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On the Reaction of Aminobis(diorganylamino)phosphanes with Halogenophosphanes—P-Hydrogeno(iminophosphoranyl)-halogenophosphanes and P-Hydrogeno(iminophosphoranyl)-σ^2,λ^3-iminophosphanes

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ABSTRACT

Reactions of triaminophosphane $(R_2N)_2P–NH_2$, (R = ^iPr) **1a**, *with aminodihalogenophosphanes $^iPr_2N–PX_2$,* **2a–c** *[X = Cl (**a**), Br (**b**), I(**c**)], in the presence of a base yielded the P-hydrogeno-iminophosphoranyl-halogenophosphanes $(R_2N)_2PH = N–PX–N(^iPr)_2$,* **4a–c** *[X = Cl (**a**), Br (**b**), I(**c**)]. Analogous reactions between* **1a** *and* **1b** *(**b**: R = c-hexyl) and chloroiminophosphane (Cl–P = N–Mes*, (Mes* = 2,4,6-$^tBu_3C_6H_2$)* **6**, *gave the P-hydrogeno(iminophosphoranyl)-σ^2,λ^3-iminophosphanes, $(R_2N)_2PH = N–P = N–Mes^*$* **8a** *and* **8b**. *In solution* **8a**, **8b** *eliminated amine, yielding σ^2,λ^3-iminophosphanyl-substituted 1,3,2,4-diazadiphosphetidines $[(R_2N)PN(P = N–Mes^*)]_2$,* **10a**, **10b**, *and* **11** *(**10a** and **10b**: cis; **11**: trans). The X-ray structure analyses of compounds* **4a**, **4b**, **8a**, *and* **11** *are discussed.* © *1996 John Wiley & Sons, Inc.*

Dedicated to Prof. Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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INTRODUCTION

Isomerization of aminophosphanes $R_2P–N(Y)R'$ via 1,2-migrations into the corresponding iminophosphoranes $R_2P(Y) = NR'$ are known for a variety of substituents Y (Y = H, SiR_3, GeR_3, $P(S)R_2$, PR_2) [1–5] and have in the past been the subject of several experimental and theoretical investigations. In a recent work, Burford et al. were able to show that amine elimination reactions from sterically overcrowded aminophosphanes $(R_2N)_2P–NHR'$ (R' = 2,4,6-$^tBu_3C_6H_2$) proceed via rearrangement into the corresponding PH-iminophosphoranes $(R_2N)_2PH = NR'$ [6] to yield $\sigma^2\lambda^3$-iminophosphanes $R_2N–P = NR'$. In this context, the recently reported synthesis and reactivity of the novel type of triaminophosphane $(R_2N)_2P–NH_2$ [7] is of interest, since the presence of two amino protons in these compounds enables the synthesis of a variety of functionalized aminophosphanes containing the $(R_2N)_2P–NH$- moiety by simple displacement reactions. To explore their potential with regard to the syntheses of novel $\sigma^2\lambda^3$-iminophosphanes, we reacted the difunctionalized aminophosphanes with dihalogenophosphanes

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X_2PR and the chloroiminophosphane Cl–P = N–R′ (R′ = 2,4,6-^{t}Bu$_3$C$_6$H$_2$).

RESULTS AND DISCUSSION

Base-induced hydrogen chloride elimination with formation of the P-hydrogeno-iminophosphoranylphosphanes **4a–c** proceeds smoothly by treatment of triaminophosphane **1a** with dihalogenophosphanes **2a–c** in hexane at room temperature (Scheme 1). The compounds **4a–c** were isolated by crystallization from a small amount of hexane as colorless crystals. Their constitution as phosphanyl(imino)phosphoranes and not their tautomeric diphosphanylamines **3a–c** becomes apparent from the characteristic ^{31}P-NMR data: (1) the observation of two significantly different shielded phosphorus nuclei and their characteristic $^2J_{PP}$ coupling constants [8] [**4**: δ = 183.7, 1.7; $^2J_{PP}$ = 128.4 Hz (a); δ = 261.2, 4.4; $^2J_{PP}$ = 102.2 Hz (b); δ = 288.2, 10.3; $^2J_{PP}$ = 92.9 Hz (c)] and (2) the large $^1J_{PH}$ coupling constant [**4**: $^1J_{PH}$ = 539.3 Hz (a), 552.0 Hz (b), 566.0 Hz (c)].

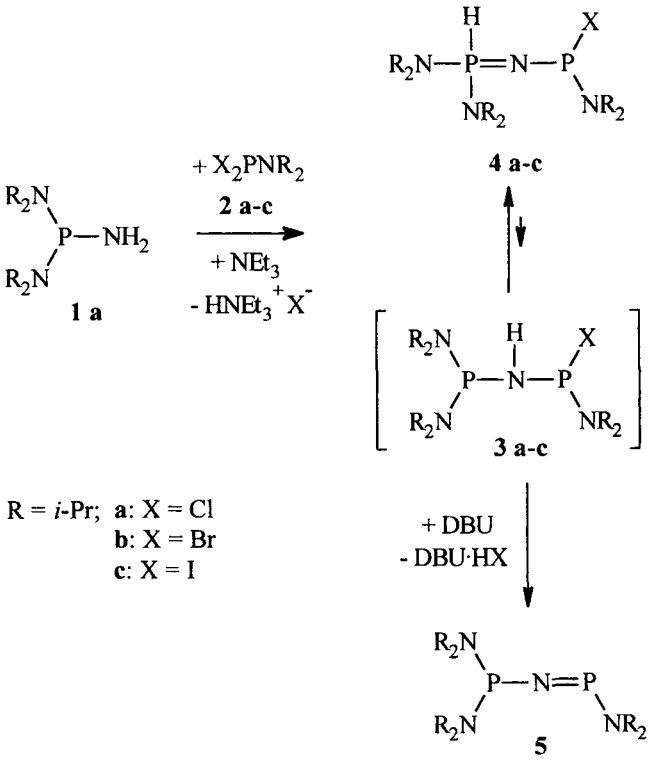
A remarkable feature for all compounds **4a–c** is the significant dependence of the ^{31}P-NMR shift of the tricoordinated phosphorus atom on the solvent polarity (Table 1). The increased deshielding of the phosphorus nucleus with increasing polarity of the solvent suggests that partial dissociation of the phosphorus halogen bond in **4a–c** takes place to give the corresponding phosphenium cations (II and III, Scheme 2), which are stabilized by both the iminophosphoranyl [9] and the amino group. The equilibrium between the covalent and the ionic species is determined by the solvent polarity. Analogous findings were previously reported for the isoelectronic phosphoniumylidyl chlorophosphines [10] and was explained by the exceptional ability of the ylidyl moiety to stabilize phosphenium cations. Complete dissociation of **4a–c** does not take place in solution; however, it can be achieved by addition of equimolar quantities of aluminum trichloride to the CH_2Cl_2 solutions. The formation of the cationic species is in this case indicated by a further downfield shift of the ^{31}P-NMR resonances (δ = 312.4) in all three cases [10,11].

