Triazinyl Phosphorus Compounds

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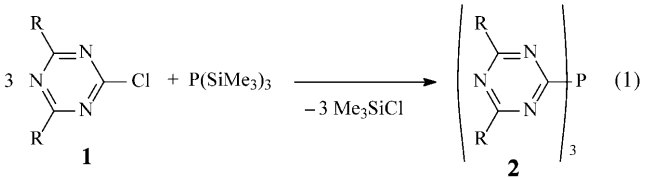
The Influence of Electron-Withdrawing Groups on the Chemistry of Phosphorus: Tautomerization of Bis(*s*-triazinyl)phosphanes**

Berthold Hoge and Waldemar Wiebe*

The influence of electron-withdrawing groups in phosphorus chemistry is essential, for example for the realization of organic electron-conducting materials[1] and chiral π-acidic phosphane ligands[2] as well as for the stabilization of phosphinous acids[3] and low-valent phosphorus species.[4,5]

1,3,5-Triazin-2-yl groups (referred to in the following as *s*-triazinyl) are strongly electron-withdrawing substituents. Their electron-withdrawing effect significantly exceeds that of the pentafluorophenyl group, as is evident by comparison of the C–O and C–N distances of the corresponding phenolate and aryl amide ions ($Ar–O^-$ and $Ar–NH^-$), respectively.[6] Although monosubstituted *s*-triazinylphosphorus compounds have been known for more than 50 years,[7] no example of bis- or tris-substituted derivatives has been reported.

The reaction of tris(trimethylsilyl)phosphane, $P(SiMe_3)_3$, with 2,4,6-trichloro- or 2,4,6-trifluoro-*s*-triazine leads to the formation of mono(*s*-triazinyl)phosphanes such as $(Me_3Si)_2P$-(s-$C_3N_3X_2$) with X = F, Cl. To find an access to bis- and tris(*s*-triazinyl)phosphane derivatives, we investigated the reaction of $P(SiMe_3)_3$ with 4,6-disubstituted 2-chloro-*s*-triazines [Eq. (1)]. When a solution of $P(SiMe_3)_3$ in diglyme was heated at reflux with an excess of a 2-chloro-*s*-triazine, the corresponding tris(*s*-triazinyl)phosphane derivative formed. The pale yellow to orange solids were isolated in almost 80% yield.[8]



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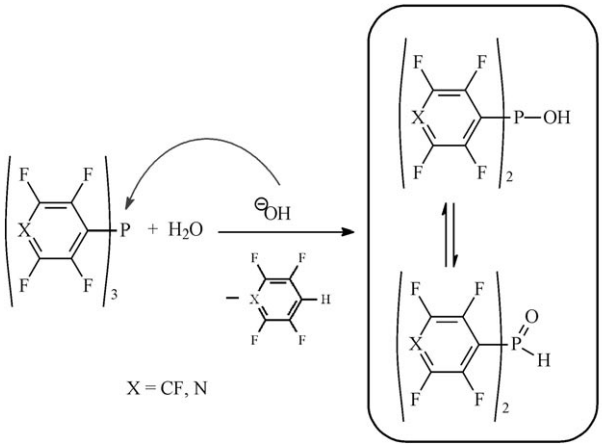
All attempts to synthesize bis(*s*-triazinyl)phosphane compounds by the reaction of $P(SiMe_3)_3$ with two equivalents of 2-chloro-*s*-triazine derivatives **1a–d** were unsuccessful. With the aim of synthesizing a novel bis(*s*-triazinyl)phosphane derivative, we investigated the hydrolysis of the tris(*s*-triazinyl)-derivatives **2a** and **2b** under basic conditions. The hydrolysis of triarylphosphanes PR_3 with electron-withdrawing pentafluorophenyl or *p*-tetrafluoropyridyl groups proceeds by means of a nucleophilic attack of a hydroxide anion at the central phosphorus atom [Eq. (2)], leading to the formation of the corresponding phosphinous acids R_2POH, which exist in a solvent-dependent equilibrium with the tautomeric phosphane oxides $R_2P(O)H$ ($R = C_6F_5$, p-C_5NF_4).[3]



