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The Reaction of Cyclohexanone Azine with PCl_3. Synthesis of Annulated Dichlorodiazaphosphole and its Unusual Transannulation

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Abstract. The N,N′-annulated dichlorodiazaphosphole **1** was prepared in 55 % yield by the reaction of cyclohexanone azine (*c*-HA) with two equivalents of PCl_3 in pyridine. Compound **1** revealed one-dimensional chains in crystal with short intermolecular interactions [3.194(1) Å] between phosphorus atoms of adjacent molecules. Treatment of *c*-HA with MeLi (2 equiv. in Et_2O) followed by addition of PCl_3 gave **1** in 33 % yield. An amount of *c*-HA isomerizes in these conditions to form corresponding hexahydroindazole derivative **3**, which further reacts with **1** to give diazaphosphole **5** as transannulation product. Copper monochloride forms an (1:1) adduct with **5**, which was characterized by its X-ray crystal structure. Only one equivalent of PCl_3 reacts with *c*-HA in Et_2O/Et_3N mixture to form diazaphospholium chloride **2** and hexahydroindazole **3**.

Introduction

Phosphorus heterocycles are versatile building blocks for the engineering of ligands used for homogeneous catalysis[1] and organic π-conjugated materials with potential application in electronic and optoelectronic devices.[2] Functional heterophospholes are currently receiving increasing attention due to their potential as precursors for these purposes.[3] Among these heterophospholes, dihydro-1,3,2-diazaphospholes are perhaps the most widely investigated precursors of phosphorus analogues of Arduengo carbenes.[4–6] The chemistry of related 1,2,3-diazaphospholes and diazaphospholenes has been extensively studied by *Schmidpeter*, *Bansal* and others.[3,7,8] These compounds are known to take part in cycloaddition reactions.[9] Dialkyl-1*H*- and -2*H*-1,2,3-diazaphospholes became available from ketone hydrazones and PCl_3.[10–13] These reactions start with formation of a P–N bond followed by cyclization involving substitution of the α-hydrogen atom of the alkyl radical *R*. Recently, it has been shown that ketazines may also react with phosphorus trichloride to form various phosphole derivatives depending on the reaction conditions.[14] Like ketones, ketazines are known to be easily deprotonated at the α-C position by alkyllithium reagents.[15] Since the azine bridge (=N–N=) prevents conjugation,[16] an excess of alkyllithium reagent usually results in a dilithium derivative. The 1,6-dianions thus formed can be used for preparation of various organic[17] or organoelement[14,18,19] compounds. Alternatively, direct reaction of a ketazine with PCl_3 is also possible. The unique example is the reaction of PCl_3 with bis(*tert*-butyl-methyl)ketazine, which affords 1,2-diaza-3-phosphacyclopenta-3,5-diene and the 1,5-diaza-2,6-diphospha-bicyclo[3.3.0]octa-3,7-diene in a 2:1 ratio, respectively.[14] The mechanism for the formation of the latter compounds is not readily apparent. Perhaps it includes direct interaction of the nitrogen lone pairs of ketazine with the electrophile PCl_3 to form the Lewis acid-base adduct.[20] Such interaction increases the acidity of α-hydrogen atoms and facilitates the dehydrochlorination process (Scheme S1, Supporting Information). So, further studies of the related reactions promise interesting findings in phosphorus-nitrogen chemistry and, in particular, in the chemistry of heterophospholes. We herein report the reaction between cyclohexanone azine and phosphorus trichloride in various conditions, which affords a novel annulated diazaphosphole and demonstrates its unusual transannulation.

Results and Discussion

The reaction of cyclohexanone azine with PCl_3 in the molar ratio of 1:2 in pyridine was carried at ambient conditions for 24 h. The abundant precipitate of Py(HCl) was filtered off; a single phosphorus-containing product (**1**) of this reaction was separated by crystallization from MeCN and purified by sublimation at 160 °C and 6.66 Pa (Scheme 1). Crystals, suitable for X-ray analysis, were obtained by crystallization from pyridine. The molecular structure of **1** with selected bond lengths and angles is shown in Figure 1; crystallographic data are summarized in Table 1.

