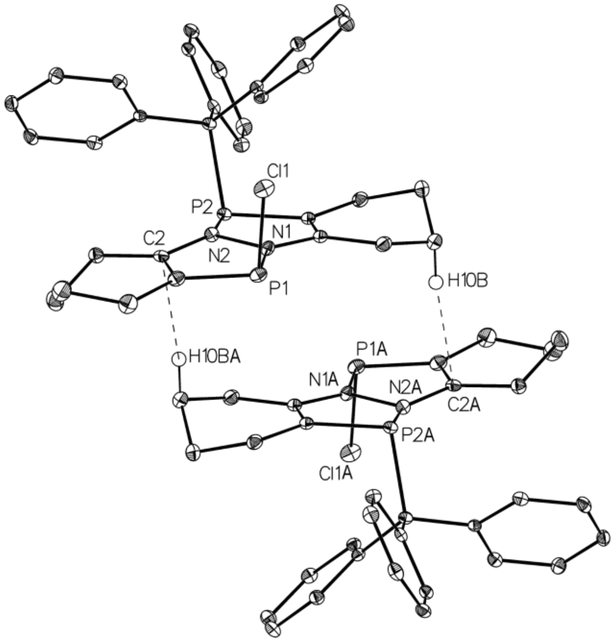
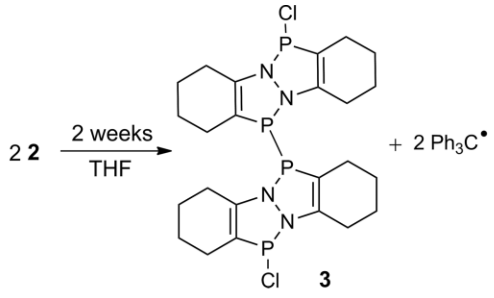


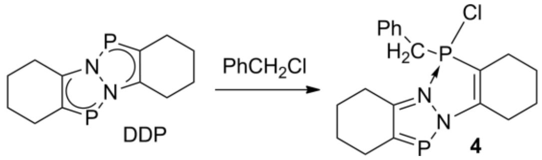
Figure 2. Arrangement of **2a** in the crystal.



3

Decomposition of **2** is accelerated to completion in about 2 h in boiling toluene. Additionally, in a control experiment we established that the triphenylmethyl radical does not react with free DDP.

Unlike Ph_3CCl, the reaction of benzyl chloride with DDP proceeds in another manner to give the 1,1-addition product **4**.



4

The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits a broadened doublet at δ = 57.5 ppm with a coupling constant $^3J(P,P)$ of 13 Hz and broad resonance at δ = 169.1 ppm. The broadened resonances indicate a rapid interchanging in solution, possibly through dissociation of the P–Cl bond. A downfield shift (δ = 169.1 ppm relative to 125.2 ppm in **2a**) is consistent with the noncoordinated P^{III} center being part of a five-membered diazaphosphole ring.[1,2,5]

X-ray analysis confirmed the formation of the 1,1-addition product. The molecular structure of **4** with its atom numbering scheme is shown in Figure 3. Crystal data and some details of the data collection and refinement are given in Table S1 in the Supporting Information.

The phosphorus atom in **4** has a four-coordinate disphenoidal geometry with an axial arrangement of nitrogen [N(2)] and chlorine [Cl(1)] atoms. The distance P(2)–N(2) [2.191(2) Å] is longer than the sum of the covalent radii of the elements (1.73 Å),[10] but sufficiently shorter than the sum of the corresponding van der Waals radii (3.35 Å). Whereas the angle N(2)–P(2)–Cl(1) is close to linear [174.77(4)°], the angle in between the P(1)N(1)N(2)C(2)C(1) mean plane and the N→P hypervalent bond is 150.0°.

There is a parallel arrangement of five-membered rings P(1)N(1,2)C(1,2) of two neighboring molecules of **4** in the crystal with a centroid–centroid distance of 3.930(2) Å (Figure S2 in the Supporting Information). These molecules are related by a crystallographically imposed inversion center.

According to the NBO analysis at the B3LYP/6-31+G(d) level of theory, a possible model for the N→P nonbonding interaction might be a negative hyperconjugation of the lone pair of electrons at the nitrogen atom with the anti-bonding orbital σ*(P–Cl) at the adjacent phosphorus[12] (Figure 4).

