Notiz / Note

Contribution to the Chemistry of Boron, 225[1]

Reactions of Monomeric Phosphanylboranes with Acyl Chlorides: 1-Oxa-3-oxonia-5-phospha-2-borata-3,5-cyclohexadienes

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Monomeric B-[bis(trimethylsilyl)phosphanyl]-9-borabicyclo-[3.3.1]nonane (1) reacts with acyl chlorides 2 in a 1:2 ratio to afford deep red derivatives of six-membered oxaoxonia-σ^2,λ^3-phosphaboratacyclohexadienes 3. In contrast, the (di-*tert*-butylboryloxy)phosphaethene 5 is obtained from tBu$_2$BP-(SiMe$_3$)$_2$ (4) and PhC(O)Cl. It is assumed that both reactions proceed via a common intermediate, an (acylphosphanyl)borane 6. The color of compounds 3, which feature a flat boat conformation, is due to a $\pi - \pi^*$ transition.

The existence of monomeric phosphanylboranes of the type R$_2$P−BR$_2$ has been definitely established only recently. Nevertheless, Ph$_2$P−BPh$_2$ is known since 1961[2], but it was not truly characterized until 1986[3]. Since then a number of other tetraarylphosphanylboranes have been reported[3–5]. Phosphanylboranes carrying alkyl substituents require sterically demanding groups such as the *tert*-butyl group on B or P atoms to be monomeric[4,5]. The same function fulfills the SiMe$_3$ group bound to the phosphorus atom[4,5]. These compounds are quite sensitive to moisture and oxygen and are in general highly reactive. The phosphanylboranes R$_2$B−P(SiMe$_3$)$_2$ are of special interest because they provide a model for studying the competition between reactions with reagents that may potentially react either with the PSi or the PB bond. In this paper we report on the behavior of this kind of phosphanylboranes towards acyl chlorides.

Reactions with Acyl Chlorides

The reaction of the phosphanylborane 1 with the acyl chlorides 2a, b produces a colorless precipitate at −78°C which dissolves on warming to give an intensly red-colored solution. The volatile material contains Me$_3$SiCl. A 1:2 ratio is required for a quantitative reaction of 1, and under these conditions a yield up to 70% of the heterocycles 3 is obtained as described by equation (1).

However, if 1 is replaced by the monomeric phosphanylborane 4 the reaction with benzoyl chloride stops at a 1:1 stoichiometry, and the product obtained is a derivative of the phosphaalkene 5, as shown in eq. (2).

It is evident from this result that the PSi bond is more reactive towards acyl chlorides than the BP bond. In addition, reaction (2) is comparable to the reaction of phosphanes RP(SiMe$_3$)$_2$ with acyl chlorides which give access to phosphaalkenes[6,7].

The formation of 3 is readily understood by assuming that the first step in the reaction, according to equation (1), is the formation of a 1:1 acid-base adduct followed by elimination of Me$_3$SiCl to produce the intermediate 6. This will then again react with the acyl chloride to produce the bis(acyl)borylphosphane 7. Boryl group
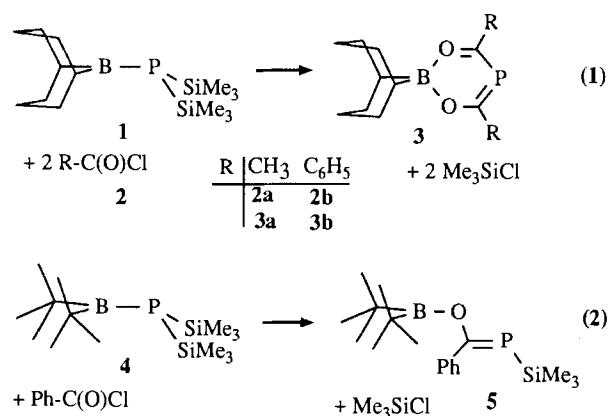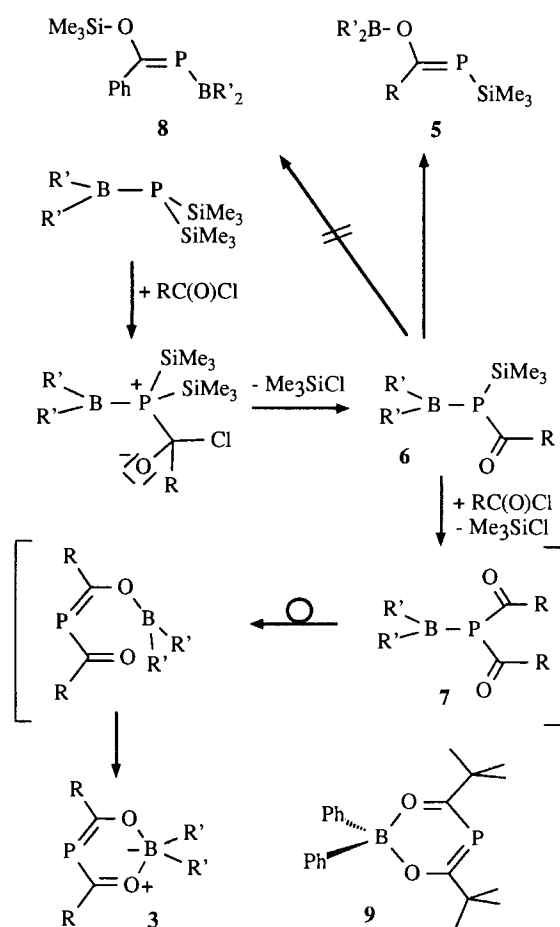