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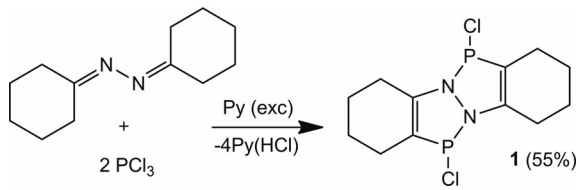
Table 1. Crystal and structure refinement for compounds **1** and **4**.

	1	**4**
Empirical formula	$C_{12}H_{16}Cl_2N_2P_2$	$C_{18}H_{26}Cl_{1.88}Cu_{0.88}N_2P$
Formula weight	321.11	423.94
Temperature, K	150(2)	100(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a /Å	7.2912(5)	7.6203(3)
b /Å	6.9859(5)	10.2144(4)
c /Å	14.1252(9)	12.9043(5)
α /°	90	106.1700(10)
β /°	102.2080(10)	99.1890(10)
γ /°	90	93.1020(10)
Volume /Å^{-3}	703.21(8)	947.15(6)
Z	2	2
Crystal size /mm^3	$0.38 \times 0.16 \times 0.16$	$0.19 \times 0.09 \times 0.08$
Absorption coefficient /mm^{-1}	0.672	1.374
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. /min. transmission	0.9001 / 0.7843	0.8980 / 0.7803
Density (calculated), Mg·m^{-3}	1.517	1.486
Reflections collected	4341	7989
Independent reflections	1521 [R(int) = 0.0157]	3628 [R(int) = 0.0215]
Data / restraints / parameters	1521 / 0 / 82	3628 / 0 / 227
R indices [$I > 2\sigma(I)$]	R_1 = 0.0314, wR_2 = 0.0863	R_1 = 0.0392, wR_2 = 0.0934
R indices (all data)	R_1 = 0.0333, wR_2 = 0.0879	R_1 = 0.0465, wR_2 = 0.0971
Largest diff. peak and hole /e·Å^{-3}	0.604 and –0.239	0.843 and –0.318



Scheme 1. *S*ynthesis of 6,12-dichloro-1,2,3,4,7,8,9,10-octahydro-6H,12H-[1,2,3]benzodiazaphospholo[2,1-a][1,2,3]benzodiazaphosphole (**1**).

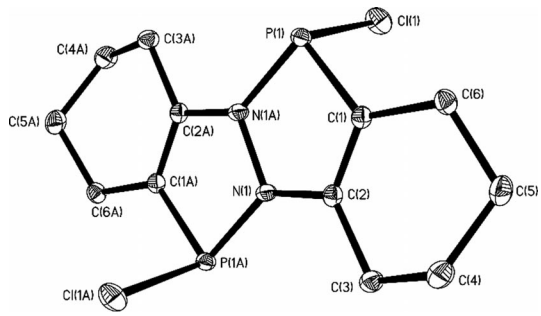


Figure 1. The molecular structure of **1** with ellipsoids of 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /° for **1**: P(1)–N(1A) 1.693(1), P(1)–C(1) 1.798(2), P(1)–Cl(1) 2.1762(6), N(1)–C(2) 1.390(2), N(1)–N(1A) 1.413(2), C(1)–C(2) 1.347(2); N(1A)–P(1)–C(1) 88.11(6), N(1A)–P(1)–Cl(1) 104.35(5), C(1)–P(1)–Cl(1) 99.09(5), C(2)–N(1)–N(1A) 109.5(1). Symmetry transformations used to generate equivalent atoms A: $-x,-y,-z$.

