Synthesis and characterization of a 2-chloro-1,3,2-diaza-phospholidine-4,5-diimine

Georgios Mourgas,[a] Zoltan Benkö,[b] Daniela Förster,[a] Martin Nieger,[c] and Dietrich Gudat[a*]

[a] Institut für Anorganische Chemie, University of Stuttgart, Pfaffenwaldring 55, 70550 Stuttgart, Germany

[b]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, H-1111 Budapest

[c]Laboratory of Inorganic Chemistry, University of Helsinki, A.I. Virtasen aukio 1, Helsinki, Finland

Email: gudat@iac.uni-stuttgart.de

Dedicated to Professor A. J. Arduengo on the occasion of his 60th birthday

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Abstract

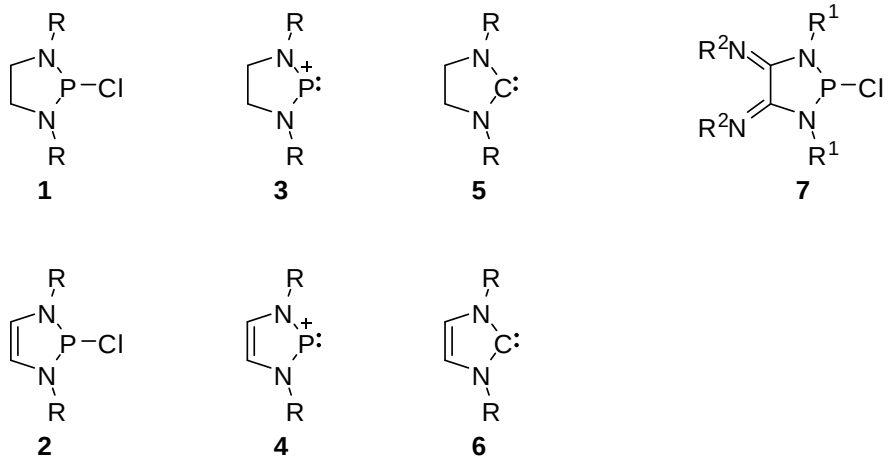
An oxalamidine **10a** was used as precursor for the synthesis of 2-chloro-1,3,2-diaza-phospholidine-4,5-diimine **7a**. Both products were characterized by single-crystal X-ray diffraction studies which revealed for **7a** the presence of an unusually short P–Cl bond distance. In contrast to other known 2-chloro-1,3,2-diazaphospholidines, **7a** fails to react with gallium trichloride, trimethylsilyl trilate, or silver triflate via heterolytic P–Cl bond fission and formation of an N-heterocyclic phosphenium ion. A computational study suggests that this unusual behavior is due to the fact that the exocyclic imino-groups stabilize the P–Cl bond in **7a** by diminishing the hyperconjugation between the lone-pairs of the ring nitrogen atoms and the σ*(P–Cl) orbital and destabilize at the same time the hypothetical phosphenium cation.

Keywords: Phosphorus heterocycles, nitrogen heterocycles, phosphenium cations, P–Cl bonds, X-ray structure, DFT calculations

Introduction

Five-membered phosphorus-nitrogen heterocycles like 1,3,2-diazaphospholidines **1** [1] and 1,3,2-diazaphospholenes **2** [2,3,4] (Scheme 1) are of central importance for the synthesis of stable phosphenium ions **3**, **4** with a cationic, two-coordinate phosphorus atom [5,6,7] which are isoelectronic analogues to neutral diaminocarbenes **5**, **6**, respectively. Whereas cations **3** with