TABLE 1 Solvent Dependency of ^{31}P-NMR Resonances δ of $\delta^3\lambda^3$-P in **4a–c**

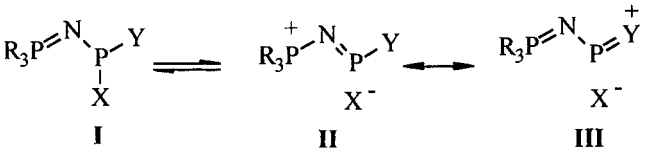
Solvent	***4a***	***4b***	***4c***
Hexane	174.9	203.4	232.4
Et_2O	177.5	208.4	243.8
THF	182.4	215.9	252.3
DME	183.8	218.3	254.5
CH_2Cl_2	205.7	254.9	288.4
$CDCL_3$	215.4	261.2	288.2
$CH_2Cl_2/AlCl_3$	312.4	312.4	312.4

Suitable crystals for X-ray structure analyses of **4a** and **4b** were obtained by crystallization from hexane at −30°C. Their molecular structures are shown in Figures 1 and 2, and relevant structural parameters are given in Table 2.

Both compounds exhibit in the solid state the expected distorted trigonal pyramidal and distorted tetrahedral environment around P1 and P2, respectively. The P2–N2–P1–N1 skeleton adopts a near-planar conformation (torsion angle $\tau_{P2-N2-P1-N1}$: **4a**: 176.7°; **4b**: 170.5°), resulting in a near-ecliptic alignment of one imino and the amino-lone pair toward the P–X bonds. This conformation enables an effective charge transfer from the nitrogen-lone pairs into the σ^*-P–X bonds, an effect that is well known as "negative hyperconjugation" [12]. This causes a



SCHEME 1



SCHEME 2

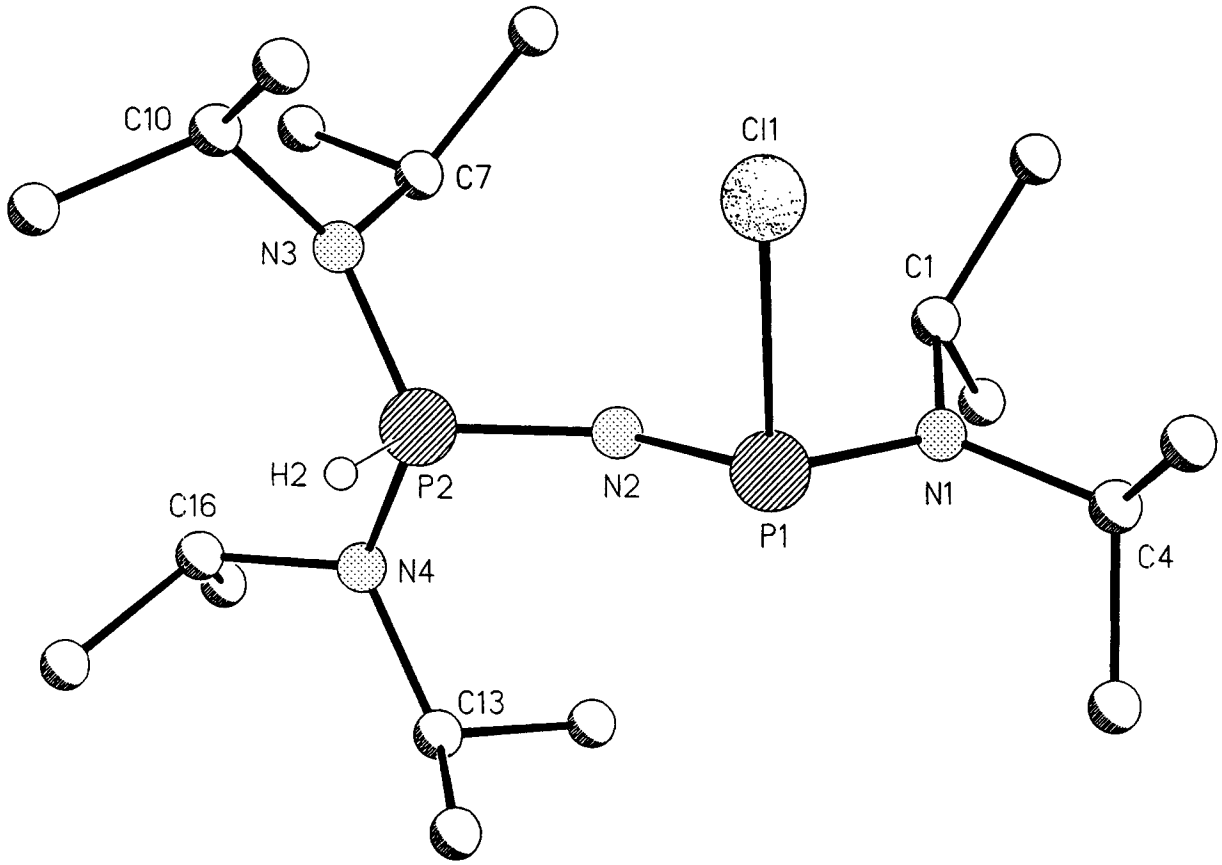


FIGURE 1 Molecular structure of **4a** in the solid state. C–H hydrogen atoms are omitted for clarity.

drastic elongation of the P–X bonds in **4a** [P1–C11: 230.6 (2) pm] and **4b** [P1–Br1: 256.5 (2) pm]. In relation to P–X single-bond lengths of 204 pm in PCl_3 and 222 pm in PBr_3 [13], these bond lengths correspond to Pauling bond orders of $n = 0.36$ in **4a** and $n = 0.26$ in **4b** [14]. These P–X bond distances are among the longest hitherto reported for P–Cl bonds [15] and, to our best knowledge, the longest P–Br bond [16]. In line with this explanation is the concomitant shortening of the two P–N bonds at P1 [P1–N1: **4a**: 166.6 (4), **4b**: 163.5 (5) pm; P1–N2: **4a**: 159.9 (4), **4b**: 161.0 (5) pm] relative to a standard P^{III}–N bond length of 170 pm [17] (**II** and **III**, Scheme 2).