migration from the phosphorus atom to an oxygen atom is favored by the formation of the thermodynamically very stable BO bond which characterizes the final product 3.
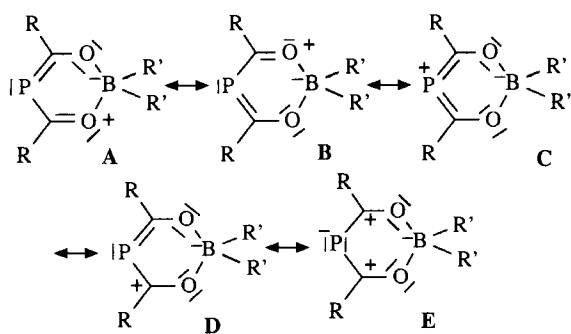
If the boron atom carries bulky R groups as in 4, then the intermediate of type 6 will react less readily with additional RC(O)Cl and therefore can rearrange to 5 but not to 8[7]. This selectivity is readily understood by considering the higher Lewis acidity of the R$_2$B group as compared to the Me$_3$Si group and the thermodynamic preference of the BO bond over the SiO bond.

NMR Spectra

The structure of compounds 3 and 5 can be readily deduced from their NMR specta. Thus, 5 exhibits an ^{11}B-NMR signal at $\delta = 49.4$ which is typical of a R$_2$BO group[8] and not indicative of a R$_2$BP group which would be present in isomer 8 ($\delta \approx 75$). Both ^{1}H- and ^{13}C-NMR spectra are in agreement with the proposed structure for 5. Two ^{31}P-NMR signals at $\delta = 134.2$ and 135.3 (very small) suggest the presence of *E*, *Z* isomers. Finally, no IR band close to a carbonyl group is observed for 5. Compounds 3 exhibit a single ^{31}P resonance ($\delta = 60.4$ for 3b, 75.1 for 3a). This is close to δ^{31}P re-

This description would correspond with a phosphaallene system of methinecyanine character. Consequently, the CO and PC bonds should be equivalent. It is conceivable that the delocalization of π electrons as described by the canonical structures is responsible for the intense color of this heterocyclic system. The most intense absorption in the UV/Vis spectrum is a band at 407 nm for 3a and at 510 nm (ε = 1800) for 3b. In addition, there are bands at 540 nm which are not well resolved and of weak intensity. The color-determining bands originate from a π − π* transition, and this assignment has been ascertained by an MNDO calculation on the model compound P[C(Me)O]₂BH₂. Figure 1 depicts the calculated bond lengths and bond angles of the planar heterocycle. Figure 2 presents a schematic representation of the orbitals involved in the color-generating electronic transitions. According to this scheme the $\sigma_{21} - \pi_{23}$ transition is calculated to be found at 308 nm, while the $\pi_{22} - \pi_{23}^{*}$ transition is calculated to have an energy difference of 9.95 eV or λ = 287 nm. Finally, the $\pi_{22} - \pi_{24}^{*}$ transition gives a calculated wave length of 216 nm, and the corresponding absorption will be expected almost in the UV region. No such transition has been observed for 3b, but for 3a it is at 258 nm[10].
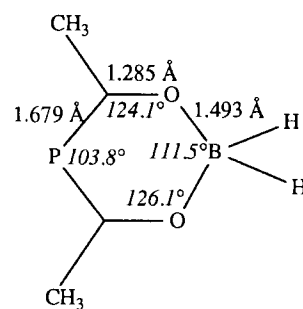

Figure 1. Calculated molecular parameters for P[C(Me)CO]₂BH₂ as obtained from geometrically optimized MNDO calculations

ported for 9 (δ = 63)[9]. δ¹¹B for 3a, b is 14.6 and 13.5, respectively, and this chemical shift is typical of tetracoordinated boron atoms in an R₂BO₂ environment[8]. The ¹H- and ¹³C-NMR spectral data are in accordance with the formula of 3. However, the IR spectra of compounds 3a and 3b are conclusive only in one respect: there is a single band in the low-frequency range of a carbonyl group. Thus, the CO stretching frequency is observed as a band at 1520 (3a) or 1478 cm⁻¹ (3b), demonstrating that the stretching frequency for the carbonyl group discloses a considerably weaker CO double bond as compared with acyl chlorides. Consequently, compounds of type 3 cannot be described by a single formula but rather in terms of canonical structures A−E or, in other words, by a delocalized system where the charge is distributed over five atoms. Even the structure E may have some significance for 3b because the positive charge at the carbon atoms may be stabilized by the phenyl groups.
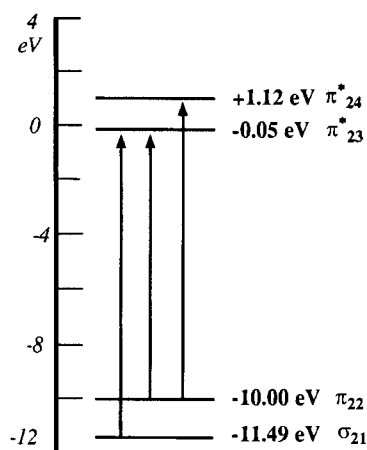