CC-saturated heterocyclic rings were among the first phosphenium ions ever prepared,[8] the interest in the CC-unsaturated N-heterocyclic phosphenium ions (NHP) **4** [2,4] developed only much later in the wake of the rise of the chemistry of stable N-heterocyclic carbenes (NHC).[9] The most widely applied synthetic approach to access both CC-saturated and unsaturated phosphenium ions involves reactions of neutral precursors **1**, **2** with suitable electrophiles (e. g. $AlCl_3$, $GaCl_3$, AgOTf, Me_3SiOTf etc.) under heterolytic cleavage of the phosphorus-chlorine bonds.[5,6,7] Cations **4** have alternatively been accessed via a [1+4]-cycloaddition route starting from a diazabutadiene and a transient P(I) fragment generated via disproportionation of PI_3, or via reduction of PCl_3 with $SnCl_2$, respectively.[10] In view of this approach we became interested in the synthesis of derivatives **7** featuring both a five-membered phosphorus-nitrogen heterocycle and a diazabutadiene moiety. Molecules of this type have not only a large potential as bridging ligands in coordination chemistry, but offer also a prospect to generate functional phosphenium ions via P–Cl bond heterolysis, or prepare novel fused heterocyclic systems via subsequent [1+4]-cycloadditions. Herein we report on our first results on synthesis and characterization of a novel 2-chloro-1,3,2-diazaphospholidine of type **7**, and its reactivity towards electrophiles.



Scheme 1. (R, R^1, R^2 = alkyl, aryl)**.**

Results and Discussion

The oxalamidine precursor **10a** was prepared as shown in Scheme 2 following a published protocol.[11] In a first step, oxalyl chloride was reacted with 2,6-diisopropyl aniline in the presence of triethylamine to give oxalic diamide **8a** which was then converted to oxalimidoyl dichloride **9a** by reaction with PCl_5. Further condensation with 2,6-dimethyl aniline finally gave oxalamidine **10a** which was isolated in reasonable yield after crystallization. A single-crystal X-ray diffraction study (Fig. 1) revealed that the oxalamidine unit adopts a transoid, strongly twisted (twist angle 45°) C_2-symmetrical conformation in which the amide protons are located at

the 2,6-dimethylphenyl groups and the C=N double bonds feature *E*-configuration. The N1–C2 (1.284(3) Å) and C2–N3 distances (1.361(2) Å) represent typical double and single bonds, and their large difference indicates a quite low degree of conjugation within the amidine NCN-moiety.[14] The observation of broadened resonances in room temperature ^{1}H NMR spectra suggests that in solution, as in the case of other oxalamidines,[11] a mixture of several rapidly equilibrating prototropic and conformational isomers is present.

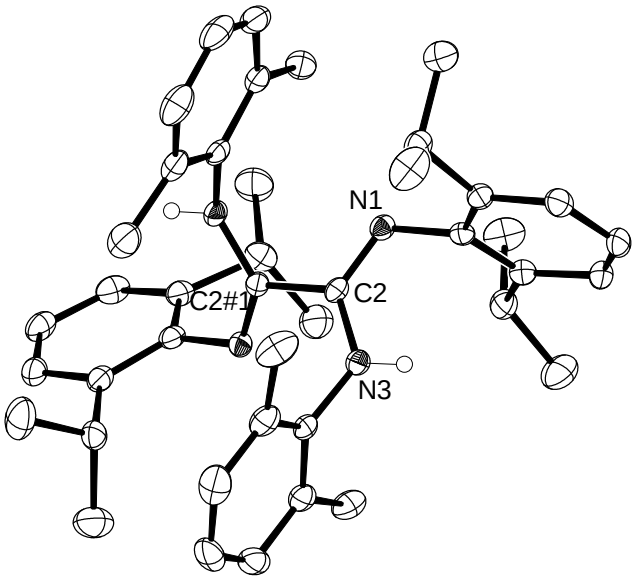
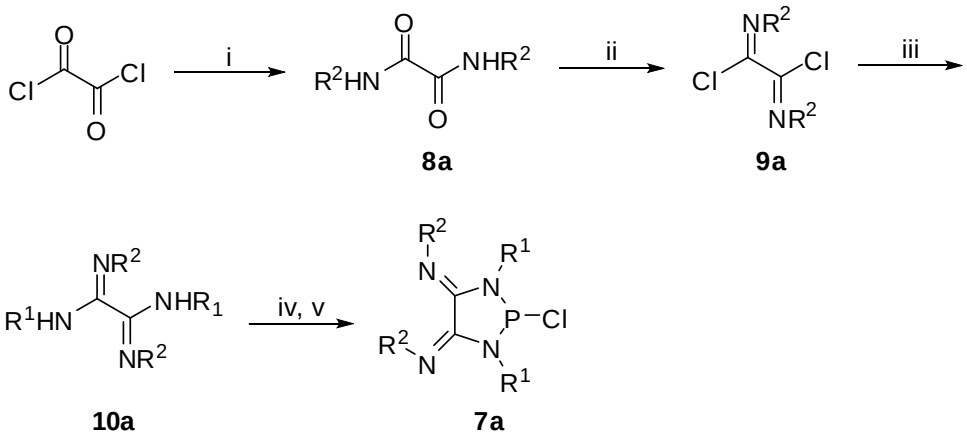


