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2-Chloro-1,3,2-diazaphospholenes – A Crystal Structural Study

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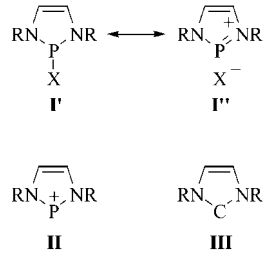
A series of 2-chloro-1,3,2-diazaphospholenes with different substitution patterns has been prepared from 1,4-diazabutadienes according to a general synthetic methodology. Subsequent chloride abstraction with Lewis acids affords the corresponding 1,3,2-diazaphospholenium salts. All products have been characterised spectroscopically and by single-crystal X-ray diffraction studies. A detailed analysis of trends in the structural parameters supports the interpretation that the unusual P–Cl bond lengthening in the diazaphospholenes is attributable to n(N)/σ*(P-Cl) hyperconjugation.

Introduction

P-Functionalised 1,3,2-diazaphospholenes (**I**) are representatives of a class of N-heterocyclic phosphanes that have recently gained interest because of their unique reactivity. In particular, P–H-substituted compounds (**I**; X = H) are selective hydride-transfer reagents that allow reductive hydrogenation of element halides as well as aldehydes and aryl ketones,[1] and phosphanyl derivatives (**I**; X = PR'_2) react with alkenes and alkynes by diphosphination to give novel unsymmetrical 1,2-bisphosphanes.[2] This unique reactivity has, in both cases, been explained by a weakening and concomitant ionic polarisation of the P–X bonds which can be expressed in terms of bond/no-bond resonance between the canonical structures **I′** and **I′′** (Scheme 1).[3] The high weight of the ionic canonical structure **I′′** is intimately connected with the exceptional stability of the corresponding phosphenium ions **II**,[4] which are isoelectronic with imidazoyl carbenes **III**[5] and are stabilised by similar electronic factors.

Another type of functional 1,3,2-diazaphospholenes, namely *P*-chloro-substituted compounds (**I**; X = Cl),[4,6,7] are of interest not only from a synthetic point of view as precursors for the cations **II** and the aforementioned P–H and P-phosphanyl derivatives but they also provide evidence for the weakening and enhanced ionic polarisation of the exocyclic P–Cl bonds.[3] Despite the high intrinsic polarity of these bonds, these phenomena still exert a visible effect on the chemical reactivity and have, for example, been considered as crucial for the use of *P*-chlorodiazaphospholenes as organocatalysts in the P–C cross-coupling between alkyl chlorides and trimethylsilyl diphenylphosphane.[8] The P–Cl bond lengthening is also significant from a structural point of view and it has been argued that its occurrence is attributable to a high degree of aromatic stabilisation in the heterocyclic ring, which induces a concomitant spontaneous dissociation of the P–Cl bond.[4,7] Although this interpretation was subsequently discredited,[3] a precise analysis of the bonding situation in *P*-chlorodiazaphospholenes is still needed.



Scheme 1.

During our investigations of the chemistry of N-heterocyclic phosphanes we have developed a general synthetic method for the preparation of 2-chloro-1,3,2-diazaphospholenes and 1,3,2-diazaphospholenium ions with a wide range of substituent patterns.[1] In this work we will give a full account of this synthetic work, and we will report on the interpretation of trends in structural parameters which were obtained from X-ray diffraction studies on a comprehensive series of these compounds.

Results and Discussion

Syntheses and Spectroscopic Studies

Known synthetic routes to 2-chloro-1,3,2-diazaphospholenes (**I**; X = Cl) include base-induced condensations of

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PCl_3 with 1,4-diazabutadienes,[6] salt-elimination reactions of PCl_3 with 1,4-diazabutadienide dianions[7] or metathesis reactions of PCl_3 with 1,3,2-diazasiloles.[4] The products can be converted into diazaphospholenium salts by subsequent treatment with Lewis acids such as $AlCl_3$, $GaCl_3$, $SbCl_5$ or Me_3SiOTf.[3,4,9] It was shown recently that triiodide or pentachlorostannate(IV) salts of cations **II** are also accessible in one step by a redox reaction between a diazabutadiene and PI_3 or a mixture of PCl_3 and $SnCl_2$, respectively.[10] The limitations of the existing methods are that their application may be restricted to the synthesis of heterocycles with specific substitution patterns, the yields of products may be low owing to the occurrence of side reactions or difficulties in purifying the products or intermediates, or that the possible redox activity of counter anions such as I_3^- or $SnCl_5^-$ may limit the use of the product in further transformations. In order to circumvent these restrictions we have developed a simple protocol for the preparation of 2-chloro-1,3,2-diazaphospholenes starting from *N*-arylated 1,4-diazabutadienes.[1] We demonstrate here that the same procedure is also applicable for the synthesis of *N*-alkylated and *C*-alkylated heterocyclic rings.

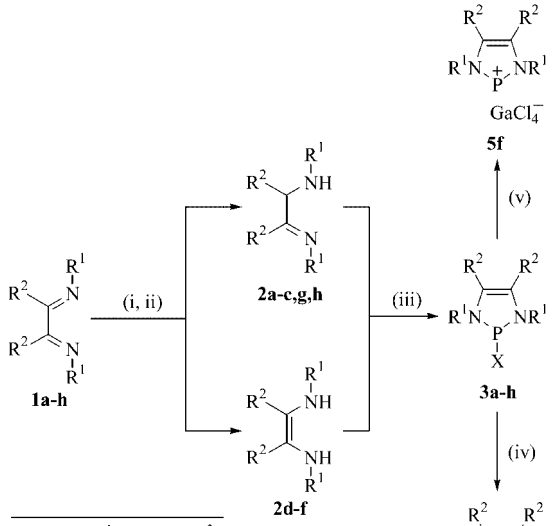
The novel *P*-chlorodiazaphospholenes **3b**,**h** and **3d**–**f** are accessible in a similar way as the previously reported derivatives **3a**,**c**,**g**[1] in a cascade reaction involving reduction of the readily available 1,4-diazabutadienes **1a**–**h** with excess lithium, quenching the resulting dianions with triethylamine hydrochloride at –78 °C, and condensation of the products formed with PCl_3 at the same temperature. All subsequent reaction steps can be carried out in a one-pot procedure without isolation of any intermediates. The triethylamine introduced to protonate the diazadienide dianions is reused to scavenge the hydrogen chloride liberated in the last step. As reported earlier,[9,11] protonation of the diazadienide dianions yields either α-aminoaldimines **2a**–**c**,**g**,**h** or 2,3-diamino-2-butenes **2d**–**f** depending on whether the central carbon atoms in the dianions bear hydrogen or alkyl substituents, respectively; both types of intermediates can be isolated as stable compounds if desired. The 2-chloro-1,3,2-diazaphospholenes **3b**,**d**–**f**,**h** were isolated as off-white to orange, moderately moisture-sensitive solids in good to excellent yields of 75–92% after work up. Reports of 4,5-dialkylated 1,3,2-diazaphospholenes are rare, although some derivatives have been obtained by condensation of a diaminoethene with substituted phosphorus dihalides according to a similar reaction to that reported here.[12]

Compounds **3b**,**c**,**g** were converted into the 1,3,2-diazaphospholenium salts **4b**,**c**,**g** by treatment with Me_3SiOTf by analogy to a previously reported method,[3] In a similar manner, **5f** was obtained by treatment of **3f** with $GaCl_3$.[13] All phosphenium salts were isolated after work-up as air- and moisture-sensitive powders in more than 90% yield.