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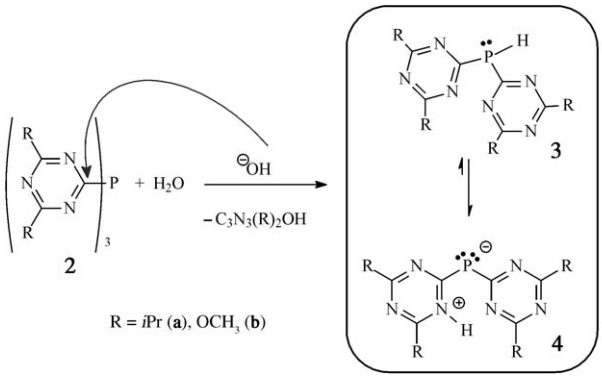
Instead of the expected nucleophilic substitution of one *s*-triazinyl group by an OH group, the hydrolysis of tris(*s*-triazinyl)phosphanes **2** proceeds by a nucleophilic attack of a hydroxide ion at the *ipso* carbon atom of one *s*-triazinyl ring, resulting in the formation of the novel bis(*s*-triazinyl)phosphanes **3** [Eq. (3)]. These compounds are not stable with respect to their zwitterionic isomers **4**, in which the hydrogen atom is bonded to a nitrogen atom of one *s*-triazinyl ring.



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[*] Priv.-Doz. Dr. B. Hoge, Dr. W. Wiebe
Institut für Anorganische Chemie, Universität zu Köln
Greinstrasse 6, 50939 Köln (Germany)
Fax: (+49) 221-470-5196
E-mail: b.hoge@uni-koeln.de
Homepage: http://www.hoge.uni-koeln.de/

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Isomers **3a** and **4a** were both detected by NMR spectroscopy in common organic solvents in all cases. The tautomeric equilibrium between **3a** and **4a** is related to both the keto–enol tautomerism observed for diacylphosphanes[9] and the isomerization of bis(benzothiazol-2-yl)phosphane, which exists both in the solid state as well as in diethyl ether solution as its N–H isomer. Surprisingly, the P–H isomer of the bis(benzothiazol-2-yl) derivative $HP(bth)_2$, although it is detectable in THF solution by NMR spectroscopic methods, is instable and dismutates into $P(bth)_3$ and $H_2P(bth)$.[10] This behavior was not observed for the *s*-triazine derivatives **3a** and **4a**,.

Exchange NMR spectroscopy (EXSY) is a very useful tool for investigating the dynamic equilibrium between compounds **3** and **4** in solution. The observation of cross peaks between the resonances of the bis(*s*-triazinyl)phosphane **3a** and the zwitterionic tautomer **4a** in the 2D $^{31}P/^{31}P$ EXSY NMR spectrum (Figure 1) proves the dynamic exchange between two forms. The dynamic behavior is also supported by 2D $^{1}H/^{1}H$ EXSY spectra.

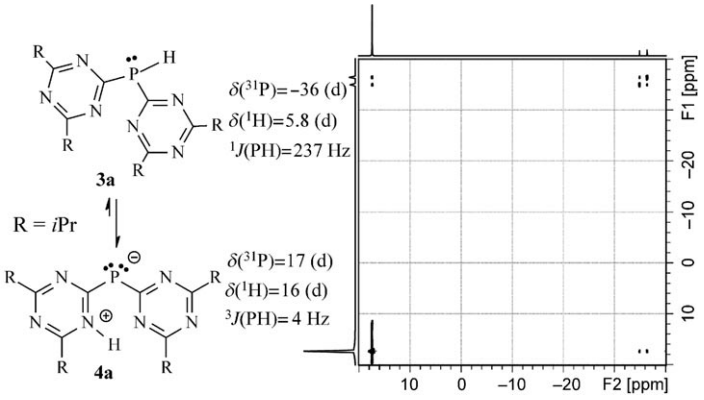


Figure 1. 2D $^{31}P/^{31}P$ EXSY NMR spectrum of the tautomeric couple **3a** and **4a** (room temperature, $[D_8]$toluene).