Figure 1. Molecular structure of **10a**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except those of NH-groups, were omitted for clarity. Equivalent atoms were was generated by symmetry transformation: #1 -x+1,y,-z+3/2. Selected bond distances [Å]: N1–C2 1.284(3), C2–N3 1.361(2), C2 –C2#1 1.518(4).

Attempts to prepare 2-chloro-1,3,2-diazaphospholidine **7a** like other derivatives of the same type [12,13] via base-induced condensation from **10a** and PCl_3 using triethyl amine as acid scavenger failed and resulted only in isolation of the corresponding oxalamidinium salt. However, conversion of **10a** to **7a** was finally accomplished after deprotonation of **10a** with two equivalents butyl lithium at -78°C and subsequent addition of PCl_3. The product was isolated after work-up as a yellow, air and moisture sensitive powder and characterized by analytical and spectral data. The ^{31}P NMR chemical shift of 134 ppm is close to the lower end of the range of approx. 138 – 155 ppm reported for other 1,3-diaryl-1,3,2-diazaphospholidines.[12,13] The occurrence of broadened signals in ^{1}H NMR spectrum can be explained as a consequence of dynamic processes associated with hindered rotation of N-aryl moieties and, possibly, inversion of imino-nitrogen atoms. A notable feature in the EI mass spectrum is the lack of an $[M\text{-}Cl]^+$ fragment peak which is a prominent attribute in the mass spectra of diamino chloro phosphines.[7]



Scheme 2. Synthesis of **7a** (R^1 = 2,6-dimethyl-phenyl; R^2 = 2,6-diisopropyl-phenyl). Conditions and reagents: i) 2 equivs. R^2NH_2, NEt_3, THF, 0°C; ii) PCl_5, toluene, 16h reflux; iii) 2 equivs. R^1NH_2, NEt_3, toluene, reflux; iv) 2 equivs, BuLi, THF, -78°C; v) 1 equiv PCl_3.

Single crystals of **7a** were obtained after crystallization from hexane at -20 C° and were characterized by single-crystal X-ray diffraction. A graphical representation of the molecular structure is shown in Fig. 2. Important bond distances and angles are summarized in Table 1.

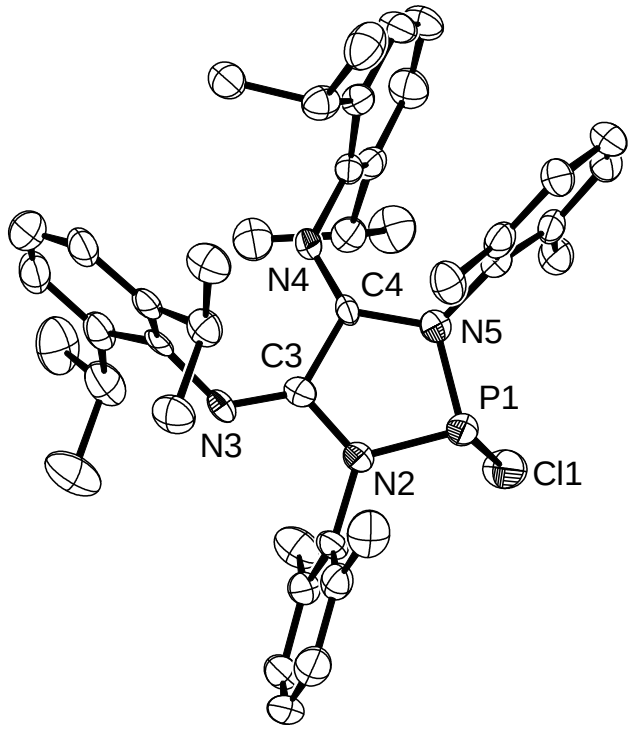


Figure 2. Molecular structure of **7a**. Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms were omitted for clarity.