Although no NMR-spectroscopic evidence was found for the tautomeric aminophosphines **3a–c**, the existence of an equilibrium between the two tautomeric forms **3** and **4** seems very likely in light of the reactivity of compounds **4a–c** (Scheme 1) and has already been shown for related compounds [18]. A ^{31}P-NMR study of the reaction of a second base equivalent (DBU) with **4a–c** shows the formation of the N-phosphanyl-substituted $\sigma^2\lambda^3$-iminophosphine **5**. This reaction is more likely to proceed via a 1,2 HCl elimination from **3a–c** than by a 1,3 HCl elimination from **4a–c**. The resonances of the two phosphorus nuclei in **5** at $\delta = 286.5$ ($\sigma^2\lambda^3$-P) and $\delta = 69.6$ ($\sigma^3\lambda^3$-P) as well as the $^2J_{PP}$ coupling constant of 210.9 Hz are in line with those of similar compounds [19]. Unfortunately, the reaction is not selective enough to allow isolation of **5** so far.

Addition of the chloroiminophosphane **6** to a solution of **1a** or **1b** in toluene in the presence of triethylamine at room temperature yields the P-hydrogeno-iminophosphoranyl-substituted iminophosphanes **8a,b**, which were isolated as yellow solids (Scheme 3). While stable as a solid under an argon atmosphere, **8a,b** quantitatively eliminate amine in solution within a week, yielding *cis*- and *trans*-diazadiphosphetidines **10a,b** and **11** as orange solids.

Whereas the elimination of amine from **8a** yields the *trans*- and *cis*-diazadiphosphetidines **10a** and **11** (in a nearly equal amount), only *trans*-diazadiphosphetidine **10b** is formed from **8b**. These results suggest that the steric and electronic influence of the aryliminophosphanyl moiety is sufficient to cause rearrangement and subsequent amine elimination from **8a,b** to generate diphosphadiazabutadienes