The ^{31}P NMR resonances of **3a** and **4a** are separated by more than 50 ppm and can be easily assigned as a result of the different $^{1}J(PH)$ and $^{3}J(PH)$ couplings of 237 and 4 Hz, respectively. By integration of the 1D ^{31}P NMR resonances at different temperatures the temperature dependency of the tautomeric equilibrium could be investigated. As the temperatures increases, the relative intensity (concentration) of the phosphane tautomer **3a** increases, indicating that the zwitterionic compound **4a** is lower in energy. Figure 2 depicts a van't Hoff plot of the equilibrium concentrations at eight temperatures. The regression yields $\Delta H° = (-24 \pm 1)\ kJ\,mol^{-1}$ for the temperature range from 233 to 333 K. This experimental result is in agreement with the results of quantum chemical calculations at the B3LYP/6-311G(d,p) level of theory which predicts that the zwitterionic isomer **4a** is stabilized by $\Delta H° = -15\ kJ\,mol^{-1}$ ($\Delta E_{ZPC} = -14\ kJ\,mol^{-1}$).[11] The deviation of the experimental value for the enthalpy difference of $(-24 \pm 1)\ kJ\,mol^{-1}$ in toluene solution and the calculated of $-15\ kJ\,mol^{-1}$ for isolated molecules in the gas phase seems acceptable, particularly when the significant

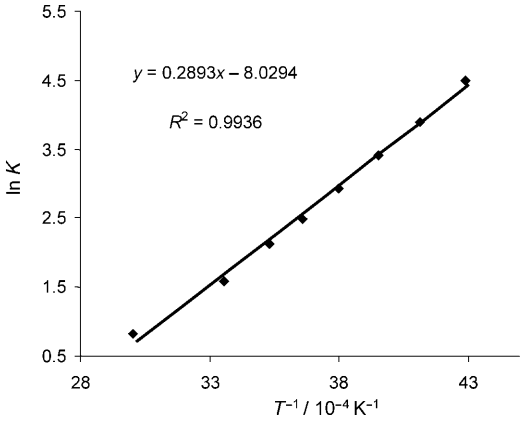
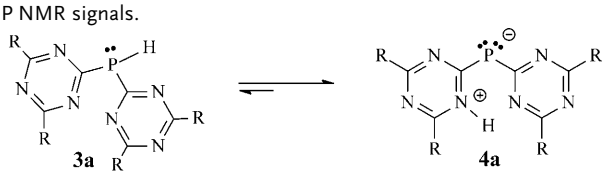


Figure 2. Van't Hoff plot of the equilibrium between tautomers **3a** and **4a** in $[D_8]$toluene solution.

solvent dependency of the equilibrium is taken into account. As outlined in Table 1, the relative concentration of the zwitterionic compound **4a** corresponds with the increasing dielectric constant of the solvent.

The ^{1}H NMR spectra of the very intense red solutions of **3a** and **4a** exhibit at room temperature three resonances for each isomer: two for the chemically different protons of the isopropyl groups and one for the hydrogen connected to the phosphorus and nitrogen atom, respectively. Lowering the temperature to 233 K decreases—as already discussed—the relative intensity (concentration) of the phosphane isomer **3a**. Simultaneously, the isopropyl resonances of the zwitterionic isomer **4a** show increasing broadening and then a separation into two independent sets of isopropyl resonances (**A** and **B** in Figure 3). The observation of two chemically different isopropyl groups can be explained by a coplanar arrangement of the two *s*-triazinyl rings, which are connected by a hydrogen bridge (Figure 3). This explains the hindered rotation of

Table 1: Solvent-dependent equilibrium of tautomers **3a** and **4a** at room temperature (R = *i*Pr). The ratio was determined by integration of the ^{31}P NMR signals.



Solvent[a]	$\delta(^{31}P)$ 20–10; $^{3}J(PH)$ 4–5 Hz	$\delta(^{31}P)$ −35; $^{1}J(PH)$ 240 Hz
pentane	42	58
diethyl ether	25	75
toluene	17	83
chloroform	12	88
THF	8	92
DME	3	97
acetone[b]	3	97
DMA	2	98

[a] THF = tetrahydrofuran, DME = dimethoxyethane, DMA = *N*,*N*-dimethylacetamide. [b] Adduct formation was not considered.