Table 1. Selected bond distances (Å) and angles (°) for **7a**

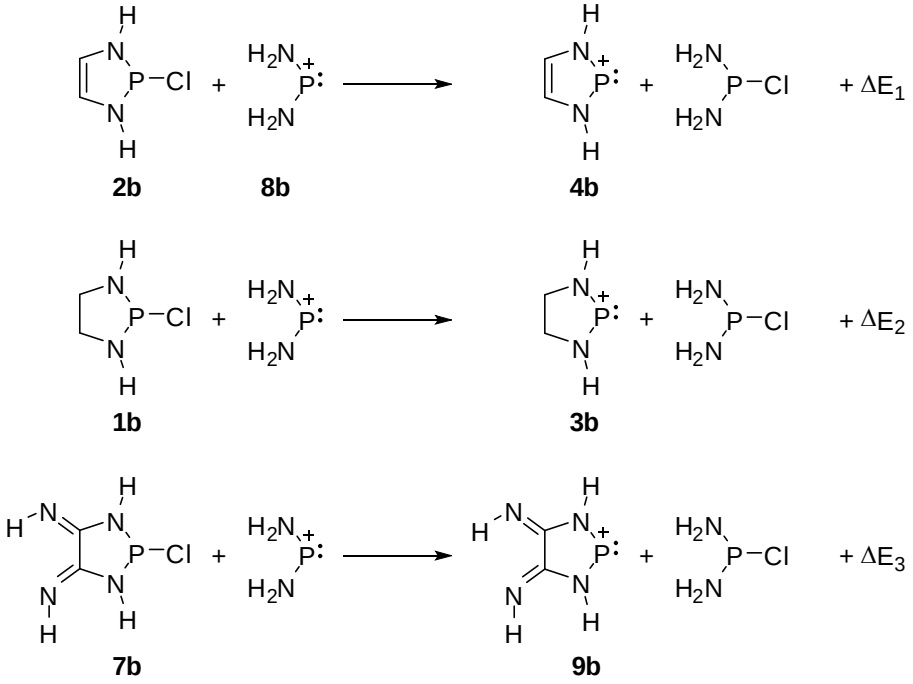
P1-Cl1	2.127(2)	N2-P1-Cl1	101.8 (2)
P1-N2	1.700(4)	N5-P1-Cl1	103.9 (2)
P1-N5	1.708(5)	N2-P1-N5	90.1 (2)
C3-N3	1.267(6)	C3-N2-P1	117.1(3)
C4-N4	1.253(6)	N2-C3-C4	108.1(4)
C3-C4	1.521(7)	C3-C4-N5	108.3 (4)
N5-C4	1.425(6)	C4-N5-P1	115.3(3)
N2-C3	1.390(6)	C4-N4-C34	123.7 (4)
		C3-N3-C22	124.7 (4)

As a consequence of the structural constraints imposed by formation of the heterocyclic ring, the oxalamidine unit in **7a** displays a cisoid conformation. The twist angle between both amidine units is much smaller (5°) than in **10a** and enforces a perceptibly non-planar conformation of the heterocyclic ring. The central C3–C4 distance is similar to that in **10a** and suggests likewise the presence of a single bond. The difference between the distances of exocyclic C3–N3/C4–N4 (1.267(6)/1.253(6) Å) and endocyclic N2–C3/C4–N5 distances (1.390(6)/1.425(6) Å) is still more pronounced than in **10a** and indicates an even lower degree of NCN-conjugation within the amidine moieties.[14] In contrast to **10a**, one of the C=N double bonds displays a Z-stereochemistry which enables presumably a minimization of steric interactions between the bulky N-aryl moieties. The coordination geometry at the endocyclic nitrogen atoms exhibits no significant deviation from planarity (sum of bond angles: N2 359.5(11)°, N5 356.7(10)°), and the phosphorus atom features the expected pyramidal coordination (sum of bond angles 295.7(6)°). The P1–N2 and P1–N5 bond distances are longer than in other known 2-chloro-1,3,2-diazaphospholidines (1.65-1.68 Å).[13,15] In contrast, the exocyclic P–Cl bond (2.127(2) Å) matches the common distance in acyclic diaminochlorophosphines (2.13(6) Å [15]) and is substantially shorter than the bond lengths in other 2-chloro-1,3,2-diazaphospholidines (2.17-2.25 Å [13,16]) or 2-chloro-1,3,2-diazaphospholenes (2.24-2.76 Å [15]). Taken together, the observed structural features seem to indicate a bonding situation in which the electron deficient imino-groups compete with the PCl-moiety for mesomeric interaction with the lone-pair of the ring nitrogen atoms. As this effect is expected to weaken the hyperconjugation between the nitrogen lone-pairs and the antibonding σ*(P–Cl)-orbital,[15] less electron density is transferred from the nitrogen lone-pairs into the σ*(P–Cl)-orbital, and the P–Cl bond can thus retain a higher covalent bond order than in other N-heterocyclic chlorophosphines.