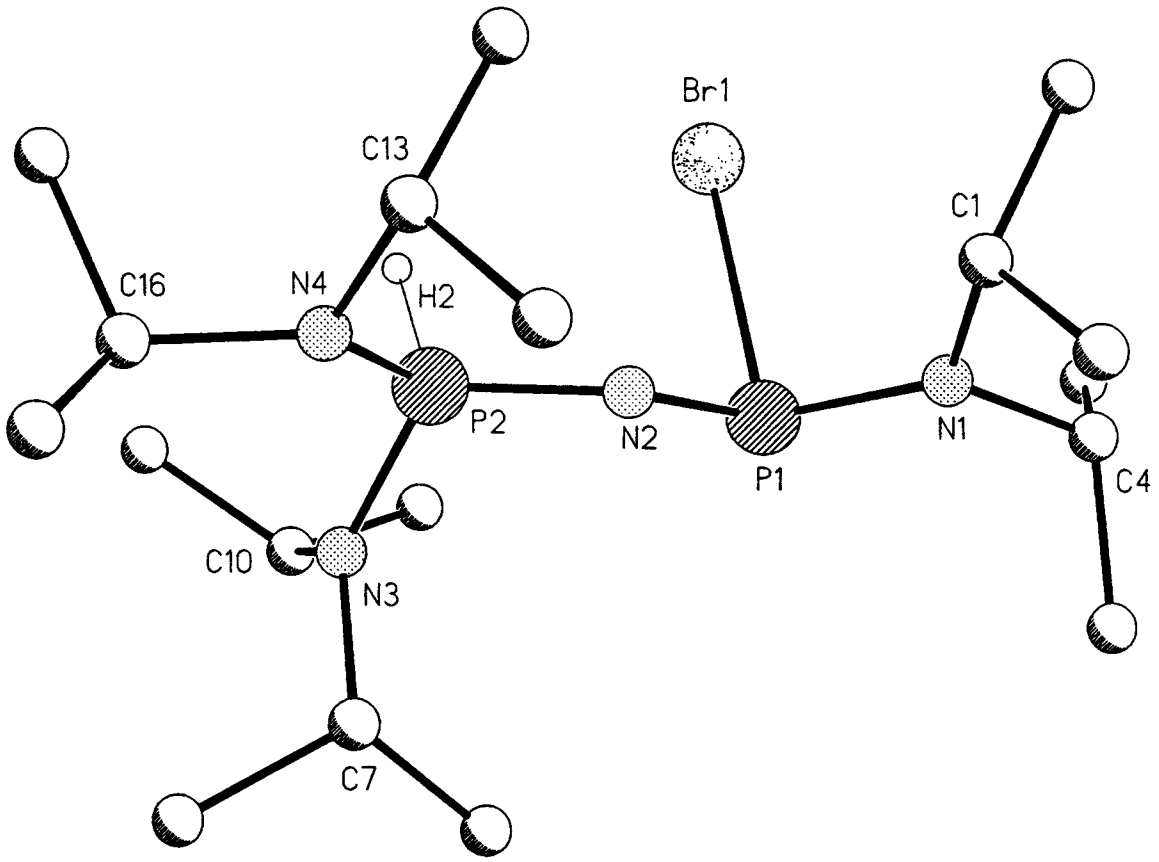


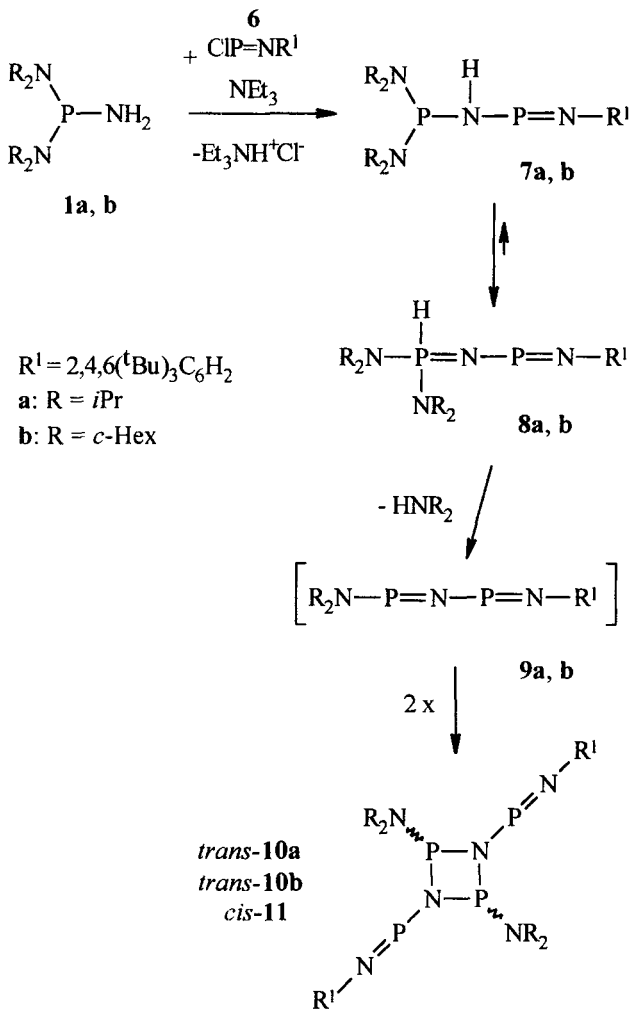
FIGURE 2 Molecular structure of **4b** in the solid state. C–H hydrogen atoms are omitted for clarity.

9a,b, but the steric protection is not sufficient to prevent its instant dimerization via a typical [2,2]-cycloaddition. The greater steric bulk of the *N*-bound cyclohexyl group in **9b** compared to the *i*-propyl residue in **9a** may be the reason for the exclusive formation of the *trans*-diazadiphosphetidines **10b**. The proposed reaction sequence is in line with that of the previously observed *α*-elimination of amine from diamino(hydrido)iminophosphoranes [6] and constitutes the first example of the formation of 2,4-diaza-1,3-diphosphetedines from such systems.

TABLE 2 Selected Structural Parameters of **4a** and **4b**—Bond Distances in (pm), Bond Angles in (°), esd in Parentheses.

Bond Distance				*Bond Angles*	
4a	***4b***			***4a***	***4b***
P1–X1	230.6 (2)	256.5 (2)	Σ° P1	305	304
P1–N1	166.6 (4)	163.5 (5)	Σ° N1	359	359
P1–N2	159.9 (4)	161.0 (5)	P2–N2–P1	136.8 (3)	124.8 (3)
P2–N2	156.1 (4)	157.9 (5)	N2–P2–N3	115.7 (2)	118.9 (3)
P2–N3	162.4 (4)	162.2 (5)	N2–P2–N4	107.8 (2)	107.3 (3)
P2–N4	164.8 (3)	164.9 (5)			

The constitution of compounds **8a,b**, **10a,b**, and **11** becomes evident from multinuclear NMR experiments, and in the case of **8a** and **10b**, single crystals suitable for X-ray structure analyses were gained by crystallization from toluene. The ^{31}P-resonances of **8a,b** are in line with the formulation stated in Scheme 2 ($\sigma^2\lambda^3$-P: **8a**: δ: 251.0, **8b**: δ: 244.1; $^2J_{PP}$: **8a**: 20.3, **8b**: 25.4 Hz; $\sigma^4\lambda^5$-P: **8a**: δ: 7.6, **8b**: δ: 4.0; $^1J_{HP}$: **8a**: 533.0, **8b**: 540.0 Hz). In contrast to the above-proposed intermediates **3a,b**, the NH-isomer **7b** of **8b** was observed by ^{31}P-NMR monitoring of the reaction solution. A second AX-spin system ($\sigma^2\lambda^3$-P: δ: 252.3, $\sigma^3\lambda^3$-P: δ: 79.5; $^2J_{PP}$ = 41.3 Hz) is found beside the resonances of **8b** and can be assigned to **7b**. These signals disappear within a few hours with concomitant increase of the resonances of **8b**, indicating the complete isomerization of **7b** into **8b**. The *cis*- and *trans*-isomers of diazadiphosphetidines **10a,b** and are observed as A_2X_2-spin systems in the ^{31}P-NMR spectra ($^2J_{PP}$: **10a**: 23.2, **10b**: 27.9, **11**: 83.3 Hz). The *cis*- and *trans*-isomers are easily distinguished by their characteristic $\sigma^3\lambda^3$-P resonances ($\sigma^3\lambda^3$-P: **10a**:



SCHEME 3

161.5, **10b**: 164.1 (*trans*), **11**: 90.2 (*cis*); $\sigma^2\lambda^3$-P: **10a**: 299.6, **10b**: 304.2, **11**: 314.2) [20]. The molecular structures of **8a** and **10b** are shown in Figures 3 and 4; relevant structural parameters are presented in Table 3.

The molecular structure of **8a** reveals a *Z*-configurated iminophosphine moiety. The P2–N2–P1–N1 backbone adopts a near-planar conformation ($\tau_{P2\text{-}N2\text{-}P1\text{-}N1}$ = 2°). P–N bond lengths and angles are very similar to those of the analogous Ph_3P = N-substituted iminophosphine [21], with the exception of the about 30° tighter P2–N2–P1 angle [131.2 (2)°] in **8a**, compared to the 160° angle observed in the Ph_3P = N derivative, which might be a result of steric interaction between the aryl and one of the diisopropylamino groups.

The suggested constitution of *trans*-diazadiphosphetidine **10b** deduced from the NMR data in solution was confirmed by the results of the X-ray structure analysis (Figure 4). **10b** shows C_i symmetry with the inversion center at the center of the four-membered ring and the *E*-configuration at the P = N double bonds. The *endo*-cyclic P–N bond lengths [P1–N1, P1–N1*a*: 175.8 (2) pm] and angles [N1–P1–N1*a*: 79.9 (1)°, P1–N1–P1*a*: 100.1 (1)°] are of typical magnitude for 1,3-diaza-2,4-diphosphetidines [20]. The relatively short *exo*-cyclic P–N bond lengths [N1–P2: 165.7 (2)] result from conjugative interaction between the ring sp^2-N atom and the π system of the P = N double bond [22], which also explains the near-coplanar orientation of the PN-π system relative to the ring plane.