The crystal structure shows that replacement of two α-hydrogen atoms in both cyclohexane rings of *c*-HA occurred. Compound **1** is centrosymmetric; the inversion center is located in the middle of the N(1)–N(1A) bond. Two PCl units are accommodated in five-membered heterocycles resulting in a tetracyclic system comprising two N,N′-annulated 1,2,3-diazaphosphole rings both attached to the cyclohexene rings. The five-membered heterocycles adopts a nearly planar conformation; mean deviation of the atoms P(1), C(1), C(2), N(1), and N(1A) from the plane is 0.051 Å; the sum of bond angles at nitrogen atoms is 358.1(4)°. The lengths of the C–C linkages in the heterocycles, 1.347(2) Å, are in the range expected for C(sp^2)–C(sp^2) bonds. The planar PCCN fragments are also coplanar. The phosphorus atoms are strongly pyramidalized and the sum of bond angles is 291.55°. The P–Cl bond length [2.1762(6) Å] lies in the normal range and is shorter than the bonds in the related 1,3,2-diazaphospholidines (2.20–2.30 Å).[21,22] The structural parameters of heterocycles in **1** are very close to those observed in the related diazadiphosphole, which was synthesized from the dilithium salt of bis(*tert*-butylmethyl)ketazine and PCl_3.[14] Crystal packing analysis of **1** revealed short intermolecular interactions between the phosphorus atoms of adjacent molecules, which form one-dimensional chains in the crystal structure. Part of the chain is depicted in Figure 2. The intermolecular distances P(1A)···P(1AB) and P(1B)···P(1AC) are notably shorter [3.194(1) Å], than the sum of van-der-Waals radii of the phosphorus atoms (3.8 Å[23]). Short intermolecular interactions are well known for pnicogens and pnicogen compounds;[24] a possible model for the P···P nonbonding interaction might be a negative hyperconjugation of the lone pair of electrons at phosphorus of one molecule with the *anti*-bonding orbital $\sigma^*_{P'N'}$ at the adjacent phosphorus and the substituent along the P···P axis[24,25].

The ^{31}P NMR chemical shift of **1** (δ =108.6 ppm) falls in the expected range for dihydro-1,2,3-diazaphospholes containing covalent P–Cl bonds at three-coordinate phosphorus atom.[14,26] The infrared spectrum of **1**, listed in Figure S1

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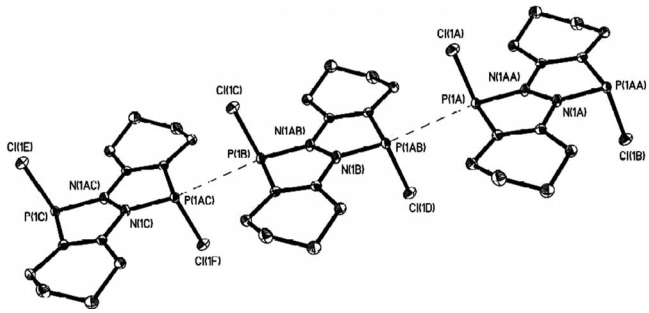
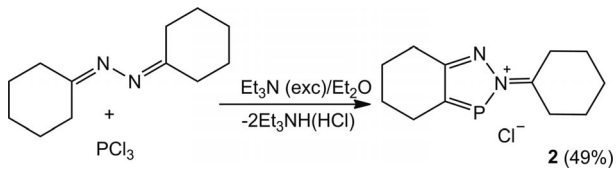


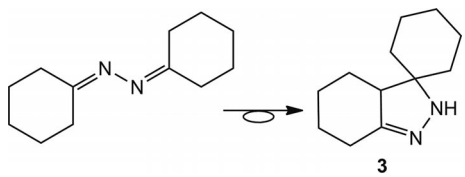
Figure 2. Crystal packing fragment of **1** with ellipsoids of 30 % probability. Hydrogen atoms are omitted for clarity.

(Supporting Information), was in agreement with the found structure. An intense absorbance between 1100 and 1300 cm^{-1} was observed. This is a characteristic of the PN skeleton of cyclic phosphorus-nitrogen compounds.[27] The bands at 465 and 480 cm^{-1} in this spectrum were assigned to the P–Cl stretching vibrations.

The reaction of cyclohexanone azine with PCl_3, was carried out in diethyl ether in the presence of triethylamine. It gave another organophosphorus product with a chemical shift at δ = 214.0 ppm in the ^{31}P NMR spectrum. In these conditions only one equivalent of PCl_3 reacts with *c*-HA to form diazaphospholium chloride **2** (Scheme 2). Microanalytical data for **2** were satisfactory and the mass spectrum gave the expected parent ion (*m*/*z* = 221.1) and fragmentation patterns (Figure S2, Supporting Information). Note that the reaction proceeds very slowly (one week) giving the hexahydroindazole derivative **3** as a side product in 15 % yield (Scheme 3).



Scheme 2. Reaction of *c*-HA with PCl_3 in diethyl ether. Formation of 2-cyclohexylidene-4,5,6,7-tetrahydro-*2H*-1,2,3-benzodiazaphosphol-2-ium chloride (**2**).