For the compound **4**, one can envision three possible positional isomers, represented graphically here as **4a**, **4b**, and **4c** (Figure 5).

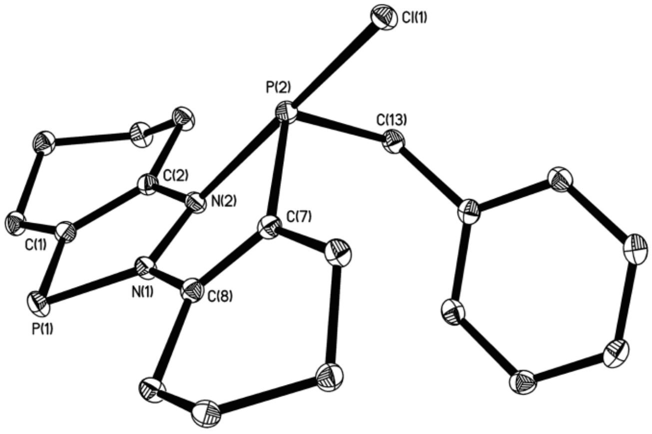


Figure 3. Molecular structure of **4** together with the atomic numbering system (thermal ellipsoids at the 30 % probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(2)–N(2) 2.191(2), Cl(1)–P(2) 2.2342(5), P(1)–N(1) 1.702(2), P(1)–C(1) 1.727(2), N(1)–N(2) 1.358(2), N(1)–C(8) 1.416(2), C(1)–C(2) 1.404(2), C(1)–C(6) 1.514(2), P(2)–C(7) 1.843(2), P(2)–C(13) 1.875(2); N(2)–P(2)–Cl(1) 174.77(4), C(7)–P(2)–C(13) 105.50(7), N(1)–P(1)–C(1) 88.84(7), C(13)–P(2)–Cl(1) 92.85(5), C(7)–P(2)–Cl(1) 95.83(5), N(2)–N(1)–C(8) 113.1(2), N(2)–N(1)–P(1) 115.7(2), N(1)–N(2)–P(2) 106.07(9), N(2)–C(2)–C(1) 115.4(2), N(2)–C(2)–C(3) 120.2(2).

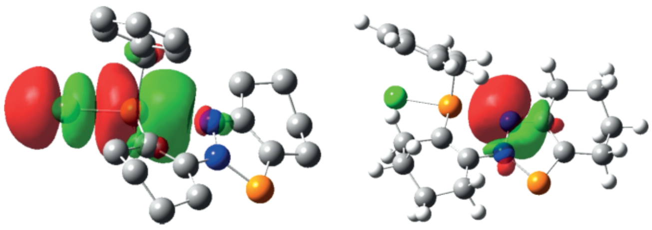


Figure 4. Hyperconjugation of the lone pairs of electrons at nitrogen (HOMO-10, right) with the unoccupied anti-bonding σ*(Cl–P) orbital (LUMO+6, left) in **4**.

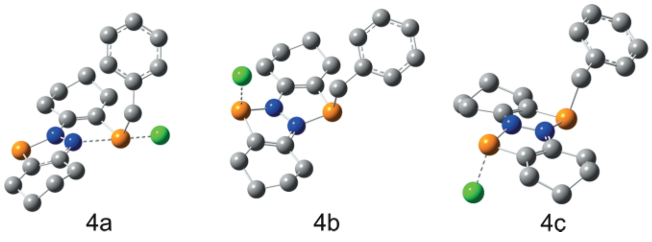
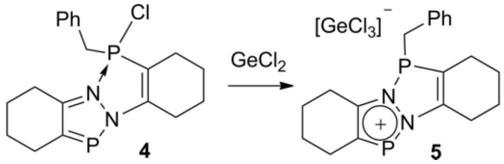


Figure 5. B3LYl P 6-31G(d)-optimized positional isomers of **4**.

Geometry optimizations of the isomers **4a**–**c** were performed using DFT calculations with method B3LYP and the 6-31G(d) basis set. The calculations revealed that the isomer **4a**, containing hypervalent phosphorus, is more favorable than **4b** and **4c** (by 4.5 and 5.7 kcal mol^{-1}, respectively).

A low-lying unshared pair of electrons (–8.9 eV, HOMO-11) in hypervalent phosphorus compound **4** is nonreactive toward the halocarbons. Prolonged heating of **4** with benzyl chloride gave no quaternization product.