EXPERIMENTAL

All manipulations were carried out with the exclusion of air and moisture in an inert gas atmosphere (argon). Solvents were dried using standard procedures. The triaminophosphanes **1a,b** [7], dihalogenophosphines **2a–c** [23], and chloro-*N*-(2,4,6-^{t}-$Bu_3C_6H_2$)-iminophosphine **6** [24] were prepared by literature methods. NMR: Bruker AMX 300; ^{31}P: 121.5 MHz, external standard 85% H_3PO_4; ^{1}H: 300.1 MHz, external standard TMS; ^{13}C: 75.5 MHz, external standard TMS, positive sign denotes shifts to lower frequencies; MS: Kratos Instruments Concept 1H, Kratos Instruments, MS 50, VG Instruments VG 12-250 (EI, 70 eV). Elemental analyses: Heraeus CHN-O-Rapid, melting points were determined in sealed glass capillaries and are uncorrected.

Procedure for the Preparation of the P–H-Iminophosphoranyl-halogenoaminophosphanes **4a–c**

To a solution of 4.92 g (20 mmol) of aminophosphane **1a** in 50 mL of hexane was quickly added a solution of 20 mmol of dihalogenophosphane (**4a**: 4.0 g, **4b**: 5.8 g, **4c**: 7.7 g) and 2.8 mL (20 mmol) of triethylamine in 20 mL hexane, and the mixture was stirred at room temperature for 30 minutes. The precipitated ammonium salt was filtered off, and the reaction product crystallized from the resulting solution at −80°C.

[Bis(diisopropylamino)-hydrogeno-iminophosphoranyl]-chlorodiisopropylaminophosphane **4a**

Yield: 5.9 g (71%); mp 65–67°C. ^{31}P[^{1}H]-NMR (C_6D_6): δ = 183.7 (d, $^2J_{PP}$ = 128.4 Hz), 1.7 (d, $^2J_{PP}$ = 128.4 Hz). ^{1}H-NMR (C_6D_6): δ = 7.62 (dd, $^1J_{HP}$ = 539.3 Hz,

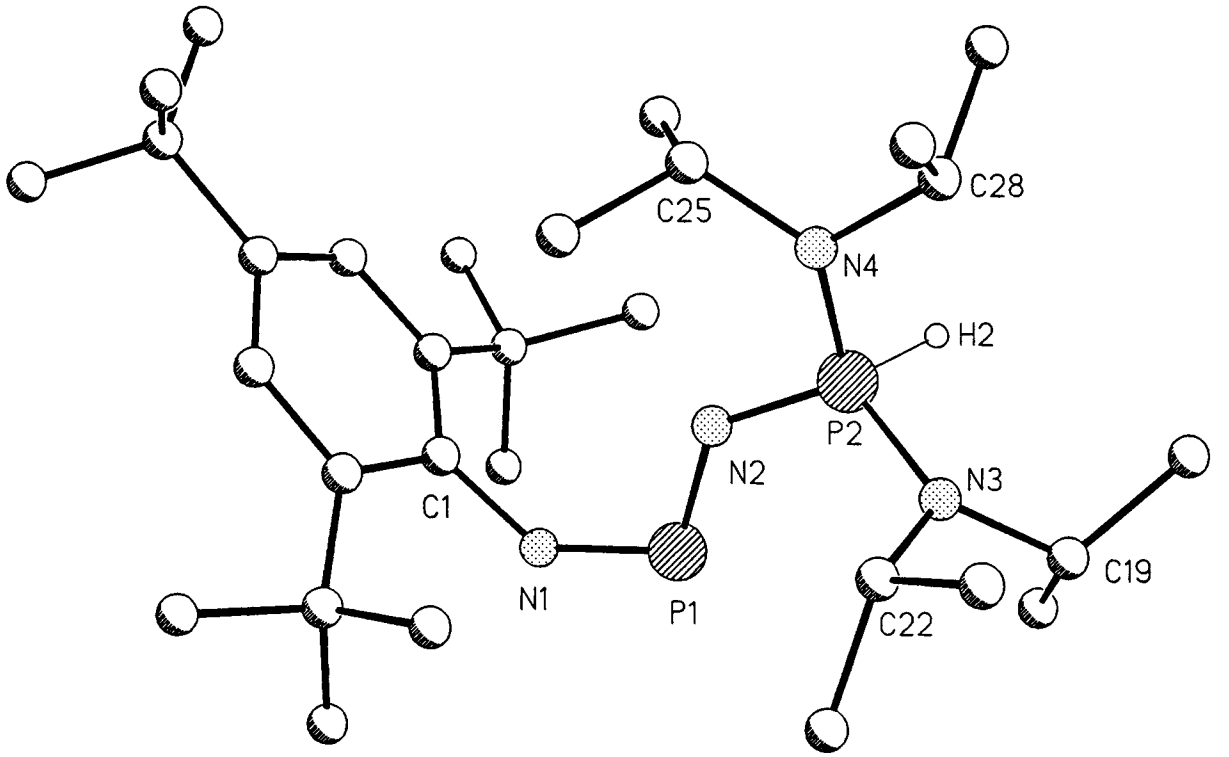


FIGURE 3 Molecular structure of **8a** in the solid state. C–H hydrogen atoms are omitted for clarity.