As a higher bond order impedes heterolytic cleavage of the P–Cl bond, it can be expected that **7a** is less prone to interact with electrophiles under formation of a phosphenium cation than other N-heterocyclic chlorophosphines. In accord with this expectation, **7a** showed no evidence to react with $GaCl_3$ (1 – 3 equivs.) or excess of Me_3SiOTf under chloride abstraction and formation of a phosphenium ion; monitoring the reaction by ^{31}P NMR indicated that even after prolonged exposure to an excess of reagent at best unspecific decomposition could be observed. Reaction of

a CH_2Cl_2 solution of **7a** with one equivalent of AgOTf produced a precipitate of AgCl together with a solution that contained according to an ^{31}P NMR spectroscopic survey a single phosphorus containing product. Although all attempts toward isolation of this product remained unsuccessful and its constitution remains therefore still in the dark, tentative assignment as a phosphenium cation salt is, however, definitely ruled out by the observed ^{31}P NMR chemical shift of 109 ppm which appears at even higher field as the signal of **7a** and lies far outside the expected range of ^{31}P NMR chemical shifts between 200 and 450 ppm for diaminophosphenium cations.[5,6,7]

The outcome of the reactions of **7a** with electrophiles suggests that the exocyclic imino moieties have an adverse effect on the stability of a diazaphospholidinium cation and its formation is therefore disfavored. This hypothesis is further substantiated by calculated energies of the isodesmic chloride transfer reactions shown in Scheme 3 which allow to estimate the stabilities of phosphenium cations **3b**, **4b**, and **9b** relative to the parent diaminophosphenium ion $[(H_2N)_2P]^+$ as reference.



	B3LYP/6-31+G*	B3LYP/6-311+G**	MP2/aug-cc-pVDZ	CBS-QB3
ΔE_1/kcal mol^{-1}	−18.5	−17.5	−23.8	−16.7
ΔE_2/kcal mol^{-1}	−7.7	−7.5	−7.2	−6.7
ΔE_3/kcal mol^{-1}	13.2	13.3	13.2	13.7

Scheme 3. Calculated reaction energies (in kcal mol^{-1}) of isodesmic chloride transfer reactions at different levels of theory.

The calculation of negative values for ΔE_1 and ΔE_2 at all levels of theory indicates that N-heterocyclic cations **3b** and **4b** are increasingly more stable than **8b** and confirms the results of earlier computational studies in which the same conclusion was derived from the calculated energies of hydride transfer reactions.[4,17] In contrast, ΔE_3 was calculated to be positive at all levels of theory. Comparison of the values of the differences ($\Delta E_1 - \Delta E_2$) and ($\Delta E_3 - \Delta E_2$) suggests that the destabilization imposed by formal replacement of the C_2H_4-backbone of **3b** by two imino-groups (~ +20 kcal mol^{-1}) is approximately twice as large as the extra stabilization brought by the presence of an additional double bond and ring aromatization in **4b** (~ -10 kcal mol^{-1}). Analysis of calculated bond distances, Wiberg Bond indices, and electron densities at the bond critical points (ρ) for the P–Cl-bonds of the model compounds **1b**, **2b**, and **7b** (Table 2) reveals further that decreasing cation stability in the order **4b**, **3b**, **8b** correlates with increasing P–Cl bond shortening in the neutral chlorophosphine precursors **2b**, **1b**, **7b**, and confirms the interpretation of this effect as arising from an increased covalent bond order. The decrease in the NPA charges q(Cl) on the chlorine atom with increasing P–Cl bond shortening suggests in line with the results of previous studies [17] that this trend is also associated with a lower degree of hyperconjugative electron transfer from the nitrogen lone-pairs into the σ*(P–Cl) orbital. Altogether, the computational results allow thus to conclude that the imino-substituents at the heterocyclic ring destabilize the phosphenium cation and strengthen at the same time the P–Cl bond in the neutral chlorophosphine precursor. Cooperation of both effects provides a reasonable explanation for the experimentally observed reluctance of N-heterocyclic chlorophosphine **7b** to undergo electrophile induced heterolytic P–Cl bond cleavage.