All phosphorus heterocycles prepared were characterised by analytical data and spectroscopic techniques. The NMR spectroscopic data of both 2-chloro-1,3,2-diazaphospholenes and phosphenium salts are unremarkable and are similar to known literature data;[1,3,4,7,10] a discussion of trends in chemical shifts (including ^{35}Cl and ^{15}N NMR spectroscopic data) has been given elsewhere[3] and is not repeated here. Methylation in the 4,5-positions of the diazaphospholene ring induces a deshielding of the ^{31}P NMR signals of **3d**,**e** by some 15 ppm with respect to **3a**,**c**. As expected, both the ^{31}P and the ^{13}C NMR signals of the ring carbon atoms in the 1,3,2-diazaphospholenium salts **4b**,**c** and **5f** are deshielded with respect to the appropriate signals in the neutral precursors **3b**,**c**,**f**. The salt **4b** exhibits the largest ^{31}P NMR shift for a 1,3,2-diazaphospholenium cation observed so far ($\delta_{^{31}P}$ = 209.4 ppm).

Crystal Structure Studies

Suitable crystals for single-crystal X-ray diffraction studies of the 1,3,2-diazaphospholenes **3b**–**h** and the 1,3,2-diazaphospholenium salts **4b**,**c**,**g** and **5f** were obtained by crystallisation of appropriate solutions at low temperature (see Scheme 2 and Exp. Sect. for further details). The salt **5f** crystallised as a solvate with one molecule of CH_2Cl_2 per formula unit.



	R^1	R^2
1a-4a	Mes	H
1b-4b	DMP	H
1c-4c	DIPP	H
1d-3d	Mes	Me
1e-3e	DIPP	Me
1f-5f	2-*t*BuC_6H_4	Me
1g-3g	*t*Bu	H
1h-3h	Cy	H

Scheme 2. Synthesis of 2-chloro-1,3,2-diazaphospholenes and 1,3,2-diazaphospholenium salts; (i) 2 Li; (ii) 2 $HNEt_3Cl$, –78 °C; (iii) PCl_3, –78 °C; (iv) Me_3SiOTf, –78 °C/–Me_3SiCl; (v) $GaCl_3$. (Mes = 2,4,6-$Me_3C_6H_2$, DMP = 2,6-$Me_2C_6H_3$, DIPP = 2,6-$iPr_2C_6H_3$).

The molecular structures of the *P*-chlorodiazaphospholene **3f** and the tetrachlorogallate salt **5f** are shown in Figures 1 and 2, respectively. The *tert*-butyl moieties in both

N-aryl substituents of **3f** are located on the same side of the diazaphospholene ring *trans* to the chlorine substituent, thereby suggesting that the direct steric interaction between the *tert*-butyl groups is lower than the repulsion between substituents at adjacent ring atoms. Interestingly, the arrangement of the *tert*-butyl groups in the cation of salt **5f** remains unchanged. As the distance between the phosphorus and the closest chlorine atom in the anion (3.75 Å) is close to the sum of the van der Waals radii (thus ruling out any substantial intermolecular interactions) and both nitrogen atoms still display planar coordination geometries [sum of bond angles of 359.4(6)° for N2 and 359.7(6)° for N5] it can be concluded that the steric strain between the bulky *N*-aryl substituents is negligible. The preference for the observed pseudo-C_s-symmetric conformation over a C_2-like conformation with *tert*-butyl moieties on opposite sides of the diazaphospholene ring is presumably due to the fact that it facilitates a closer stacking of molecules in the crystal.

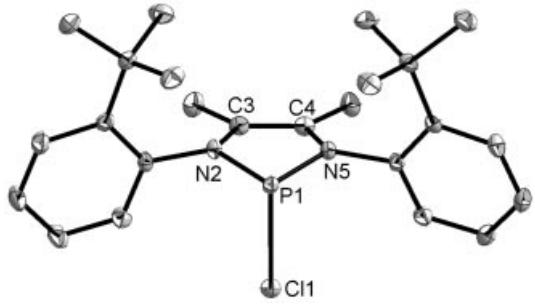


Figure 1. Molecular structure of **3f**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

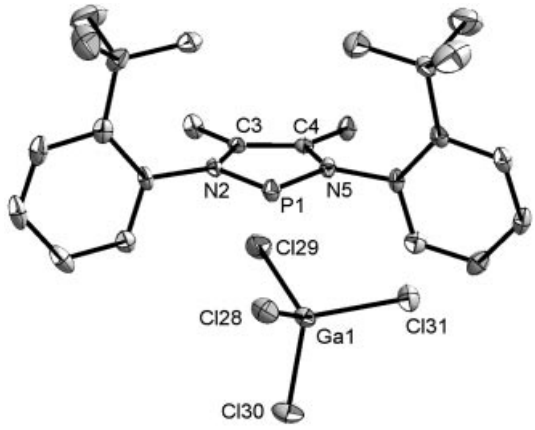


Figure 2. Molecular structure of **5f**. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Selected bond lengths and angles of all neutral *P*-chlorodiazaphospholenes and the cations of phosphenium salts are summarised in Table 1 together with the previously reported structural data for **3a**,**g** and **4a**[3] for comparison. The five-membered rings of all *P*-chlorodiazaphospholenes feature a similar flat envelope conformation to that already found for **3a**,**g**,[3] while the rings of the cations display no significant deviations from planarity. All molecules exhibit only insignificant deviations between the two crystallographically independent P-N2/N5 and C3/4-N2/5 distances.

The endocyclic P–N and C–C bond lengths in all studied 2-chloro-1,3,2-diazaphospholenes are similar and match the values for **3a** and **3g**. The C–N bonds in **3b** and **3h** are likewise similar to those of **3a** and **3g** while the C-methylated derivatives **3d**–**f** display a small (1–2 pm) yet crystallographically significant bond lengthening. The most important variation is found for the exocyclic P–Cl bond lengths, which range from 2.243(1) Å in **3c** to 2.692(4) Å in **3g**. All distances are thus considerably longer than standard P–Cl bonds in diaminochlorophosphanes (2.13 ± 0.06 Å[14]), although the bond length in **3c**, which is the shortest P–Cl bond in a 2-chloro-1,3,2-diazaphospholene reported to date, comes quite close to the normal range. A comparison between compounds with N-Mes (**3a**,**d**) and N-DIPP (**3c**,**e**) substituents reveals that the P–Cl bonds in the latter are 3–8 pm shorter, although the reason for this effect is not obvious. The longest P–Cl bonds are found for the *N*-alkyl-substituted compounds **3g**,**h**.

Table 1. Selected bond lengths [Å] and angles [°] for the 2-chloro-1,3,2-diazaphospholenes **3a**–**h** and the cations of the 1,3,2-diazaphospholenium salts **4a**–**c**, **4g**, and **5f**.