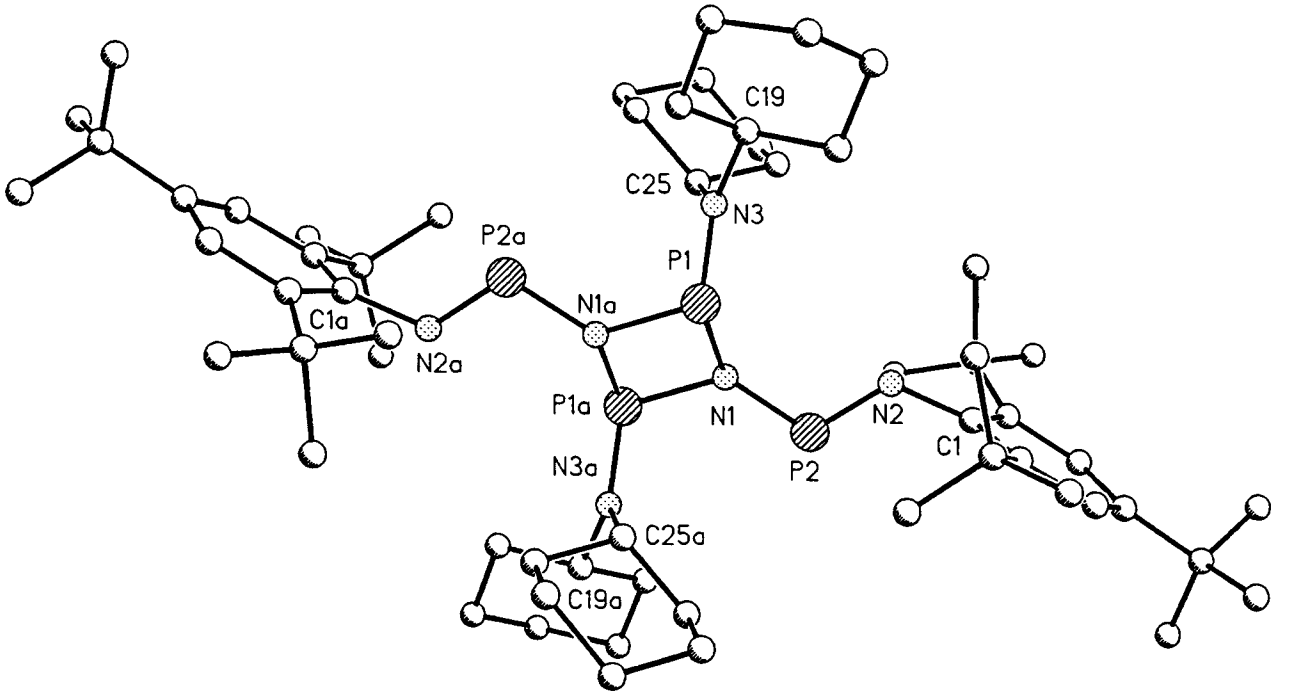


FIGURE 4 Molecular structure of *trans*-**10b** in the solid state. C–H hydrogen atoms are omitted for clarity.

TABLE 3 Relevant structural parameters of **8a** and *trans*-**10b**. Bond distances in (pm), bond angles in (°), esd in parentheses. Atoms denoted with an *a* were generated by symmetry transformation $-x, -y + 1, -z$.

8a				*trans*-**10b**			
Bond Distance		*Bond Angle*		*Bond Distance*		*Bond Angle*	
P1–N1	154.8 (3)	N2–P1–N1	112.7 (2)	P1–N1	175.8 (2)	N1*a*–P1–N1	79.9 (1)
P1–N2	161.6 (3)	P2–N2–P1	131.2 (2)	P1–N1*a*	175.8 (2)	P1–N1–P1*a*	100.1 (1)
P2–N2	156.4 (3)	P1–N1–C1	129.8 (3)	N1–P2	165.7 (2)	N1–P2–N2	107.1 (1)
P2–N3	163.8 (3)	N3–P2–N2	118.9 (2)	P2–N2	156.2 (2)	P2–N2–C1	118.6 (2)
P2–N4	164.2 (3)	N3–P2–N4	108.2 (2)	P1–N3	165.2 (2)	Σ°P1	293
N1–C1	141.5 (5)	N4–P2–N2	107.9 (2)	N2–C1	142.3 (3)	ΣN1	357

TABLE 4 Crystallographic Data

	4a	**4b**	**8a**	*trans*-**10b**
Crystal Data				
Formula	$C_{18}H_{43}ClN_4P_2$	$C_{18}H_{43}BrN_4P_2$	$C_{30}H_{58}N_4P_2$ toluene	$C_{60}H_{102}N_6P_4$ (4 • 0.5) toluene
M	413.0	457.4	628.9	1215.6
Color	colorless	colorless	yellow	orange
Dimension [mm]	0.20 × 0.30 × 0.55	0.10 × 0.40 × 0.65	0.40 × 0.40 × 0.50	0.10 × 0.20 × 0.40
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	P-1 (no. 2)	$P2_1$ (no. 4)	P-1 (no. 2)	P-1 (no. 2)
a (Å)	9.567(3)	10.310(2)	10.024(1)	10.167(2)
b (Å)	10.200(3)	12.524(3)	11.504(1)	13.598(1)
c (Å)	14.218(5)	10.978(2)	17.733(2)	13.901(1)
α (°)	105.09(2)		92.79(1)	88.14(1)
β (°)	95.72(2)	114.61(2)	90.46(1)	88.52(1)
γ(°)	105.28(2)		97.21(1)	73.98(1)
V (Å^3)	1271(1)	1288.7(5)	2026.1(4)	1845.9(4)
Z	2	2	2	1
ρ (g cm^3)	1.08	1.18	1.03	1.09
μ (mm^{-1})	0.29	1.73	1.17	1.26
F(000)	452	488	692	664
Structure Solution and Refinement				
Full matrix least squares				
Refinement on	F^2	F^2	F^2	F^2
Parameter/restraints	229/4	241/2	392/18	375/105
Measured reflection	4705	4767	6214	5740
Unique reflection				
Used in refinement	4441	4527	5988	5474
*w*R2	0.189	0.139	0.209	0.175
R_1 [for $I > 2\sigma(I)$]	0.070	0.055	0.065	0.065
Largest Diff.				
Peak and hole (eÅ^{-3})	0.41/−0.44	0.44/−0.64	0.76/0.31	0.56/−0.64
Data collection parameter				
Diffractometer	Nicolet R3m	Nicolet R3m	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
λ (Å)	0.71073	0.71073	1.54178	1.54178
T (K)	293(2)	293(2)	293(2)	200(2)
$2\theta_{max}$ (°)	50	50	120	120
	$-11 \le h \le 11$	$-12 \le h \le 11$	$-11 \le h \le 11$	$-11 \le h \le 11$
	$-12 \le k \le 11$	$-14 \le k \le 14$	$-12 \le k \le 12$	$-15 \le k \le 15$
	$0 \le l \le 16$	$0 \le l \le 13$	$0 \le l \le 19$	$-15 \le l \le 0$