Scheme 3. Isomerization of *c*-HA into 2′,3a′,4′,5′,6′,7′-hexahydrospiro-[cyclohexane-1,3′-indazole] (**3**).

Cyclohexanone azine can be converted into 4,5-dihydropyrazoles by reaction in acidic conditions, as reported by *Stolle* and *Hanusch* in 1930.[28] The hydrochloride of **3** was isolated in crystalline form and characterized by ^1H NMR spectroscopy, elemental analysis and mass spectrometry. It demonstrated some differences in comparison with the spectrum of isomeric *c*-HA (Figures S3 and S4, Supporting Information). By using tetrahydrofurane instead of Et_2O in the reaction of cyclohexanone azine with PCl_3 in the presence of triethytlamine, a mixture of the products **1** and **2** was observed. It thus became obvious that the solvent plays a crucial role in this reaction.

Additionally, the reaction of PCl_3 with the dilithium derivative of cyclohexanone azine was carried out. Lithiation of *c*-HA was performed by addition of MeLi to a diethyl ether solution of *c*-HA. The first equivalent of MeLi reacted for a few minutes; the process was accompanied by a fast methane evolution. Reaction with the second equivalent of MeLi was completed after 48 h. The dilithium derivative of *c*-HA further reacted with two equivalents of PCl_3 in diethyl ether to give a yellow solution and precipitated LiCl. Compound **1** was separated from the reaction mixture in 33 % yield. Note, that only two P–Cl groups are consumed by the dilithium derivative. This may be one of the reasons of the smaller yield of **1** compared to the reaction in pyridine. The remaining two P–Cl fragments may react with *c*-HA due to its basic properties. Actually, *c*-HA hydrochloride was found in the reaction products in a small amount, together with the hydrochloride of its isomer **3**. Furthermore, the ^{31}P NMR spectrum of the oily residue showed two novel signals at δ = 199.8 and 196.7 ppm. The chromatography-mass spectrometry measurements (Figure S5 and Figure S6, Supporting Information) revealed formation of two novel compounds with highest mass peaks at 301 and 140 *m*/*z*. The CuCl adduct **4** of one of the products (**5**), having highest mass peak at 301 *m*/*z* was isolated and fully characterized. According to the X-ray analysis it turned to be the transannulation product, which was formed by side reaction of the dichloro derivative **1** with hexahydroindazole **3**. The molecular structure of **4** with selected bond lengths and angles is shown in Figure 3. The crystallographic data of **4** are summarized in Table 1.

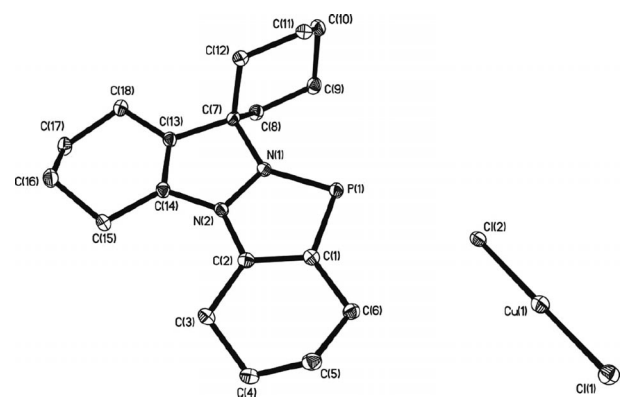
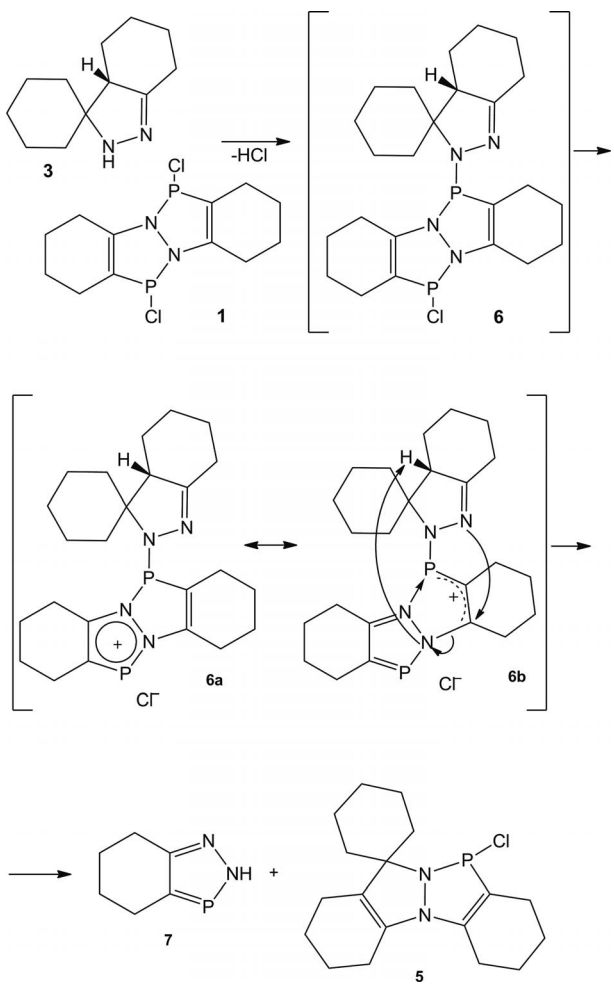