	R^1	R^2	P1–Cl1	P1–N2	P1–N5	N2–C3	N5–C4	C3–C4	N2–P1–N5
3a[a]	Mes	H	2.324(1)	1.673(1)	1.675(1)	1.406(2)	1.402(2)	1.338(2)	89.7(1)
3b	DMP	H	2.362(1)	1.678(2)	1.675(2)	1.400(2)	1.398(2)	1.335(3)	89.3(1)
3c	DIPP	H	2.243(1)	1.684(1)	1.679(1)	1.408(2)	1.402(2)	1.333(2)	89.4(1)
3d	Mes	Me	2.354(1)	1.664(2)	1.673(1)	1.427(2)	1.430(2)	1.331(2)	89.9(1)
3e	DIPP	Me	2.325(1)	1.679(1)	1.674(1)	1.425(2)	1.423(2)	1.345(2)	89.8(1)
3f	2-*t*Bu-C_6H_4	Me	2.331(1)	1.671(1)	1.669(1)	1.427(2)	1.422(2)	1.344(2)	89.5(1)
3g[a]	*t*Bu	H	2.692(4)	1.663(1)	1.665(1)	1.391(1)	1.391(1)	1.349(1)	90.6(1)
3h	Cy	H	2.567(1)	1.671(2)	1.669(2)	1.403(3)	1.401(3)	1.339(3)	90.2(1)
4a[a]	Mes	H	–	1.666(2)	1.671(1)	1.374(2)	1.378(2)	1.351(2)	89.6(1)
4b	DMP	H	–	1.664(1)	1.664(1)	1.373(2)	1.373(2)	1.351(3)	89.5(1)
4c	DIPP	H	–	1.677(1)	1.675(1)	1.365(2)	1.371(2)	1.356(2)	88.9(1)
4g	*t*Bu	H	–	1.658(2)	1.660(2)	1.365(3)	1.368(3)	1.349(4)	90.6(1)
5f[b]	2-*t*Bu-C_6H_4	Me	–	1.663(2)	1.674(2)	1.386(3)	1.372(3)	1.379(3)	89.1(1)

[a] Data from ref.[3] [b] Different crystallographic numbering scheme.

The P–N bond lengths in the cations of the phosphenium salts **4a**–**c**,**g** and **5f** match the values in **3a**–**h** closely, whereas the adjacent C–N bonds are approximately 3 pm longer than in the neutral compounds. The C–C bonds in the cations are also longer than in **3a**–**h**, although the difference in this case is less pronounced (approx. 1 pm) and on the verge of being significant when compared with the magnitude of the estimated standard deviations (see data in Table 1). The cation of **5f** is an exception and displays a significant lengthening of the C–C bond length, which is possibly influenced by the presence of methyl substituents at both ring carbon atoms. Apart from this effect, the variation of bond lengths in the phosphenium cations shows no clear connection with the changes in the substituent pattern.

The existence of a series of crystal structure analyses of similar compounds stimulated us to attempt a discussion of common trends in the sense of a structure correlation. This principle, which was coined by Bürgi and Dunitz,[15] states that structural changes that occur during a chemical reaction can be manifested in the ground-state structure as deviations of bond lengths and angles from "normal values" along the reaction coordinate. In the case of *P*-chlorodiazaphospholenes the extraordinary P–Cl bond lengthening, which was first reported for **3g**, can be interpreted as a consequence of spontaneous bond heterolysis that is energetically driven by the aromatisation of the cyclic phosphenium cation fragment.[4,7] Given the validity of this hypothesis, the application of the structure-correlation principle implies that a comparison of the crystal structure data of all compounds included in this study might reveal a systematic correlation between the P–Cl bond lengthening, the lengthening of the C–C double bond, and a concomitant shortening of the C–N and P–N single bonds, respectively.

Inspection of a plot of the P–Cl versus average P–N distances for the diazaphospholenes **3a**–**h** (Figure 3) reveals that the P–Cl bond lengthening indeed appears to coincide with a general shortening of the P–N bonds. A linear regression analysis reveals that this correlation is not particularly strong, and the magnitude of the correlation coefficient (r = 0.78) implies the presence of some scattering which suggests that additional factors also have a major impact on both bond lengths. If one considers that the individual compounds are not isostructural but crystallise in different space groups, and thus exhibit different types of crystal packing, the observed scattering is presumably due, at least in part, to variations in intermolecular interactions (the validity of this assumption is substantiated by the observed difference in P–Cl bond lengths between pure **3g** and its toluene solvate[3]). Even though an analysis of the crystallographic data of all diaminochlorophosphanes of the type $(R_2N)_2PCl$ (except **3a**,**g**) listed in the CSD data base reveals a similar relation between the changes in P–N and P–Cl bond lengths, the two regression lines deviate substantially from each other (Figure 3). In principle, this finding underlines, in a quantitative way, the previously mentioned hypothesis of the P–Cl bond in the N-heterocyclic derivatives **3a**–**h** being much "softer" (i.e. more easily polarisable) than in diaminochlorophosphanes in general.

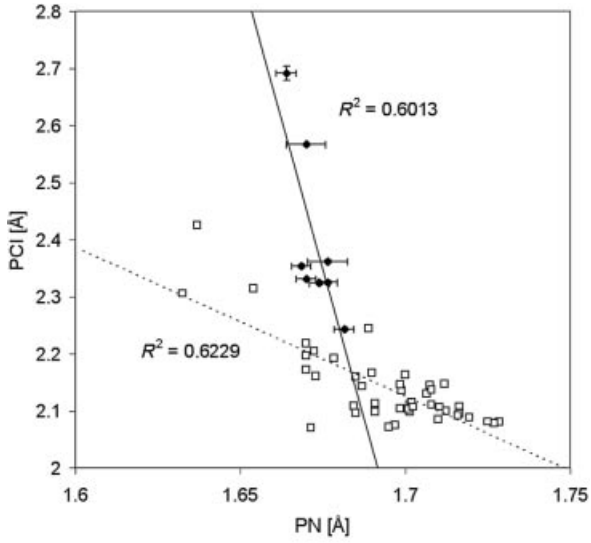


Figure 3. Plot of P–Cl distances [Å] vs. average P–N distances [Å] for **3a**–**h** (diamonds) and for all $(R_2N)_2PCl$ compounds (except **3a**,**g**) listed in the CSD data base (open squares). The solid and dashed lines represent the result of linear regression analyses. Error bars at the data points for **3a**–**h** denote a range of ±3σ, where σ is the estimated standard deviation. R^2 is the square of the correlation coefficient in the regression analysis.