There is an interplay between covalent and nonvalent N(2)–P(2) bonding interactions in **4** dependent on the possible dissociation of the P(2)–Cl(1) bond. Abstraction of the chloride ion should cause the transformation of the nonvalent P–N interaction to the covalent one. Indeed, addition of germanium dichloride, which is prone to form the complex anion $[GeCl_3]^-$, affords the complex salt **5** containing a "normal" P–N bond in the cationic fragment.



The structure of **5** with its atom numbering scheme is shown in Figure 6. Crystal data and some details of the data collection and refinement are given in Table S1 in the Supporting Information.

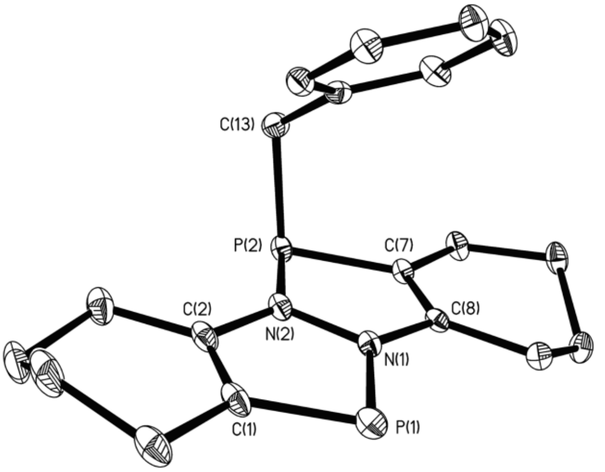


Figure 6. Structure of **5** (cationic part) together with the atomic numbering system (thermal ellipsoids at the 30 % probability level). Hydrogen atoms and $GeCl_3^-$ anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–N(1) 1.685(2), P(2)–N(2) 1.785(3), P(1)–C(1) 1.738(3), P(2)–C(7) 1.815(3), P(2)–C(13) 1.867(3), N(1)–N(2) 1.360(3), N(1)–C(8) 1.418(3), N(2)–C(2) 1.356(4), C(1)–C(2) 1.381(5), C(7)–C(8) 1.329(4); N(1)–P(1)–C(1) 89.0(2), N(2)–P(2)–C(7) 86.6(2), N(2)–P(2)–C(13) 98.7(2), C(7)–P(2)–C(13) 102.9(2), N(2)–N(1)–C(8) 110.9(2), N(2)–N(1)–P(1) 114.8(2), C(8)–N(1)–P(1) 134.0(2), C(2)–N(2)–N(1) 111.8(2), N(1)–N(2)–P(2) 114.7(2), C(2)–C(1)–P(1) 111.4(2), C(6)–C(1)–P(1) 127.7(3), N(2)–C(2)–C(1) 112.9(3).

The phosphorus–nitrogen bond P(2)–N(2) is shortened from 2.191(2) Å in **4** to 1.785(3) Å in **5**, becoming covalent. The anion $[GeCl_3]^-$ has close contacts Cl•••P of 3.411(2) and 3.489(2) Å with neighboring cationic parts in the crystal (Figure S3 in the Supporting Information). The five-membered heterocycles are almost planar, with only negligible deviations of atoms (0.03 Å) from the mean plane.

The $^{31}P\{^1H\}$ NMR spectrum of **5** shows two single resonances at 86.2 and 214.3 ppm corresponding to the three- and two-coordinate phosphorus, respectively. It is remarkable that no coupling is observed between magnetically nonequivalent phosphorus atoms. At the same time, the ^1H NMR spectrum of **5** reveals two multiplets from inequivalent methylene protons of the benzyl group at δ = 3.91 and 3.50 ppm with coupling constants $^2J_{H,P}$ = 12 Hz and $^2J_{H,H*}$ = 16 Hz, respectively. Apparently, the phenyl group in **5** has a fixed position as shown in the crystal structure and no rotation is observed around the P–C bond in solution.

Conclusions

In conclusion, we have shown that 3a,6a-diaza-1,4-diphosphapentalene (**1**) reacts with benzyl chloride and chlorotriphenylmethane providing 1,1- and 1,4-addition products (**4** and **2**, respectively). We suppose that the mechanism of RCl addition to DDP is a usual nucleophilic substitution of the halogen-like formation of phosphonium salts. However, the final location of the halogen atom depends mainly on two factors: the strength of the nonvalent interaction N→P (which is governed by electronegativity of substituents at phosphorus) and steric hindrances. Because of the sterically crowded Ph_3C group in **2** the existence of a 1,1-addition product is not possible.