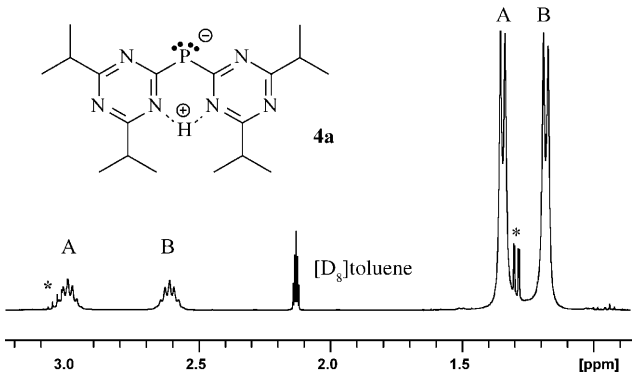
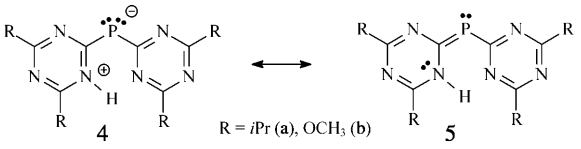


Figure 3. ^{1}H NMR resonances of the isopropyl groups of **4a** in [D_8]toluene solution at 233 K. The resonances of **3a** are indicated by an asterix.

the two *s*-triazinyl rings, which will cause a chemical differentiation of the two isopropyl groups at each *s*-triazinyl ring.

The coplanar arrangement of the *s*-triazinyl rings—as postulated in solution at lower temperature—was determined in the solid state of **4a**[8] and **4b**[12] by X-ray structure analysis of the corresponding intense red single crystals. As a result of the lacking hydrogen bond, the comparable bis(*s*-triazinyl)-amine derivatives $HN(C_3N_3X_2)$ with $X = Cl$[13] and NH_2[14] exhibit twisted *s*-triazinyl rings.

The methoxy derivative **4b** crystallizes in the orthorhombic space group *P*mnb (no. 62) with all non-hydrogen atoms lying on special positions—the mirror plane of the molecule (Figure 4). The C–N distances exhibit a broad variance from 130 to 138 pm. The P–C bond lengths of **4b** (174.5(3) and 179.4(3) pm) are shorter than those in corresponding tris(*s*-triazinyl)phosphane derivative **2b** (184.9(2) pm).[8] This shortening in **4b** may be interpreted in terms of partial double-bond character. The apparent difference between the two P–C distances can be described by the formulation of an additional mesomeric structure, the phosphaalkene derivative **5** [Eq. (4)]. The P–C bond length of 174.5(3) pm is in the typical range for C-amino phosphaalkenes.[15] The two P–C distances in **5b** (174.5(3) and 179.4(3) pm) are in an excellent agreement with data calculated at the B3PW91/6-311G(2d,p) level of theory (175.8 and 181.6 pm).[11]



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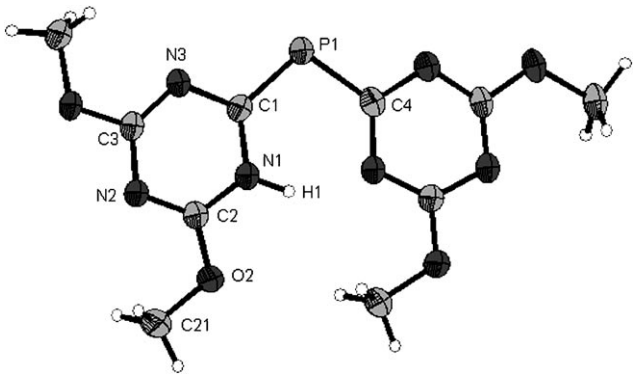

Figure 4. Molecular structure of **4b**/**5b**; the anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [pm] and angles [°]: P1–C1 174.5(3), P1–C4 179.4(3), N1–C2 134.6(4), N1–C1 137.9(3), N2–C2 130.3(3), N2–C3 136.0(3), N3–C3 131.3(3), N3–C1 136.9(3), C2–O2 132.0(3), O2–C21 145.3(4); C1-P1-C4 103.4(1), C2-N1-C1 120.4(2), C2-N2-C3 112.7(2), C3-N3-C1 116.5(2).