An analysis of the trends in endocyclic P–N, N–C and C–C bond lengths in the diazaphospholenes **3a**–**h** and the salts **4a**–**c**,**g** and **5f** shows that the observed changes are essentially uncorrelated. A regression analysis of the changes in P–N and C–N distances for all compounds (Figure 4) gave a statistical correlation coefficient (r = 0.41) which suggests no significant connection between both parameters. Furthermore, a positive slope for the computed regression curve indicates parallel trends of the lengths of

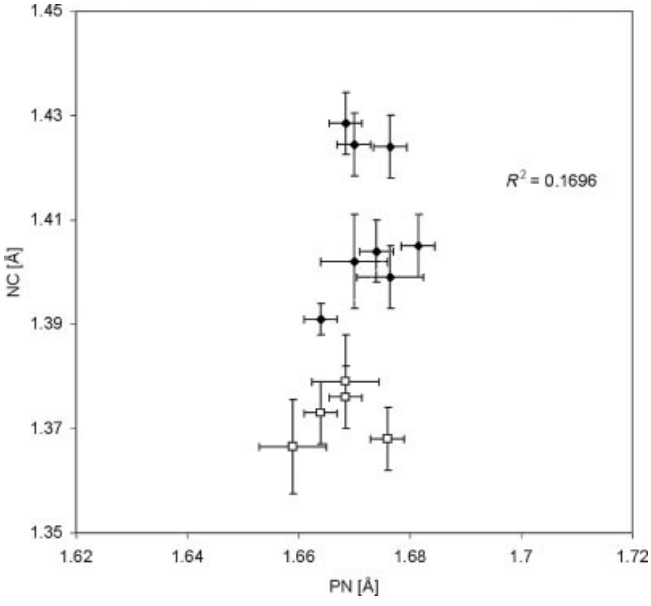


Figure 4. Plot of the average P–N distances [Å] vs. average C–N distances [Å] of **3a**–**h** (diamonds) and **4a**–**c**, **5f** (open squares). Error bars at each data point denote a range of ±3σ, where σ is the estimated standard deviation.

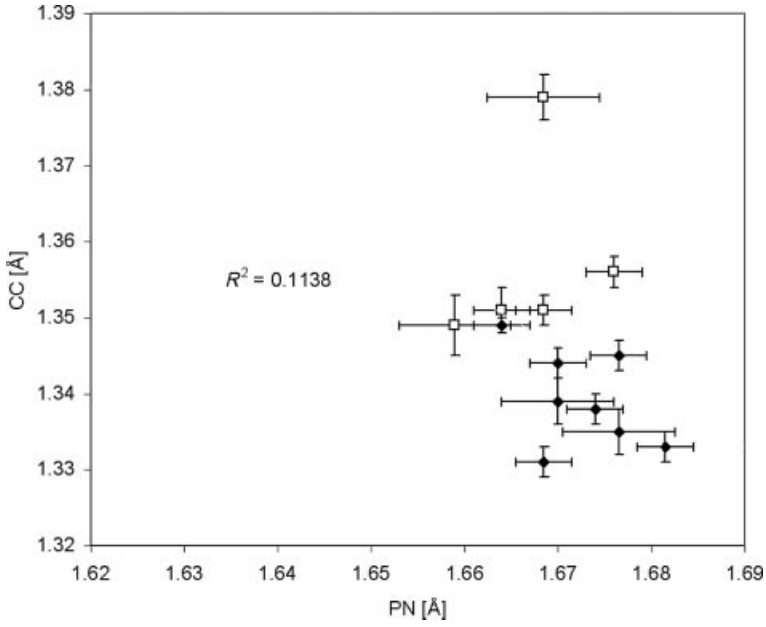


Figure 5. Plot of the average P–N distances [Å] vs. C–C distances [Å] of **3a**–**h** (diamonds) and **4a**–**c**, **5f** (open squares). Error bars at each data point denote a range of ±3σ, where σ is the estimated standard deviation.

both types of bonds, which is hardly compatible with a connection between P–Cl bond dissociation and increasing aromaticity in the ring.[4] A regression analysis of the connection between changes in P–N and C–C distances (Figure 5) indicated a statistically still weaker correlation (r = 0.34), the physical interpretation of which is further complicated by the fact that the observed differences in C–C bond lengths are rather small when compared with the estimated standard deviations of the experimental data. Further regression analyses which included only data for neutral diazaphospholenes, or involved correlations between P–Cl and C–N/C–C bond lengths, gave similar or even lower values for the correlation coefficients.

On the whole, the regression analyses performed suggest a weak statistical correlation between P–Cl and P–N distances in the diazaphospholenes **3a**–**h**, whereas the variations in the endocyclic N–C and C–C bonds appear to be fairly uncorrelated. In contrast, inspection of Figures 3, 4 and 5 suggests that the data for the neutral compounds **3a**–**h** and the salts **4a**–**c**,**g** and **5f** lie in different regions of the scatter plots that are more or less well separated owing to systematic deviations in C–N and (less pronounced) C–C bond lengths between both types of compounds. All these features are very well compatible with the explanation of the bond lengthening in *P*-chlorodiazaphospholenes being due to n(N)/σ*(P-Cl) hyperconjugation, which has also been derived from earlier computational and experimental studies,[3] but do not support the interpretation as beginning P–Cl dissociation driven by increasing aromatic character of the diazaphospholene ring.

Conclusions

We have shown that the previously reported one-pot route to 1,3,2-diazaphospholenes by reduction/protonation of 1,4-diazadienes and subsequent condensation with phosphorus trichloride offers a generally applicable and economic access to 2-chloro-1,3,2-diazaphospholenes with a wide range of substituents at both the ring nitrogen and carbon atoms. All products were obtained in high yields and purity and are suitable starting materials for further transformations.[1,3,16] In particular, subsequent Lewis acid-induced chloride abstraction permits the synthesis of N-heterocyclic phosphenium cations in overall yields that compare well with those of a recently reported one-step synthesis involving the redox reaction between a diazabutadiene and PI_3.[10] Systematic single-crystal X-ray diffraction studies have revealed that the P–Cl bond lengths in *P*-chlorodiazaphospholenes vary between 2.24 and 2.70 Å, with the *N*-alkyl derivatives showing systematically longer bonds than the *N*-aryl derivatives. An analysis of trends in the structural parameters underlines that the P–Cl bonds in diazaphospholenes are more easily polarised than in compounds of the type $(R_2N)_2PCl$ in general, but gives no evidence that the bond lengthening can be interpreted in terms of the onset of spontaneous bond heterolysis driven by an increase in the aromatic character of the diazaphospholene ring. This analysis supports the results of earlier experimental and computational studies which have explained this effect as being mainly the result of n(N)/σ*(P-Cl) hyperconjugation.

Experimental Section

All manipulations were carried out under argon in flame-dried glassware. Solvents were dried prior to use according to common procedures. Compounds **1a**–**h** were synthesised according to literature procedures.[17] The synthesis of **3a**–**h** was carried out according

to the procedure reported in ref.[1] All other chemicals were purchased from commercial suppliers. NMR Spectra: Bruker Avance 400 (^{1}H: 400.13 MHz; ^{31}P: 161.9 MHz; ^{13}C: 100.4 MHz) at 30 °C; chemical shifts referred to ext. TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P); positive signs of chemical shifts denote shifts to lower frequencies; coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of aryl substituents. MS: Varian MAT 711, EI, 70 eV. Elemental analysis: Perkin–Elmer 2400CHSN/O analyser. Melting points were determined in sealed capillaries.