Figure 3. The molecular structure of **4** with ellipsoids of 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths / Å and angles /° for **4**: P(1)–N(1) 1.686(2), P(1)–C(1) 1.731(2), N(1)–N(2) 1.364(2), N(1)–C(7) 1.500(2), N(2)–C(2) 1.349(3), N(2)–C(14) 1.414(2), C(1)–C(2) 1.397(3), C(13)–C(14) 1.326(3), Cu(1)–Cl(2) 2.0762(6), Cu(1)–Cl(1) 2.0982(7); Cl(2)–Cu(1)–Cl(1) 179.47(3), N(1)–P(1)–C(1) 89.73(9), N(2)–N(1)–C(7) 109.3(2), N(2)–N(1)–P(1) 113.8(1), C(7)–N(1)–P(1) 136.9(1), C(2)–N(2)–N(1) 112.9(2), C(2)–N(2)–C(14) 137.0(2), N(1)–C(7)–C(13) 100.1(2).

The organic (cationic) component of compound **4** may be considered as hexahydroindazole **3**, attached to a half part of

compound **1**. The polycyclic system of **4** includes two five-membered N,N′-annulated heterocycles (C_3N_2 and C_2N_2P) both attached to the cyclohexene rings. The phosphole ring exhibits planar conformation whereas the C_3N_2 ring is nearly planar. The mean deviation of the atoms N(1), N(2), C(14), C(13), C(7) from the mean plane C_3N_2 is 0.022 Å. The angle between the C_2N_2P and C_3N_2 planes is 2.9°; the sums of bond angles at the nitrogen atoms are 360.0° (N1) and 359.9° (N2). The nitrogen–nitrogen bond length in **4** [1.364(2) Å] is notably shorter than that [1.413(2) Å] in **1**. The C(1)–C(2) distance of 1.397(3) closely resembles the aromatic C–C bond. These data are indicative of better cyclic conjugation in the positively charged diazaphosphole ring of **4** relative to that in **1**. Note that the C(13)–C(14) distance of 1.326(3) Å is close to a normal carbon–carbon double bond in alkenes. The presence of a quaternary carbon atom [C(7), Figure 3] impedes the cyclic conjugation in the C_3N_2 heterocycle. The anionic part of **4** is the linear $[CuCl_2]^-$ anion, which is formed by chloride ion transfer from dihydrodiazaphosphole **5** to CuCl. In the crystal of **4**, the short intermolecular interaction occurs between the P(1) atom of the organic cation and the Cl(2) atom of the $[CuCl_2]^-$ anion. The distance of intermolecular P(1)···Cl(2) contact [3.311(1) Å] is substantially shorter than the sum of corresponding van der Waals radii (3.7 Å).[23] Schematic representation of the formation of **5** is shown in Scheme 4. Tentatively, the first step of the reaction between the chlorophosphine **1** and the secondary amine **3** is the P–N bond formation resulting in the intermediate product **6**, which undergoes subsequent fragmentation. The nitrogen (sp^2) atom of hexahydroindazole part of **6** coupled with the carbon (sp^2) atom of the diazadiphosphole fragment. This interaction is facilitated in transition state by positive charge transfer from phosphorus to conjugated sp^2-carbon, as depicted in structure **6b**. Presumably, the hydrogen atom at the tertiary carbon atom of the hexahydroindazole part is transferred to the nitrogen atom of the diazadiphosphole fragment followed by cleavage of the N–P and N–C bonds to form two novel diazaphospholes **5** and **7**. It seems that compound **5** may easily extrude the halide anion to form diazaphospholium cation with a highest mass peak at 301 *m*/*z* in the mass spectrum. This is in agreement with the 6e-aromatic delocalization found in similar $C_2N_2P^+$ five membered heterocycles.[11,29]