The compound **4** contains a hypervalent phosphorus (trivalent, four-coordinate) atom showing a N•••P nonvalent interaction of 2.191(1) Å. The abstraction of the chloride ion from **4** by $GeCl_2$ affords the complex salt **5** containing the $GeCl_3^-$ anion and a cationic heterocyclic fragment demonstrating covalent P–N bonding. The 1,4-addition product of Ph_3CCl (**2**) is slowly decomposed in solution to form the Ph_3C radical and coupling product **3** with a P–P bond.

Experimental Section

General Procedures: All preparations were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen or argon. All solvents were distilled from appropriate drying agents immediately prior to use:[13] diethyl ether and THF were dried and distilled from Na/benzophenone, and pyridine was distilled from KOH and kept over CaH_2. Toluene and hexane were thoroughly dried and distilled from sodium prior to use. 3a,6a-Diaza-1,4-diphosphapentalene was prepared according to the method described in ref.[5] Chlorotriphenylmethane, benzylchloride, and $GeCl_2$(diox) were purchased from Sigma–Aldrich Chemical Co. and used as is. NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions using Bruker DPX-200 and AV-400 spectrometers. Infrared spectra were recorded with a Perkin–Elmer 577 spectrometer from 4000 to 400 cm^{-1} in nujol or with a Perkin–Elmer FTIR Spectrometer System 2000 as KBr mulls.

X-ray Crystallography: The X-ray diffraction data were collected with Bruker AXS SMART APEX (for **4**) and Agilent Xcalibur E (for **2a** and **5**) diffractometers (Mo-K_α radiation, ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by the SAINT (**4**)[14] and CrysAlisPro (**2a** and **5**)[15] programs. All structures were solved by direct methods and were refined on F_{hkl}^2 using the SHELXTL package.[16] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS (**4**)[17] and SCALE3 ABSPACK (**2a** and **5**)[18] were used to perform absorption corrections. The main crystallographic data and structure refinement details for **2a**, **4**, and **5** are presented in Table S1 in the Supporting Information.

CCDC 1438537 (for **2a**), 1438538 (for **4**), and 1438539 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational Details: DFT calculations were performed with the Gaussian 03 software package (for details see the Supporting Information) at the B3LYP/6-31+G(d) level of theory. The optimized geometries of **3a**–**e** correspond to energy minima, as indicated by frequency computations. There are no imaginary frequencies in the calculation.

Synthesis

Adduct of DDP with Ph_3CCl (2): A solution of chlorotriphenylmethane (0.28 g, 1.0 mmol) in THF (15 mL) was added to an orange solution of 3a,6a-diaza-1,4-diphosphapentalene (**1**) (0.25 g, 1.0 mmol) in the same solvent at room temperature. The reaction mixture turned yellow after 10 min of stirring. The solvent was removed under reduced pressure and replaced by hexane. On leaving the concentrated hexane solution in the ice bath, yellow crystals separated, yield 0.51 g (96 %). ^{1}H NMR (C_6D_6, 300 K): δ = 6.6–7.8 (m, 15 H, Ph), 0.7–3.0 (m, 16 H, *c*-Hexyl) ppm. ^{13}C NMR: δ = 67.1 (dd, $^{1}J_{C,P}$ = 53, $^{4}J_{C,P}$ = 16 Hz, Ph_3*C*-P) ppm. Other ^{13}C signals are not possible to assign because of the decomposition of **2** over time. ^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ = 125.2 (d, $^{3}J_{P,P}$ = 17 Hz), 76.2 (d, $^{3}J_{P,P}$ = 17 Hz) ppm. IR (Nujol): $\tilde{\nu}$ = 1618 (m), 1593 (w), 1546 (m), 1346 (w), 1290 (m), 1263 (m), 1207 (w), 1180 (m), 1159 (s), 1138 (w), 1080 (w), 1021 (m), 915 (m), 856 (w), 801 (m), 750 (m), 700 (s), 624 (w), 585 (w), 545 (m), 505 (m), 486 (m), 463 (w) cm^{-1}. $C_{31}H_{31}ClN_2P_2$ (528.99): calcd. C 70.39, H 5.91, Cl 6.70, N 5.30, P 11.71; found C 70.31, H 6.00, Cl 6.67, N 5.35, P 11.69.