1-[(2,6-Dimethylphenyl)imino]-2-[(2,6-dimethylphenyl)amino]ethane (2b): Compound **1b** (18.5 g, 70 mmol) was dissolved in thf (200 mL), and lithium turnings (1.1 g, 150 mmol) were added. After stirring for 24 h the unreacted lithium was filtered off and the solution cooled to –78 °C. Triethylamine hydrochloride (15.1 g, 150 mmol) was added and the reaction mixture slowly warmed to room temperature. After the solution had become colourless all volatiles were removed in vacuo. The residue was dissolved in *n*-hexane (150 mL) and the precipitate filtered off. The solution was concentrated and the product crystallised at –20 °C. The yellow needles obtained were filtered off and dried in vacuo. Yield 12.0 g (65%), m.p. 136 °C. ^{1}H NMR ($CDCl_3$): δ = 7.83 (t, $^3J_{H,H}$ = 2.1 Hz, 1 H, C*H*=N), 7.25–6.80 (m, 6 H, C*H*), 5.42 (s, 1 H, N*H*), 4.15 (d, $^3J_{H,H}$ = 2.1 Hz, 2 H, CH_2-N), 2.42 (s, 6 H, *o*-CH_3), 2.14 (s, 6 H, *o*-CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 163.7 (s, *C*H=N), 150.2 (s, *i*-*C*), 146.4 (s, *i*-*C*), 128.9 (s, *m*-*C*), 128.2 (s, *o*-*C*), 128.0 (s, *m*-*C*), 126.8 (s, *p*-*C*), 123.8 (s, *o*-*C*), 121.3 (s, *p*-*C*), 52.9 (s, *C*H_2-N), 19.0 (s, *o*-*C*H_3), 18.2 (s, *o*-*C*H_3) ppm.

1,4-Bis(2-*tert*-butylphenyl)-2,3-dimethyl-1,4-diazabuta-2-ene (2f): Compound **1f** (10.4 g, 30 mmol) was dissolved in thf (300 mL), and lithium (0.5 g, 60 mmol) was added. The mixture was stirred for 24 h. The remaining lithium was filtered off, the solution cooled to –78 °C, and triethylamine hydrochloride (6.1 g, 60 mmol) was added. The reaction mixture was slowly warmed to room temperature, and all volatiles were removed in vacuo. The residue was dissolved in *n*-hexane (100 mL) and the insoluble portion filtered off. The filtrate was concentrated to 30 mL and stored at –20 °C. The yellow powder formed was filtered off and dried in vacuo. Yield 9.4 g (89%). ^{1}H NMR ($CDCl_3$): δ = 7.27 (dt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*), 7.12 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*), 6.83 (dt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*), 6.82 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*), 5.29 (s, 2 H, N*H*), 1.91 (s, 6 H, CH_3), 1.37 (s, 18 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 143.2 (s, *i*-*C*), 138.0 (s, *o*-*C*), 126.7 (s, *o*-*C*H), 126.3 (s, *m*-*C*H), 122.2 (s, N-*C*CH$_3$), 119.9 (s, *m*-*C*H), 119.2 (s, *p*-*C*H), 34.4 (s, *C*), 30.0 [s, C(*C*H$_3$)$_3$], 15.7 (s, *C*H$_3$) ppm.

2-Chloro-1,3-bis(2,6-dimethylphenyl)-1,3,2-diazaphospholene (3b): Crystallisation from acetonitrile at –30 °C; colourless crystals; yield 21.2 g (92%); m.p. 184 °C. ^{1}H NMR ($CDCl_3$): δ = 7.18 (m, 6 H, *m*/*p*-C*H*), 6.46 (s, 2 H, N-C*H*), 2.46 (s, 12 H, *o*-CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 136.9 (d, $^2J_{P,C}$ = 4.5 Hz, *i*-*C*), 129.5 (d, $^4J_{P,C}$ = 1.3 Hz, *m*-*C*), 128.7 (s, *p*-*C*), 128.2 (s, *o*-*C*), 120.8 (d, $^2J_{P,C}$ = 8.4 Hz, N-*C*), 19.4 (d, $^4J_{P,C}$ = 2.9 Hz, *o*-*C*H_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 149.2 (s) ppm. MS (EI): *m*/*z* (%) 330.1 (23.9) [M]$^+$, 295.2 (100.0) [M – Cl]$^+$, 190.1 (27.5) [M – C_8H_9Cl]$^+$. $C_{18}H_{20}ClN_2P$ (330.80): calcd. C 65.36, H 6.09, N 8.47; found C 64.55, H 6.80, N 7.84.

2-Chloro-1,3-dimesityl-4,5-dimethyl-1,3,2-diazaphospholene (3d): Crystallisation from dichloromethane at –20 °C, colourless crystals; yield 22.6 g (90%); m.p. 219 °C. ^{1}H NMR ($CDCl_3$): δ = 6.96 (s, 4 H, *m*-C*H*), 2.30 (s, 6 H, *p*-CH_3), 2.28 (s, 12 H, *o*-CH_3), 1.82 (d, $^4J_{P,H}$ = 1.3 Hz, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 138.7 (s, *i*-*C*), 137.0 (d, $^5J_{P,C}$ = 5.5 Hz, *p*-*C*), 131.8 (d, $^3J_{P,C}$ = 10.0 Hz, *o*-*C*), 129.7 (d, $^4J_{P,C}$ = 1.0 Hz, *m*-*C*H), 125.8 (m, N-*C*H), 21.0 (d, $^6J_{P,C}$ = 0.8 Hz, *p*-*C*H$_3$), 19.1 (d, $^4J_{P,C}$ = 1.3 Hz, *o*-*C*H$_3$), 11.1 (d, $^3J_{P,C}$ = 2.0 Hz, *C*H$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 165.0 (s) ppm. MS (EI): *m*/*z* (%) 386.2 (21.9) [M]$^+$, 351.2 (100.0) [M – Cl]$^+$, 363.0 (19.2) [M – CH_3Cl]$^+$, 305.2 (2.7) [M – $C_3H_{10}Cl$]$^+$. $C_{22}H_{28}ClN_2P$ (386.90): calcd. C 68.30, H 7.29, N 7.24; found C 68.24, H 7.35, N 7.13.

2-Chloro-1,3-bis(diisopropylphenyl)-4,5-dimethyl-1,3,2-diazaphospholene (3e): Crystallisation from dichloromethane at –20 °C; colourless crystals; yield 8.7 g (93%); m.p. 204 °C. ^{1}H NMR ($CDCl_3$): δ = 7.45–7.13 (m, 6 H, *m*/*p*-C*H*), 3.14 (sept, $^3J_{H,H}$ = 6.7 Hz, 4 H, C*H*), 1.84 (d, $^4J_{P,H}$ = 0.9 Hz, 6 H, NC-CH_3), 1.31 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.21 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 148.9 (d, $^4J_{P,C}$ = 5.0 Hz, *m*-*C*H), 131.0 (d, $^2J_{P,C}$ = 12.1 Hz, *i*-*C*), 129.8 (d, $^5J_{P,C}$ = 1.5 Hz, *p*-*C*H), 129.4 (s, *o*-*C*), 128.6 (s, *o*-*C*), 125.7 (s; N-*C*), 125.0 (d, $^4J_{P,C}$ = 1.0 Hz, *m*-*C*H), 28.9 (d, $^5J_{P,C}$ = 1.0 Hz, *C*H$_3$), 26.1 (d, $^5J_{P,C}$ = 1.3 Hz, *C*H$_3$), 25.0 (s, *C*H), 11.9 (d, $^3J_{P,C}$ = 3.4 Hz, NC-*C*H$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 157.0 (s) ppm. MS (EI): *m*/*z* (%) 470.3 (15.1) [M]$^+$, 435.3 (100.0) [M – Cl]$^+$. $C_{28}H_{40}ClN_2P$ (471.07): calcd. C 71.39, H 8.56, N 5.95; found C 71.30, H 8.64, N 6.14.