Table 2. Bond distances (P–Cl), electron densities at bond critical points (ρ), Wiberg bond indices (WBI) and atomic charges q(P), q(Cl) obtained from Natural Population Analysis (NPA) for the P–Cl bonds in the model compounds **1b**, **2b**, and **7b** as calculated at the B3LYP/6-311+G**-level of theory

	P−Cl / Å	ρ / a.u.	WBI	q(P) / a.u.	q(Cl) / a.u.
1b	2.267	0.0872	0.6905	1.206	−0.477
2b	2.305	0.0822	0.6334	1.162	−0.500
7b	2.185	0.1030	0.8055	1.193	−0.376

Conclusions

A 2-chloro-1,3,2-diazaphospholidine-4,5-diimine was synthesized by reaction of a doubly metalated oxalamidine with PCl_3. The product displays an extraordinarily short P–Cl bond and fails to undergo electrophile induced bond cleavage to give a phosphenium ion. A computational study allows to relate these features to the presence of the exocyclic imino-groups which destabilize the hypothetical phosphenium cation and exert at the same time a stabilizing effect on the P–Cl bond.

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Experimental Section

General. All manipulations were carried out under an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried by standard procedures. Compounds **8a** and **9a** were prepared as previously described.[11] All other chemicals were commercially available and used as received. NMR spectra were recorded on a Bruker Avance 250 (^{1}H, 250.1 MHz; ^{13}C, 62.8 MHz; ^{31}P, 101.2 MHz) spectrometer at 303 K; chemical shifts are referenced to external $SiMe_4$ (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Elemental analyses were determined on a Perkin-Elmer 24000 CHN/O Analyzer. Melting points were determined in sealed capillaries at a Büchi Melting Point B-545 apparatus. Computational studies were carried out with the Gaussian03 package,[18] and the program AIM 2000 [19] was used for Bader analysis of electron densities. The reaction energies listed in Scheme 3 and further data listed in Table 2 were calculated at different levels of theory using molecular structures of model compounds that had previously been optimized at the same level of theory.

***N*'^{1}, *N*'^{2}-Bis(2,6-diisopropylphenyl)- *N*^{1}, *N*^{2}-bis (2,6-dimethylphenyl)oxalamidine (10a).**
Compound **10a** was prepared by the same procedure as had previously been described for other symmetrical oxalamidines. [11] Yield: 56%, light beige powder, mp.: 127°C.
^{1}H NMR (250 MHz, $CDCl_3$, 300K) δ = 1.18 (d, 20H, d, 6.8 Hz, CH_3), 1.25 (d, 4H, 6.8 Hz, CH_3), 2.1 (broad s, 12H, CH_3), 3.15 (broad m, 4H, CH_{iPr}), 6.79-7.0 (broad m, 9H, CH_{aryl}), 7.14 (bs, 2H, CH_{aryl}), 7.20 (broad s, 1H, CH_{aryl}).
Anal. Calcd. for $C_{42}H_{54}N_4$ (614.90): C, 82.04; H, 8.85; N, 9.11% Found: C, 82.05; H, 9.13; N, 8.44%. (+)-EI-MS (70 eV): *m/z (%)* = 614.4 (100) $[M]^+$, 571.3 (80) $[M\text{-}C_3H_7]^+$. IR (ν, cm^{-1}): 3211 (w) (NH); 1635 (m) (C=N).
Preparation of 2-chloro-*N*,*N*'-bis(2,6-diisopropylphenyl)-1,3-bis(2,6-dimethylphenyl)-1,3,2-diazaphospholidine-4,5-diimine (7a). A solution of **10a** (1.0 mmol, 614 mg) in THF (10 ml) was cooled to -78°C, and butyl lithium (2.4 mmol, 960μL of 2.5M soln in hexane) was added slowly**.** The reaction mixture was allowed to warm up to room temperature, stirred for 20 minutes, and cooled down again to -78°C. Then PCl_3 (1.2 mmol, 105μL) was added slowly. The color of the solution turned immediately into yellow. The reaction mixture was allowed to warm to room temperature and stirred overnight. Solvents were evaporated in vacuum to give a yellow foam which was dissolved in hexanes (20 ml) and filtered over Celite. Evaporation of the solvent