Adduct of DDP with $PhCH_2Cl$ (4): A solution of benzylchloride (0.13 g, 1.0 mmol) in THF (10 mL) was added to an orange solution of 3a,6a-diaza-1,4-diphosphapentalene (**1**) (0.25 g, 1.0 mmol) in the same solvent at room temperature. The reaction mixture turned yellow after 30 min of stirring. The solvent was removed under reduced pressure and replaced by toluene. On leaving the concentrated toluene solution in the ice bath, yellow crystals separated, yield 0.35 g (94 %). ^{1}H NMR (C_6D_6, 300 K): δ = 6.8–7.8 (m, 5 H, Ph), 3.3 (d, $^{2}J_{H,P}$ = 13 Hz, 2 H), 1.0–2.8 (m, 16 H, *c*-Hexyl) ppm. ^{13}C NMR: δ = 149.3 (m, *C*=CPBn), 140.5 [t, $^{2}J_{C,P}$ = 6 Hz, (*C*NPBn)]; Ph: 136.5, 129.3, 128.1, 125.9, 120.5; 43.8 (m, *C*PBn), 25.9 (m, CH_2Ph), 23.7–21.4 (m, CH_2, c-Hex) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ = 57.5 (d, $^{3}J_{P,P}$ = 13 Hz), 169.1(s, br) ppm. IR (Nujol): $\tilde{\nu}$ = 1597 (w), 1336 (m), 1281 (m), 1256 (m), 1219 (m), 1180 (w), 1135 (m), 1071 (m), 1032 (m), 961 (m), 908 (m), 853 (m), 819 (m), 794 (m), 771 (s), 736 (m), 708 (s), 602 (w), 581 (w), 566 (w), 536 (w), 472 (m) cm^{-1}. $C_{19}H_{23}ClN_2P_2$ (376.8): calcd. C 60.54, H 6.15, Cl 9.41, N 7.43, P 16.44; found C 60.62, H 6.20, Cl 9.37, N 7.40, P 16.39.

Reaction of 4 with $GeCl_2$(diox): A solution of $GeCl_2$(diox) (0.23 g, 1.0 mmol) in THF (10 mL) was added to a solution of **4** (0.37 g, 1.0 mmol) in the same solvent (15 mL) at room temperature. The mixture was kept for 24 h at 20 °C. On leaving the concentrated THF solution in the ice bath, yellow crystals separated, yield 0.47 g (92 %). ^{1}H NMR ([D_8]THF, 300 K): δ = 6.8–7.3 (m, 5 H, Ph), 3.91 (m, $^{2}J_{H,P}$ = 12, $^{2}J_{H,H*}$ = 14 Hz, 1 H, C*H*H*Ph), 3.50 (m, $^{2}J_{H,P}$ = 12, $^{2}J_{H,H*}$ = 14 Hz, 1 H, CH*H**Ph), 1.8–3.1 (m, 16 H, *c*-Hexyl) ppm. ^{13}C NMR: δ = 153.7 (m, *C*=CPBn), 151.0 (m, *C*NPBn), Ph: 140.8, 137.4, 132.2, 128.8, 128.2, 127.9; 125.9 (dd, $^{2}J_{C,P}$ = 27 Hz, 7 Hz, P*C*CNPBn), 66.7 (m), 37.5 (dd, $^{1}J_{C,P}$ = 39, $^{3}J_{C,P}$ = 7 Hz, *C*PCH$_2$Ph), 24.6 (m, *C*H$_2$Ph), 23.5–20.0 (m, CH_2, c-Hex) ppm. ^{31}P{^{1}H} NMR ([D_8]THF, 300 K): δ = 86.2 (s) (triplet in ^{31}P NMR, with $^{2}J_{P,H}$ = 8 Hz), 214.3 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1628 (m), 1597 (m), 1345 (m), 1277 (m), 1246 (m), 1227 (m), 1195 (m), 1183 (w), 1162 (m), 1138 (s), 1074 (m), 1037 (m), 990 (m), 959 (s), 912 (s), 853 (m), 814 (m), 800 (s), 763 (vs), 700 (vs), 631 (w), 613 (w), 586 (s), 563 (s), 537 (m), 469 (vs) cm^{-1}. $C_{19}H_{23}Cl_3GeN_2P_2$ (519.96): calcd. C 43.86, H 4.46, Cl 20.44, N 5.38; found C 43.93, H 4.40, Cl 20.39, N 5.42.

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