1,3-Bis(2-*tert*-butylphenyl)-2-chloro-4,5-dimethyl-1,3,2-diazaphospholene (3f): Crystallisation from a mixture of dichloromethane/diethyl ether (2:1) at –20 °C; colourless crystals; yield 8.7 g (74%); m.p. 196 °C. ^{1}H NMR ($CDCl_3$): δ = 7.72 (dd, $^3J_{H,H}$ = 7.0, $^4J_{H,H}$ = 2.0 Hz, 2 H, C*H*), 7.53 (dd, $^3J_{H,H}$ = 7.0, $^4J_{H,H}$ = 2.0 Hz, 2 H, C*H*), 7.35 (dt, $^3J_{H,H}$ = 7.0, $^4J_{H,H}$ = 2.4 Hz, 2 H, C*H*), 7.31 (dt, $^3J_{H,H}$ = 7.0, $^4J_{H,H}$ = 2.4 Hz, 2 H, C*H*), 1.81 (d, $^4J_{P,H}$ = 0.5 Hz, 6 H, CH_3), 1.37 (s, 18 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 147.8 (d, $^3J_{P,C}$ = 6.9 Hz, *o*-*C*), 135.0 (d, $^2J_{P,C}$ = 8.4 Hz, *i*-*C*), 134.0 (d, $^3J_{P,C}$ = 7.9 Hz, *o*-*C*), 129.0 (d, $^4J_{P,C}$ = 1.8 Hz, *m*-*C*), 127.8 (d, $^5J_{P,C}$ = 0.8 Hz, *p*-*C*), 126.8 (d, $^4J_{P,C}$ = 1.3 Hz, *m*-*C*), 125.8 (d, $^2J_{P,C}$ = 6.6 Hz, N-*C*), 36.0 [d, $^4J_{P,C}$ = 1.0 Hz, *C*(CH$_3$)$_3$], 32.1 (d, $^5J_{P,C}$ = 4.1 Hz, *C*H$_3$), 12.0 (d, $^3J_{P,C}$ = 3.1 Hz, *C*H$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 161.9 (s) ppm. MS (EI): *m*/*z* (%) 414.2 (17.2) [M]$^+$, 379.2 (86.2) [M – Cl]$^+$, 174.1 (19.3) [M – $C_{12}H_{16}NPCl$]$^+$. $C_{24}H_{32}ClN_2P$ (414.96): calcd. C 69.47, H 7.77, N 6.75; found C 68.91, H 7.86, N 6.77.

2-Chloro-1,3-dicyclohexyl-1,3,2-diazaphospholene (3h): Crystallisation from a mixture of *n*-hexane and thf at –28 °C, colourless crystals; yield 2.46 g (43%), m.p. 148 °C. ^{1}H NMR ($CDCl_3$): δ = 6.91 (s, 2 H, N-CH), 3.98–3.77 (m, 2 H, CH), 2.40–2.25 (m, 8 H, CH_2), 1.97–1.60 (m, 8 H, CH_2), 1.51–1.21 (m, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 116.7 (d, $^2J_{P,C}$ = 8.0 Hz, N-CH), 53.5 (d, $^3J_{P,C}$ = 11.1 Hz, CH), 29.0 (d, $^4J_{P,C}$ = 9.3 Hz, CH_2), 28.1 (d, $^5J_{P,C}$ = 1.2 Hz, CH_2), 19.9 (s, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 176.5 ppm. MS (EI): *m*/*z* (%) 286.1 (14.4) [M]$^+$, 251.1 (100.0) [M – Cl]$^+$, 169.1 (7.7) [M – $C_6H_{10}Cl$]$^+$, 87.0 (44.5) [M – $C_{12}H_{20}Cl$]$^+$. $C_{14}H_{24}ClN_2P$ (286.78): calcd. C 58.71, H 8.45, N 9.79; found C 58.55, H 8.62, N 9.65. IR: $\tilde{\nu}$ = 1566 (m) cm^{-1}.

1,3-Bis(2,6-dimethylphenyl)-1,3,2-diazaphospholenium Trifluoromethanesulfonate (4b): Compound **3b** (1.32 g, 4 mmol) was dissolved in toluene (50 mL) and cooled to –78 °C. Trimethylsilyl trifluoromethanesulfonate (1.78 g, 8 mmol) was added and the solution stirred for 2 h. All volatiles were then evaporated in vacuo and the residue dissolved twice in diethyl ether (15 mL) followed by removal of the solvent. The product was dissolved in diethyl ether/dichloromethane (5 mL/10 mL) and crystallised at –20 °C. The colourless crystals were filtered off and dried in vacuo. Yield 1.26 g (95%); m.p. 236 °C. ^{1}H NMR (CD_3CN): δ = 8.14 (s, 2 H, N-C*H*), 7.53–7.35 (m, 6 H, C*H*), 2.23 (d, $^4J_{P,H}$ = 0.6 Hz, 12 H, *o*-CH_3) ppm.

$^{13}C\{^1H\}$ NMR (CD_3CN): δ = 137.7 (d, $^3J_{P,C}$ = 2.5 Hz, *o-C*), 135.3 (d, $^2J_{P,C}$ = 3.6 Hz, *i-C*), 134.9 (d, $^2J_{P,C}$ = 6.7 Hz, N-*C*H), 131.6 (d, $^5J_{P,C}$ = 0.7 Hz, *p-C*), 129.9 (s, *m-C*), 17.4 (d, $^4J_{P,C}$ = 1.7 Hz, *o-C*H_3) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN): δ = 209.4 (s) ppm. MS (EI): *m/z* (%) 444.0 (20.3) $[M]^+$, 295.1 (100.0) $[M - CF_3SO_3]^+$. $C_{19}H_{20}F_3N_2O_3PS$ (444.41): calcd. C 51.35, H 4.54, N 6.30; found C 52.09, H 5.10, N 6.06.

1,3-Bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholenium Trifluoromethanesulfonate (4c): A solution of **3c** (0.89 g, 2 mmol) in toluene

Table 2. Crystallographic data, structure solution and refinement of **3b**–**f**.