The transannulation reaction described above seems to be energetically favorable since two non-aromatic molecules after interaction gave the aromatic diazaphosphole **7** and compound **5**, which is the precursor of the aromatic diazaphosphonium cation. It should also be noted that the control reaction of dichlorodiazaphosphole **1** with cyclohexanone azine gave no products. The structure of the intermediate **6** was fully optimized by the B3LYP/6-31G(d) method and characterized as energy minimum on the hypersurface by means of a vibrational analysis. The arrangement and selected bond lengths for **6** are shown in Figure 4 and Table 2 respectively. Notably, that the P_{26}–N_{23} (1.787 Å) and N_{22}–C_{24} (1.400 Å) bonds are significantly elongated, whereas the nitrogen atom (N_8) of the pyrazolyl fragment is coordinated to the positively charged sp^2



Scheme 4. Schematic representation of the proposed mechanism for the reaction of **1** with hexahydroindazole **3**.

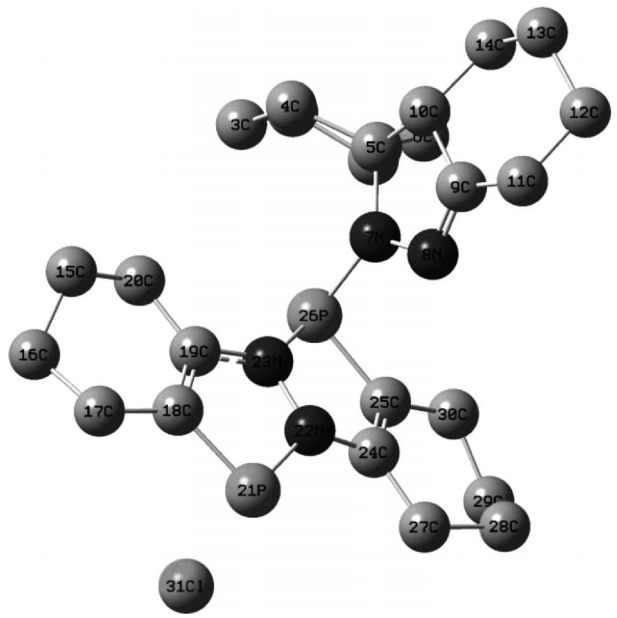


Figure 4. The molecular structure of the intermediate **6** optimized at the B3LYP/6-31G(d) level.

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carbon atom (C_{24}) of diazadiphosphole, which explains the ease of the transformation to **5** and **7**. The Cl_{31}–P_{21} bond is quite long (2.312 Å) that may be explained by hyperconjugation effects between the six π electrons in the C_2N_2 unit and the σ*(P-Cl) orbital.[4] The Mulliken charges for the intermediate **6** are shown in Figure S7 (Supporting Information).

Table 2. Calculated bond lengths in **6**.

Cl_{31}–P_{21}	2.312
P_{21}–N_{22}	1.727
N_{22}–N_{23}	1.408
N_{23}–P_{26}	1.787
P_{26}–N_7	1.726
C_{19}–N_{23}	1.368
C_{24}–N_{22}	1.400
C_{18}–C_{19}	1.370
C_{24}–C_{25}	1.349
N_{22}–C_{24}	1.400
N_{23}–C_{19}	1.368

Surprisingly, a better yield of **4** was observed when a solution of $Cu(MeCN)_4BF_4$ was added to the mother liquor containing diazaphospholes **5** and **7**. This is possibly due to fast ion exchange and better solubility of copper(I) tetrafluoroborate unlike CuCl.