$^3J_{HP}$ = 3.9 Hz, 1H, P*H*), 3.54 [m, 6H, NC*H*, (λ^3-P, λ^5-P)], 1.57 [d, $^3J_{HH}$ = 6.8 Hz, 12H, CCH_3, (λ^3-P)], 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CCH_3, λ^5-P). ^{13}C-NMR (C_6D_6): δ = 45.3 [d, $^2J_{CP}$ = 9.8 Hz, N*C* (λ^3-P)], 45.2 [d, $^2J_{CP}$ = 6.2 Hz, N*C* (λ^5-P), 23.8 [d, $^3J_{CP}$ = 2.7 Hz, N*C* (λ^5-P)], 23.7 [d, $^3J_{CP}$ = 2.7 Hz, N*C* (λ^3-P)], 22.7 [d, $^3J_{CP}$ = 1.9 Hz, N*C* (λ^3-P)]. MS (*m/z*) (%): 412 (2) [M$^+$], 377 (6) [M$^+$ − Cl], 277 (51) [M$^+$ − Cl − *i*-Pr_2N], and other fragments.

[Bis(diisopropylamino)-hydrogeno-iminophosphoranyl]-bromodiisopropylaminophosphane **4b**

Yield: 4.8 g (53%); mp 78–80°C. ^{31}P-NMR ($CDCl_3$): δ = 261.2 [d, $^2J_{PP}$ = 102.2 Hz, (λ^3-P)], 4.4 [ddqui, $^1J_{PH}$ = 552.0 Hz, $^2J_{PP}$ = 102.2 Hz, $^3J_{PH}$ = 16.9 Hz, (λ^5-P)].

[Bis(diisopropylamino)-hydrogeno-iminophosphoranyl]-iododiisopropylaminophosphane **4c**

Yield: 3.7 g (37%); mp 95–97°C. ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 288.2 (d, $^2J_{PP}$ = 92.9 Hz), 10.3 (d, $^2J_{PP}$ = 92.9 Hz). ^{1}H-NMR (C_6D_6): δ = 7.82 (dd, $^1J_{HP}$ = 566.0 Hz, $^3J_{HP}$ = 2.7 Hz, 1H, P*H*), 3.75 [m, 6H, NC*H*, (λ^3-P, λ^5-P)], 1.63 [d, $^3J_{HH}$ = 6.6 Hz, 6H, CCH_3, (λ^3-P)], 1.57 [d, $^3J_{HH}$ = 6.8 Hz, 6H, CCH_3, λ^3-P)] 1.44 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CCH_3, λ^5-P), 1.38 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CCH_3, λ^5-P). ^{13}C-NMR (C_6D_6): δ = 46.9 [d, $^2J_{CP}$ = 9.8 Hz, N*C* (λ^3-P)], 46.3 [d, $^2J_{CP}$ = 6.3 Hz, N*C* (λ^5-P)], 24.1 [d, $^3J_{CP}$ = 3.2 Hz, N*C* (λ^5-P)], 24.0 [d, $^3J_{CP}$ = 3.2 Hz, N*C* (λ^3-P)], 23.4 [d, $^3J_{CP}$ = 2.2 Hz, N*C* (λ^3-P)]. MS (*m/z*) (%): 504 (1) [M$^+$], 377 (100) [M$^+$ − Cl], 277 (5) [M$^+$ − Cl − *i*-Pr_2N], and other fragments.

P-[Bis(diisopropylamino)-hydrogeno-iminophosphoranyl]-N-(2,4,6-tris-tert-butylphenyl)-$\sigma^2\lambda^3$-iminophosphane **8a** *and P-[Bis (dicyclohexylamino) -hydrogeno-iminophosphoranyl]-N-(2,4,6-tris-tert-butylphenyl)-$\sigma^2\lambda^3$-iminophosphane* **8b**

To a solution of 5 mmol **1** (**a**: 1.23 g; **b**: 2.03 g) in 40 mL of toluene was quickly added a solution of 1.63 g (5 mmol) of chloriminophosphane **6** and 0.7 mL (5 mmol) of triethylamine. The resulting yellow solution was stirred for 30 minutes, then the precipitated ammonium chloride was filtered off, and **8a,b** were crystallized from this solution at −30°C.

8a: Yield: 1.7 g (63%); mp 76°C. ^{31}P{^{1}H}-NMR (C_6D_6): δ = 251.0 (d, $^2J_{PP}$ = 20.3 Hz), −7.1 (d, $^2J_{PP}$ = 20.3 Hz). ^{1}H-NMR (C_6D_6): δ = 7.6 (s, 2H, aryl-*H*), 7.33 (d, $^1J_{HP}$ = 533 Hz, 1H, P*H*), 3.44 (d sept, $^3J_{HP}$ = 17.1 Hz, $^3J_{HH}$ = 6.9 Hz, 4H, NC*H*), 1.90 (s, 18H, *o*-aryl-CCH_3), 1.51 (s, 9H, *p*-aryl-CCH_3). ^{13}C-NMR (C_6D_6): δ = 148.7 (d, $^2J_{CP}$ = 41.9 Hz, *ipso*-aryl-*C*), 139.7 (d, $^2J_{CP}$ = 5.8 Hz, *o*-aryl-*C*), 137.2 (d, $^5J_{CP}$ = 10.0 Hz, *p*-aryl-*C*), 121.5 (d, $^4J_{CP}$ = 2.6 Hz, *m*-aryl-*C*), 44.9 (d, $^2J_{CP}$ = 6.5 Hz, NCCH$_3$), 36.7 (s, *o*-*C*CH$_3$), 33.6 (s, *o*-C*C*H$_3$), 32.5 (s, *p*-*C*CH$_3$), 32.0 (s, *p*-C*C*H$_3$), 23.6 (d, $^3J_{CP}$ = 3.05 Hz, NC*C* H$_3$). MS (*m/z*) (%): 536 (7) [M$^+$], 494 (13) [M$^+$ − C_3H_6], 436 (35) [M$^+$ − *i*-Pr_2N], 291 (100) [M$^+$ − aryl], and other fragments.