	3b	**3c**	**3d**	**3e**	**3f**
Empirical formula	$C_{18}H_{20}ClN_2P$	$C_{26}H_{36}ClN_2P$	$C_{22}H_{28}ClN_2P$	$C_{28}H_{40}ClN_2P$	$C_{24}H_{32}ClN_2P{\cdot}CH_2Cl_2$
Formula weight	330.78	442.99	386.88	471.04	499.86
Temperature [K]	123(2)	123(2)	123(2)	173(2)	123(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	14.9453(3)	9.7599(2)	7.7200(2)	16.899(4)	10.9942(3)
b [Å]	7.2778(2)	10.6976(2)	18.7452(6)	10.5903(17)	11.0029(2)
c [Å]	16.4943(4)	12.3357(3)	14.4230(4)	16.434(3)	12.6859(3)
α [°]	90	90	90	90	115.005(2)
β [°]	113.926(2)	92.891(1)	97.635(2)	114.480(13)	97.615(2)
γ [°]	90	90	90	90	105.485(2)
V [Å^3]	1639.90(7)	1286.30(5)	2068.69(10)	2676.8(8)	1286.29(5)
Z	4	2	4	4	2
$D_{calcd.}$ [g cm^{-3}]	1.340	1.144	1.242	1.169	1.291
Abs. coeff. [mm^{-1}]	0.328	0.225	0.270	0.220	0.434
F(000)	696	476	824	1016	528
Crystal size [mm]	0.60 × 0.35 × 0.25	0.50 × 0.25 × 0.15	0.40 × 0.20 × 0.20	0.65 × 0.50 × 0.45	0.60 × 0.50 × 0.40
θ range for data collection [°]	2.98–25.03	2.52–24.99	3.05–27.48	2.33–28.01	3.07–27.48
Reflections collected	9610	13453	13602	6664	11453
Unique reflections	2881	4524	4651	6444	5698
R_{int}	0.0229	0.0354	0.0348	0.0250	0.0279
Data/restraints/parameters	2881/0/203	4524/1/271	4651/0/243	6444/0/304	5698/0/282
GOF on F^2	1.062	1.044	0.938	1.005	1.058
$R1$ [$I > 2\sigma(I)$]	0.0433	0.0257	0.0381	0.0426	0.0328
wR_2 (all data)	0.1153	0.0628	0.0906	0.1237	0.0864
Largest diff. map peak/hole [e Å^{-3}]	1.240/–0.271	0.220/–0.298	0.456/–0.304	0.496/–0.266	0.328/–0.302

Table 3. Crystallographic data, structure solution and refinement for **3h**, **4b**,**c**,**g** and **5f**.

	3h	**4b**	**4c**	**4 g**	**5f**
Empirical formula	$C_{14}H_{24}ClN_2P$	$C_{19}H_{20}F_3N_2O_3PS$	$C_{27}H_{36}F_3N_2O_3PS$	$C_{11}H_{20}F_3N_2O_3PS$	$C_{24}H_{32}Cl_4GaN_2P$
Formula weight	286.77	444.40	556.61	348.32	591.01
Temperature [K]	123(2)	123(2)	173(2)	123(2)	123(2)
Crystal system	triclinic	orthorhombic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	*Pnma*	$P\bar{1}$	*Pnma*	$P2_1/n$
a [Å]	6.995(2)	10.2721(3)	9.875(2)	12.4780(3)	10.1559(2)
b [Å]	9.164(2)	17.4393(8)	10.708(2)	8.5135(2)	9.4609(2)
c [Å]	12.244(2)	11.7441(5)	14.739(3)	15.3270(4)	28.6877(7)
α [°]	100.67(2)	90	95.172(14)	90	90
β [°]	92.28(2)	90	104.567(15)	90	98.102(1)
γ [°]	98.03(2)	90	100.759(15)	90	90
V [Å^3]	762.0(3)	2103.82(15)	1466.4(5)	1628.21(7)	2728.92(10)
Z	2	4	2	4	4
$D_{calcd.}$ (g cm^{-3})	1.250	1.403	1.261	1.421	1.439
Abs. coeff. [mm^{-1}]	0.342	0.278	0.214	0.337	1.474
F(000)	308	920	588	728	1216
Crystal size [mm]	0.40 × 0.30 × 0.20	0.50 × 0.30 × 0.15	0.70 × 0.35 × 0.25	0.40 × 0.25 × 0.15	0.15 × 0.15 × 0.15
θ range for data collection [°]	3.10–25.02	3.47–27.48	1.96–27.50	3.12–27.48	2.96–27.48
Reflections collected	8795	10939	7127	9671	14785
Unique reflections	2654	2463	6731	1982	6068
R_{int}	0.0510	0.0337	0.0224	0.0406	0.0473
Data/restraints/parameters	2654/0/163	2463/0/141	6731/0/327	1982/0/115	6068/0/291
GOF on F^2	1.058	1.017	1.051	1.075	0.918
$R1$ [$I > 2\sigma(I)$]	0.0369	0.0357	0.0425	0.0428	0.0358
wR_2 (all data)	0.0960	0.0950	0.1131	0.1186	0.0792
Largest diff. map peak/hole [e A^{-3}]	0.338/–0.266	0.262/–0.282	0.387/–0.378	0.484/–0.408	0.843/–0.544

(30 mL) was cooled to –78 °C and trimethylsilyl trifluoromethanesulfonate (1.08 g, 5 mmol) was added. After stirring for 2 h at room temperature all volatiles were evaporated in vacuo and the residue dissolved twice in 15 mL of diethyl ether, followed by removal of the solvent. The product was dissolved in a mixture of *n*-hexane, toluene, and dichloromethane (5 mL/5 mL/1 mL) and crystallised at –28 °C. The colourless needles were filtered off and dried in vacuo. Yield 0.78 g (73%); m.p. 259 °C. ^{1}H NMR ($CDCl_3$): δ = 8.62 (d, $^3J_{P,H}$ = 0.9 Hz, 2 H, N-C*H*), 7.64 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, *p*-C*H*), 7.43 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, *m*-C*H*), 2.50 (sept, $^3J_{H,H}$ = 6.8 Hz, 4 H, C*H*), 1.36 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3), 1.27 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 144.2 (d, $^2J_{P,C}$ = 3.6 Hz, *i*-*C*), 140.2 (s, *o*-*C*), 137.1 (s, *o*-*C*), 131.5 (d, $^2J_{P,C}$ = 1.2 Hz, N-*C*H), 128.3 (s, *m*-*C*), 127.5 (s, *m*-*C*), 124.6 (s, *p*-*C*), 124.2 (s, *p*-*C*), 30.9 (s, *C*H), 30.1 (s, *C*H), 24.5 (s, *C*H_3), 23.0 (s, *C*H_3), 21.9 (s, *C*H_3), 20.7 (s, *C*H_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 205.0 (s) ppm. MS (EI): *m*/*z* (%) 556.1 (12.3) $[M]^+$, 407.2 (100.0) $[M - CF_3SO_3]^+$. $C_{27}H_{36}F_3N_2O_3PS$ (556.62): calcd. C 58.26, H 6.52, N 5.03; found C 58.46, H 6.70, N 4.95.

1,3-Di-*tert*-Butyl-1,3,2-diazaphospholenium Trifluoromethanesulfonate (4g): M.p. 168 °C. ^{1}H NMR ($CDCl_3$): δ = 8.17 (s, 2 H, N-CH), 1.69 (d, $^4J_{P,H}$ = 1.8 Hz, 18 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 132.9 (d, $^3J_{P,H}$ = 3.8 Hz N-C), 62.8 (d, $^2J_{P,H}$ = 7.6 Hz, 1 C), 31.4 (d, $^3J_{P,H}$ = 6.5 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 205.5. $C_{11}H_{20}F_3N_2O_3PS$ (348.32): calcd. C 36.93, H 5.79, N 8.04; found C 36.85, H 5.69, N 7.82.