Conclusions

The results of our study illustrate that the annulated dichlorodiazaphosphole **1** may be easily synthesized by reaction of cyclohexanone azine with two equivalents of PCl_3 in pyridine in 55 % yield. The reaction of dilithiated cyclohexanone azine with PCl_3, which gives a 33 % yield of **1**, is a complicated process that is accompanied by isomerization of *c*-HA into 4,5-dihydropyrazole. The latter further reacts with **1** to give the product of re-annulation **5**, in which one of the diazaphosphole rings replaced by the dihydropyrazole fragment. Copper(I) chloride reacts with **5** to form the adduct **4**, which could be structurally characterized.

Experimental Section

General Remarks: Solvents were purified following standard methods.[30] Toluene and pyridine were thoroughly dried with sodium hydride and distilled prior to use. Diethyl ether and THF were dried and distilled over Na/benzophenone. Phosphorus trichloride and cyclohexanone azine were purchased from Sigma-Aldrich Chemical Co. and distilled before use. All manipulations were performed in a vacuum or in an argon atmosphere using standard Schlenk techniques. NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions with a Bruker DPX-200 device. Infrared spectra were recorded with a Perkin-Elmer 577 spectrometer from 4000 to 400 cm^{-1} in nujol or with a Perkin-Elmer FT-IR spectrometer System 2000 as KBr mulls. GC-MS spectra were recorded with an "Trace GC Ultra"-"Polaris Q" device with ion trap mass analyzer.

Computational Details: DFT calculations performed in this work were carried out at the B3LYP/6-31G(d) level of theory with the Gaussian 03 package (Supporting general information). The optimized geometry of **6** corresponds to energy minima, as indicated by frequency computations. For the geometry optimization we used the full structure without simplification and the B3LYP/6-31G(d) level of theory. The structure corresponds to an energy minimum.

X-ray Crystallography: Intensity data for **1** and **4** were collected with a Smart Apex diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) in the ω-ϕ scan mode (ω = 0.3°, 10 sec on each frame). The intensity data were integrated by SAINT program.[31] SADABS[32] was used to perform area-detector scaling and absorption corrections. The structures of **1** and **4** were solved by direct methods and were refined on F^2 using all reflections with SHELXTL package.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined in the "riding-model" and refined isotropically. In crystal of **4** the $[CuCl_2]^-$ anion is disordered with Cl^- anion occupancies of disordered anions of 0.88 and 0.12, respectively.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-848933 (**1**) and CCDC-848934 (**4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Reaction of *c*-HA with PCl_3 in Pyridine. Synthesis of 1: Phosphorus trichloride (1.09 g,7.9 mmol) was added to a solution of cyclohexanone azine (0.46 g, 2.4 mmol) in pyridine (15 mL) at 0 °C. The color immediately turned to yellow. The resulting solution was allowed to stand at room temperature for 24 h, upon which pyridine hydrochloride precipitated. The mixture was filtered; the solvent was evaporated under reduced pressure and changed for acetonitrile. Soon after dissolution in acetonitrile, yellow crystals of the crude product precipitated. Sublimation at 160 °C (2.67 Pa) gave 0.42 g (55 %) of **1**. $C_{12}H_{16}Cl_2N_2P_2$: calcd. C 44.88; H 5.02; N 8.72; P 19.29 %; found C 44.82; H 5.08; N 8.69; P 19.32 %. **^{1}H NMR** ($CDCl_3$, 295 K): δ = 1.50–2.10 (m, 8 H, CH_2 at 2,3,8,9 C-atoms); 2.32–2.56 (m, 4 H, CH_2 at 4 and 10 C-atoms), 2.65–2.80 (m, 4 H, CH_2 at 1 and 7 C-atoms) ppm. **^{13}C NMR** ($CDCl_3$, 295 K): δ = 23.1–23.6 [m, 2C (4, 10)], 22.1–22.6 [m, 2C (1,7)]; 21.3–22.1 [m, 4C-(2,3,8,9)]; 144.9 [m, 2C, (4a, 10a)]; 116.6 [m, 2C, (6a, 12a)] ppm. **^{31}P{^{1}H} NMR**: δ = 108.6 ppm. **IR** (nujol): $\tilde{\nu}$ = 1589 m, 1347 w, 1287 m, 1247 m, 1181 m, 1161 m, 1130 w, 1025 m, 960 m, 920 m, 854 w, 807 m, 756 w, 723 w, 684 m, 610 w, 589 m, 545 s, 480 m, 466 w cm^{-1}.