8b: Yield: 2.8 g (83%); mp 82°C. ^{31}P{^{1}H}-NMR (C_6D_6): δ = 244.1 (d, $^2J_{PP}$ = 25.4 Hz), 4.0 (d, $^2J_{PP}$ = 25.4 Hz). ^{1}H-NMR (C_6D_6): δ = 7.46 (d, $^1J_{HP}$ = 540.3 Hz, 1H, P*H*), 7.25 (s, 2H, aryl-*H*), 3.07 (m, 4H, NC*H*), 1.9–0.9 (m, 40H, *c-Hex*), 1.51 (s, 18H, *o*-aryl-CCH_3), 1.27 (s, 9H, *p*-aryl-CCH_3), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, NCCH_3), 1.1 (d, $^3J_{HH}$ = 6.9 Hz, 12H, NCCH_3). ^{13}C-NMR (C_6D_6): δ = 146.2 (d, $^3J_{CP}$ = 5.7 Hz, *o*-aryl-*C*), 139.7 (d, $^3J_{CP}$ = 2.27 Hz, *ipso*-aryl-*C*), 136.6 (d, $^5J_{CP}$ = 9.9 Hz, *p*-aryl-*C*), 121.7 (d, $^4J_{CP}$ = 2.3 Hz, *m*-aryl-*C*), 54.9 (d, $^2J_{CP}$ = 5.73 Hz, NCCH$_3$), 36.4 (s, *o*-*C*CH$_3$), 34.8 (s, *o*-C*C*H$_3$), 34.5 (s, NC*C*H$_2$), 33.7 (s, *p*-*C*CH$_3$), 32.1 (s, *p*-C*C*H$_3$), 27.0 (s, NCC*C*H$_2$), 25.8 (s, NCCC*C*H$_2$).

Procedure for the Preparation of Diazadiphosphetidines **10a**, **10b**, *and* **11**

4 mmol of the P-hydrogenoiminophosphoranyl-iminophosphane **8** (**8a**: 2.14 g; **8b**: 2.38 g) was dissolved in 20 mL of toluene. After 1 week, an orange precipitate containing the *trans*-diazadiphosphetidine was isolated by filtration and recrystallized from dichloromethane (**10a**) or toluene (**10b**), respectively. From the reaction filtrate of **8a**, the *cis*-diazadiphosphetidine **11** was isolated by crystallization at −30°C.

trans-2,4-Bis(diisopropylamino)-1,3-bis(N'-2,4,6-tri-tert-butylphenyliminophosphanyl)-1,3,2,4-diazadiphosphetidine **10a**.

Yield: 0.62 g (36%); mp 195°C (dec.). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ = 299.6 (t, $^2J_{PP}$ = 23.2 Hz), 161.5 (t, $^2J_{PP}$ = 23.2 Hz). ^{1}H-NMR (C_6D_6): δ = 7.70 (s, 4H, aryl-*H*), 4.42 (m, 4H, NC*H*), 1.75 (s, 36H, *o*-CCH_3), 1.52 (s, 18H, *p*-CCH_3), 1.45 (d, $^3J_{HH}$ = 6.9 Hz, 24H, NCCH_3). ^{13}C-NMR (C_6D_6): δ = 145.2 (d, $^3J_{CP}$ = 17.93 Hz, *o*-aryl-*C*), 142.3 (s, *p*-aryl-*C*), 138.5 (d, $^3J_{CP}$ = 8.77 Hz, *ipso*-aryl-*C*), 121.7 (s, *m*-aryl-*C*), 53.7 (s, NCH), 36.6 (s, *p*-*C*CH$_3$), 34.9 (s, *o*-*C*CH$_3$), 33.4 (s, *p*-*C*CH$_3$), 32.1 (s, NCCH$_3$), 30.7 (s, *p*-CCH$_3$). EA: calcd: C, 66.18; H, 9.95; N, 9.65. Found: C, 66.13; H, 9.92; N, 9.63.

trans-2,4-Bis(dicyclohexylamino)-1,3-bis(N'-

2,4,6-tri-tert-butylphenyliminophosphanyl)-1,3,2,4-diazadiphosphetidine **10b**. Yield: 1.09 g (53%); mp 165°C. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 304.2 (t, $^2J_{PP}$ = 27.9 Hz), 164.1 (t, $^2J_{PP}$ = 27.9 Hz). ^1H-NMR (C_6D_6): δ = 7.29 (s, 4H, aryl-*H*), 3.95 (m, 4H, NC*H*), 2.1–1.0 (m, 40H, *c*-Hex), 1.46 (s, 36H, *o*-CCH_3), 1.31 (s, 18H, *p*-CCH_3). ^{13}C-NMR (C_6D_6): δ = 145.2 (d, $^3J_{CP}$ = 20.8 Hz, *o*-aryl-*C*), 142.3 (s, *p*-aryl-*C*), 138.1 (d, $^3J_{CP}$ = 8.8 Hz, *ipso*-aryl-*C*), 122.0 (s, *m*-aryl-*C*), 56.4 (d, $^3J_{CP}$ = 14.3 Hz, NCH), 36.7 (s, *o*-CCH_3), 34.9 (s, *p*-CCH_3), 33.5 (s, *p*-CCH_3), 33.3 (s, NCCH_2), 32.1 (s, *p*-CCH_3), 27.4, 26.8 (s, NCCCH_2), 26.0, 25.8 (s, NCCCCH_2).

cis-2,4-Bis(diisopropylamino)-1,3-bis(N'-2,4,6-tri-tert-butylphenyliminophosphanyl)-1,3,2,4-diazadiphosphetidine **11**

Yield: 0.38 g (22%); mp 183°C (dec.). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ = 314.2 (t, $^2J_{PP}$ = 83.3 Hz), 90.2 (t, $^2J_{PP}$ = 83.3 Hz). ^1H-NMR (C_6D_6): δ = 7.72 (s, 4H, aryl-*H*), 4.02 (m, 4H, NC*H*), 1.75 (s, 36H, *o*-CCH_3), 1.54 (s, 18H, *p*-CCH_3), 1.40 (d, $^3J_{HH}$ = 6.9 Hz, 24H, NCCH_3).

X-ray Structure Determination of **4a,b**, **8a**, *and trans-*10b

The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Absorption corrections on the basis of ψ scans were applied to **8a** and *trans*-**10b**. In **4b**, the absolute structure was determined. In *trans*-**10b**, an *o*-^{t}Bu-group was disordered. Details of data collection and refinement are given in Table 4. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen (FRG) on quoting the depository numbers CSD-391046 (4a), CSD-391047 (46), CSD-391044 (8a), and CSD-391045 (10b).

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