Experimental Section

Synthesis of **4a**: A solution of tris(4,6-diisopropyl-*s*-triazin-2-yl)phosphane (3.8 g, 7.3 mmol) in THF (40 mL) and 1M NaOH (20 mL) was stirred for 72 h at room temperature. After the addition of a concentrated NaCl solution (40 mL), the organic phase was separated and all volatiles were evaporated in vacuo. The resulting residue was extracted with pentane and concentrated in vacuo. On cooling of the intense red pentane solution ($\lambda_{max} = 424$ nm) to −28 °C, **4a** (2.1 g, 78%) precipitated as intense red crystals (m.p. 110 °C). Elemental analysis (%) calcd for **4a**: C 59.98, N 23.32 H 8.11; found: C 60.10, N 23.31, H 8.51. MS (20 eV): *m*/*z* (%) 524 (4) [$P\{C_3N_3(iPr)_2\}_3^+$], 360 (100) [M^+], 345 (15) [M^+-CH_3], 222 (26) [$\{C_3N_3(iPr)_2\}PHCN^+$], 166 (7) [$\{HC_3N_3(iPr)_2\}H^+$].

NMR data of **5a**: ^{1}H NMR (300 MHz, [D_8]toluene, 25 °C, TMS): $\delta = 16.0$ (d, $^3J(HP) = 4$ Hz, 1H), 2.8 (sept, $^3J(HH) = 7$ Hz, 4H), 1.2 ppm (d, $^3J(HH) = 7$ Hz, 24H); $^{13}C\{^1H\}$ NMR (75 MHz, [D_8]toluene, 25 °C, TMS): $\delta = 194.5$ (d, $^1J(PC) = 33.9$ Hz), 179.7 (br s), 36.6 (s, CH) 20.2 ppm (s, CH_3); ^{31}P NMR (81 MHz, [D_8]toluene, 25 °C, H_3PO_4): $\delta = 17.4$ ppm (d, $^3J(HP) = 4$ Hz).

NMR data of **3a:** ^{1}H NMR (300 MHz, [D_8]toluene, 25 °C, TMS): $\delta = 5.8$ (d, $^1J(HP) = 237$ Hz, 1H), 3.0 (sept, $^3J(HH) = 7$ Hz, 4H), 1.28/1.27 ppm (d, $^3J(HH) = 7$ Hz, diastereotopic CH_3 groups 12/12H); $^{13}C\{^1H\}$ NMR (75 MHz, [D_8]toluene, 25 °C, TMS): $\delta = 181.9$ (d, $^1J(PC) = 13$ Hz), 181.8 (d, $^3J(PC) = 5$ Hz), 37.1 (s, CH) 20.6/20.5 ppm (s, diastereotopic CH_3 groups); ^{31}P NMR (81 MHz, [D_8]toluene, 25 °C, H_3PO_4): $\delta = -35.6$ ppm (d, $^1J(HP) = 237$ Hz).

CCDC 692201 (**5b**) contains 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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[12] Data collection for X-ray structure determination was performed on a STOE IPDS II diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (71.073 pm). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data (X-Shape 2.01, Crystal Optimisation for Numerical Absorption Correction (C) 2001 STOE & Cie GmbH Darmstadt). The programs used in this work are Stoe's X-Area (X-Area 1.16, Stoe & Cie GmbH Darmstadt, 2003), including X-RED and X-Shape for data reduction and numerical absorption correction (X-RED32 1.03, Stoe Data Reduction Program (C) 2002 Stoe & Cie GmbH Darmstadt), and X-Step32 program (X-STEP32 1.06f, 2000 Stoe & Cie GmbH Darmstadt), including SHELXS-97 (G. M. Sheldrick, SHELXS-97, University of Göttingen, **1998**) and SHELXL-97 (G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**) for structure solution and refinement.

[13] The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all of the hydrogen atoms. Intensity data for **5b**, $C_{10}H_{13}N_6O_4P$ (313.23 g mol^{-1}), collected at 170(2) K, red polyhedron, orthorhombic space group *Pmnb* (no. 62); $a = 663.5(1)$, $b = 839.9(1)$, $c = 2420.3(4)$ pm, $V = 1.3487(3)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.538$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.232$ cm^{-1}, $F(000) = 648$; 20608 reflections with $3.4 < 2\theta < 54.7°$, 1651 independent in structure solution and refinement for 158 parameters, R_1 ($I \geq 2\sigma(I)$) = 0.049, wR_2 (all data) = 0.136, $w = 1/\{\sigma^2(F_o^2) + [0.0946(F_o^2 + 2F_c^2)/3]^2\}$.

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