Reaction of *c*-HA with PCl_3 in Et_2O. Formation of 2 and 3: Phosphorus trichloride (1.13 g, 8.2 mmol) was added to a mixture of cyclohexanone azine (1.00 g, 5.2 mmol) and Et_3N (1.99 g, 19.7 mmol) in Et_2O (20 mL) at 0 °C. The resulting solution was allowed to stand at room temperature for a week, upon which triethylamine hydrochloride precipitated. The mixture was filtered and concentrated under reduced pressure. Pale yellow crystals of **2** were obtained overnight from a concentrated solution at 0 °C. Yield 0.65 g (49 %). $C_{12}H_{18}N_2PCl$ (**2**): calcd. C 56.14; H 7.07; N 10.91; P 12.07; Cl 13.81 %; found C 56.08; H 7.11; N 10.88; P 12.10; Cl 13.76 %. **^{1}H NMR** ($CDCl_3$, 295 K): δ = 3.0–2.5 (m, 4H, (CH_2 at 9 and 13 C-atoms), 2.5–1.4 (m, 14H, CH_2 at 4,5,6,7,10,11,12 C-atoms) ppm. **^{31}P{^{1}H} NMR:** δ = 214.0 (s) ppm. **MS**, *m/z* (%): 221.1 (16) $[M]^+$-Cl, 220.1 (100) $[M]^+$-HCl, 192.3 (60), 141.2 (37).

The Remaining solvent was fully removed from the mother liquor under reduced pressure, and CH_2Cl_2 was added. Colorless crystals of **3**·HCl were precipitated overnight. Yield 0.15 g (15 %). $C_{12}H_{21}ClN_2$ (**3**·HCl): calcd. C 63.00; H 9.25; Cl 15.50; N 12.25 %; found C 62.93;

H 9.30; Cl 15.47; N 12.21 %. **^{1}H NMR** ($CDCl_3$, 295 K): δ = 11.8 (s, broad, 2 H, HN^+), 3.0–2.6 (2 H, N = CCH_2), 2.50–1.10 (m, 17 H, CH and 7 CH_2) ppm. **MS**: *m/z* (%):192.3 (20) $[M]^+$, 149.4 (100) $[M-C_3H_7]^+$, 136.3 (60), 107.2 (32). **IR** (nujol): $\tilde{\nu}$ = 2613 s, 2495 s, 1398 m, 1270 w, 1240 m, 1173 m, 1036 m, 1007 m, 954 w, 877 w, 807 m cm^{-1}.

Reaction of Lithiated *c*-HA with PCl_3. Synthesis of 1 and 4: A solution of MeLi in diethyl ether (1 M, 20.0 mL) was added dropwise at 0 °C to a solution of cyclohexanone azine (1.92 g, 10 mmol) in the same solvent. The mixture was allowed to stand for a 43 h, at room temperature for completing the reaction, afterwards PCl_3 (2.75 g, 72 mmol) in E_2O (20 mL) was added at 0 °C under vigorous stirring. The mixture was filtered and the solvent was evaporated under reduced pressure. Yellow crystals of **1**, precipitated overnight were collected. The yield of the crude product **1** was 33 %. The mother liquor was separated from the crystals of **1**, and allowed to react with an excess of $Cu(MeCN)_4BF_4$ (3.14 g, 10.0 mmol) in THF solution. Colorless crystals of **4** were precipitated overnight. Yield 1.22 g (28 %). $C_{18}H_{26}Cl_2CuN_2P$: calcd. C 49.60; H 6.01; Cl 16.27; N 6.43 %; found C 49.22; H 6.12; Cl 16.31; N 5.39 %. **IR** (nujol): $\tilde{\nu}$ = 1285 m, 1270 w, 1247 w, 1180 m, 1138 m, 1096 m, 1040 w, 1012 w, 962 w, 922 m, 873 w, 839 w, 817 w, 772 m, 722 s, 578 m, 542 m, 500 w cm^{-1}. The compound **4** decomposed at 190 °C (0.1 Torr) to give pure **5** and copper(I) chloride.

Supporting Information (see footnote on the first page of this article): Nomenclature and atom numbering schemes for the polycyclic compounds **1**, **2**, **3**, **5**, and **7**. IR spectrum of **1**; mass spectra for compounds **2**, **3**, **5**, and **7**; Mulliken charges for the intermediate **6**.

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