gave **7a** as bright yellow microcrystalline powder which was purified by recrystallization from hexanes at -20 °C. Yield: 516 mg, 76% , mp.: 74.5°C. ^{31}P NMR (250 MHz, $CDCl_3$, 300K) δ = 134.8 (s). ^{1}H NMR (250 MHz, $CDCl_3$, 300K) δ = 0.81 (d, 6H, 7 Hz, CH_{3iPr}), 0.8 – 1.2 (broad, 12H, CH_{3iPr}), 1.16 (broad d, 7 Hz, 6H, CH_{3iPr}), 2.37 (broad, 6H, CH_3), 2.46 (s, 6H, CH_3), 2.64 (broad, 2H, CH_{iPr}), 3.05 (broad septet, 2H, CH_{iPr}), 6.48-7.13 (broad m, 12H, CH_{aryl}). Anal. Calcd. for $C_{42}H_{52}ClN_4P$ (679.33): C, 74.26; H, 7.72; N, 8.25% Found: C, 73.27; H, 7.62; N, 8.42%. (+)-EI-MS (70 eV): *m/z (%)* = 678.3 (4) $[M]^+$, 614.4 (70), 244.2 (100). IR (ν, cm^{-1}): 1660 (m) (C=N); 1580(m), 1463 (s); 797 (m); 752 (s).

Crystal structure determinations

Crystallographic data were collected on a Bruker Nonius Kappa CCD diffractometer at 123(2) K (**7a**) or on a Nonius Kappa CCD diffractometer at 100(2) K **(10a)** using Mo-K_α radiation (λ = 0.71073). Direct Methods (SHELXS-97 [20]) were used for structure solution, and non-hydrogen atoms were refined anisotropically (SHELXL-97,[20] full-matrix, least-squares on F^2). Hydrogen atoms were refined using a riding model (H(N) free). The absolute structre of **7a** was determined by refinement of Flack's x-parameter (x = -0.04(13)).[21] –**7a**: Bright yellow crystals, $C_{42}H_{52}N_4PCl$, M = 679.30 g mol^{-1}, crystal size 0.30 x 0.12 x 0.06 mm, monoclinic, space group $P2_1$ (No.4), a = 11.481(1) Å, b = 11.015(1) Å, c = 15.381(2), β = 98.96(1)°, V = 1921.4(3) $Å^3$, Z = 2, ρ_{calcd} = 1.174 Mg m^{-3}, F(000) = 728, μ = 0.175 mm^{-1}, 24699 reflections ($2\theta_{max}$ = 50°), 6754 unique [R_{int} = 0.107], 437 parameters, 1 restraint, goodness-of-fit on F^2: 1.05, $R1$ ($I > 2\sigma(I)$) = 0.078, w$R2$ (all data) = 0.183, largest diff. peak and hole 0.722 and -0.319 eA^{-3}. – **10a**: Colorless crystals, $C_{42}H_{54}N_4$, M = 614.89 g mol^{-1}, crystal size 0.25 x 0.20 x 0.10 mm, monoclinic, space group $C2/c$ (No.15), a = 23.7202(10) Å, b = 10.5633(4) Å, c = 16.7118(6), β = 119.624(2)°, V = 3640.0(2) $Å^3$, Z = 4, ρ_{calcd} = 1.122 Mg m^{-3}, F(000) = 1336 μ = 0.065 mm^{-1}, 8451 reflections ($2\theta_{max}$ = 50°), 4398 unique [R_{int} = 0.060], 213 parameters, 1 restraint, goodness-of-fit on F^2: 1.075, $R1$ ($I > 2\sigma(I)$) = 0.080, w$R2$ (all data) = 0.180, largest diff. peak and hole 0.364 and -0.263 eA^{-3}.

CCDC 832278 (**7a**) and 832948 (**10a**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif

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