1,3-Bis(2-*tert*-butylphenyl)-4,5-dimethyl-1,3,2-diazaphospholenium Tetrachlorogallate (5f): Compound **3f** (207 mg, 0.5 mmol) and gallium trichloride (88 mg, 0.5 mmol) were dissolved in acetonitrile (10 mL) and stirred for 5 min. Storage of the solution at –35 °C afforded colourless crystals, which were filtered off and dried in vacuo. Yield 280 mg (95%). ^{1}H NMR (CD_3CN): δ = 7.84 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.6 Hz, 2 H, o -C*H*), 7.65 (dddd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.6, $^6J_{P,H}$ = 0.9 Hz, 2 H, *m*-C*H*), 7.48 (dddd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.6, $^5J_{P,H}$ = 0.9 Hz, 2 H, *p*-C*H*), 7.28 (ddd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.6, $^5J_{H,H}$ = 0.4 Hz, 2 H, m′-C*H*), 2.21 (d, $^4J_{P,H}$ = 1.8 Hz, 6 H, CH_3), 1.34 (s, 18 H, CH_3) ppm. ^{13}C{^{1}H} NMR (CD_3CN): δ = 146.9 (d, $^2J_{P,C}$ = 3.4 Hz, *i*-*C*), 144.6 (s, *o*-*C*), 132.5 (d, $^4J_{P,C}$ = 1.3 Hz, *m*-*C*H), 132.1 (s, *m*-*C*H), 132.0 (d, $^2J_{P,C}$ = 5.5 Hz, N-*C*), 130.9 (s, *m*-*C*H), 128.8 (s, *p*-*C*H), 37.3 (d, $^4J_{P,C}$ = 0.8 Hz, 1 *C*), 32.7 (d, $^5J_{P,C}$ = 2.6 Hz, *C*H_3), 13.8 (d, $^3J_{P,C}$ = 3.9 Hz, *C*H_3) ppm. ^{31}P{^{1}H} NMR (CD_3CN): δ = 205.8 (s) ppm. MS (EI): *m*/*z* (%) 379.2 (100.0) $[M - GaCl_4]^+$. $C_{24}H_{32}Cl_4GaN_2P$ (591.04): calcd. C 48.77, H 5.46, N 4.74; found C 48.49, H 5.39, N 4.74.

Crystal Structure Studies: Single-crystal X-ray diffraction studies were carried out at low temperatures on a Nonius Kappa-CCD diffractometer or a Siemens P3 or P4 diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Direct methods (SHELXS-97[18]) were used for structure solution and refinement (SHELXL-97,[19] full-matrix least-squares on F^2). An empirical absorption correction was applied for **5f**, and H atoms were refined using a riding model. The absolute structure of **3c** was determined by refinement of Flack's *x*-parameter [*x* = 0.04(4)].[20] Important data regarding the data collection and structure solution and refinement are listed in Tables 2 and 3.

CCDC-650776 (for **3b**), -650777 (for **3c**), -650778 (for **3d**), -650770 (for **3e**), -650779 (for **3f**), -650780 (for **3h**), -650781 (for **4b**), -650771 (for **4c**), -651156 (for **4g**), and -650782 (for **5f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) D. Gudat, A. Haghverdi, M. Nieger, *Angew. Chem.* **2000**, *112*, 3211–3214; *Angew. Chem. Int. Ed.* **2000**, *39*, 3084–3087; b) S. Burck, D. Gudat, M. Nieger, W.-W. du Mont, *J. Am. Chem. Soc.* **2006**, *128*, 3946–3955.
[2] a) S. Burck, D. Gudat, M. Nieger, *Angew. Chem.* **2004**, *116*, 4905–4908; *Angew. Chem. Int. Ed.* **2004**, *43*, 4801–4804.
[3] D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, *Chem. Eur. J.* **2000**, *6*, 3414–3425.
[4] M. Denk, S. Gupta, R. Ramachandran, *Tetrahedron Lett.* **1996**, *37*, 9025–9028.
[5] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[6] A. M. Kibardin, I. A. Litvinov, V. A. Naumanov, Y. T. Struchkov, T. V. Gryaznova, Y. B. Mikhailov, A. N. Pudovik, *Dokl. Akad. Nauk SSSR* **1988**, *298*, 369–372.
[7] C. J. Carmalt, V. Lomeli, B. G. McBurnett, A. H. Cowley, *Chem. Commun.* **1997**, 2095–2096.
[8] S. Burck, D. Förster, D. Gudat, *Chem. Commun.* **2006**, 2810–2812.
[9] a) A. H. Cowley, R. A. Kemp, J. C. Wilburn, *Inorg. Chem.* **1981**, *20*, 4289–4293; b) I. A. Litvinov, V. A. Naumov, T. V. Gryaznova, A. M. Kibardin, A. N. Pudovik, *Dokl. Akad. Nauk SSSR* **1990**, *324*, 623–625.
[10] a) G. Reeske, C. R. Hoberg, N. J. Hill, A. H. Cowley, *J. Am. Chem. Soc.* **2006**, *128*, 2800–2801; b) B. D. Ellis, C. L. B. Macdonald, *Inorg. Chim. Acta* **2007**, *351*, 329–344; c) G. Reeske, A. H. Cowley, *Inorg. Chem.* **2007**, *46*, 1426–1430.
[11] a) T. Gans-Eichler, D. Gudat, M. Nieger, *Angew. Chem.* **2002**, *114*, 1966–1969; *Angew. Chem. Int. Ed.* **2002**, *41*, 1888–1891; b) T. Gans-Eichler, D. Gudat, K. Nättinen, M. Nieger, *Chem. Eur. J.* **2006**, *12*, 1162–1173.
[12] a) A. M. Kibardin, T. V. Gryaznova, T. A. Zyablikova, Sh. K. Latypov, R. Z. Musin, A. N. Pudovik, *Zh. Obshch. Khim.* **1993**, *63*, 33–39; b) A. M. Kibardin, T. V. Gryaznova, A. N. Pudovik, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1987**, *36*, 1554.
[13] a) A. Dumitrescu, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Eur. J. Inorg. Chem.* **2002**, 1953–1956; b) N. Burford, P. Losier, C. Macdonald, V. Kyrimis, P. K. Bakshi, T. S. Cameron, *Inorg. Chem.* **1994**, *33*, 1434–1439; c) N. Burford, P. Losier, P. K. Bakshi, T. S. Cameron, *J. Chem. Soc. Dalton Trans.* **1993**, 201–202; d) N. Burford, T. S. Cameron, J. A. C. Clyburne, K. Eichele, K. N. Robertson, S. Sereda, R. E. Wasylishen, W. A. Whitla, *Inorg. Chem.* **1996**, *35*, 5460–5467.
[14] Average and standard deviation of the result of a query in the CSD database for P–Cl distances in phosphorus compounds $(R_2N)_2P$–Cl neglecting the entries for 1,3,2-diazaphospholenes.
[15] a) *X-ray Analysis and the Structure of Organic Molecules* (Ed.: J. Dunitz), Cornell University Press Ltd., London, **1979**; b) H. B. Bürgi, J. D. Dunitz, *Acc. Chem. Res.* **1983**, *16*, 153–161; c) *Structure Correlation* (Eds.: H. B. Bürgi, J. D. Dunitz), Verlag Chemie, Weinheim, **1994**.
[16] S. Burck, D. Gudat, M. Nieger, J. Tirree, *Dalton Trans.* **2007**, 1891–1897.
[17] a) H. tom Dieck, M. Svoboda, T. Greiser, *Z. Naturforsch., Teil B* **1981**, *36*, 823–832; b) H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378–1399; c) D. J. Tempel, L. K. Johnson, R. L. Huff, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **2000**, *122*, 6686–6700.
[18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[19] G. M. Sheldrick, University of Göttingen, Germany, **1997**.
[20] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

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