Figure 2. Schematic representation of highest occupied and lowest unoccupied molecular orbitals of the model compound P[C(Me)-CO]₂BH₂

Although the MNDO calculation on P[C(Me)O]₂BH₂ suggests the ring system to be planar, larger substituents at the carbon and boron atoms may disturb this geometry. There should, however, be no strong steric influence originating from the 9-BBN group because the neighboring oxygen atoms should not interfere sterically with the 9-BBN group. However, the phenyl group may interfere, depending on whether its ring plane is coplanar or orthogonal to the PC₂O₂B ring plane. Therefore, we have decided to investigate 3b by a single-crystal X-ray structural analysis.

Figure 3 shows the molecule of **3b** in the crystal in two orientations, in a perspective and side view. The latter reveals an almost planar arrangement of the PC_2O_2 ring atoms (the CP1C1 plane is bent to the CO1C1O2 plane by 10.6°) while the boron atom is located outside of the ring plane (0.52 Å above the C_2O_2 ring plane). Also the phenyl rings are close to be coplanar with the PC_2O_2 plane, the angle between the normals of the two planes are 15.3 and 18.9°, respectively.
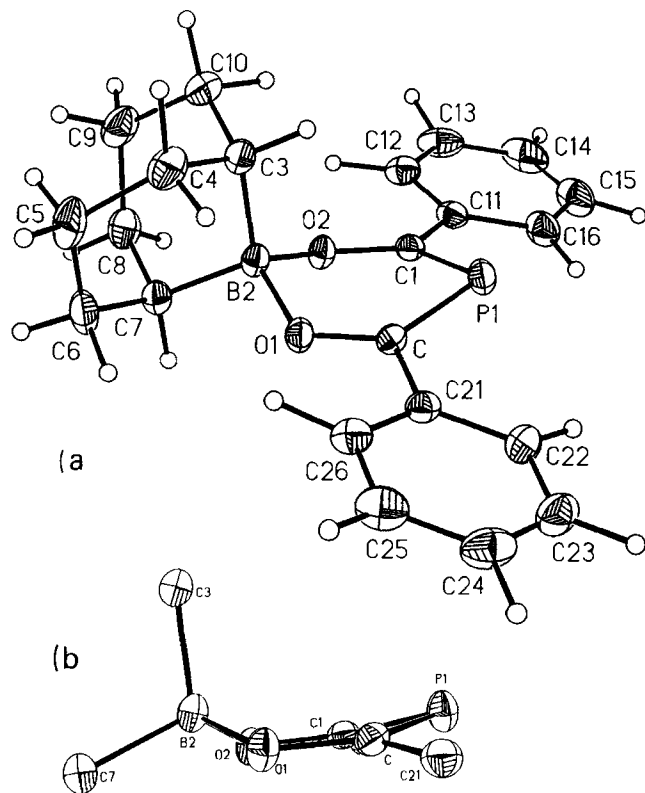

(a

(b

Figure 3. a) ORTEP-type representation of the molecular structure of **3b** in the crystal. Thermal ellipsoids are represented on a 25-% probability level. Selected bond lengths [Å]: P1−C 1.777(3), P1−C1 1.760(3), C−O1 1.286(4), C1−O2 1.292(4), O1−B2 1.539(4), O2−B2 1.536(4), C−C21 1.472(4), C1−C11 1.475(4), B2−C3 1.603(5), B2−C7 1.589(5). − Selected bond angles [in °]: C1−P1−C 97.7(1), P1−C−O1 126.7(2), C−O1−B2 123.9(2), O1−B2−O2 106.5(2), B2−O2−C1 123.4(2), P1−C1−O2 126.0(2). b) Side view of the molecule with H atoms omitted

The C−P−C bond angle is determined as 97.7° and, therefore, the P atom is far from being sp²-hybridized. This is reminiscent of the C−P−C bond angles for phosphabenzenes which range from 101 to 103°[11]. Both the P−C and the C−O bond lengths lie between a single and double bond, with the C−O bond lengths of 1.29 Å being closer to the accepted standard double bond length (1.215 Å). Thus, the mesomeric contributions **A** and **B** to the ground state of **3b** are obviously significant and in line with the P−C bond length (1.67 Å for P=C, and 1.85 Å for P−C). The P=C bond length found for **3b** (average 1.768 Å) is close to that found for phosphabenzenes (1.74 Å). No obvious reason can be envisaged for the boron atom to be forced out of the PC_2O_2 plane. However, the BO bond lengths (average 1.537 Å) are fairly long for a B−O bond to a tetracoordinated boron atom suggesting considerable polarity for this bond[12]. Thus, the heterocyclic compounds **3a** and **3b** are interesting examples of π-electron delocalization over part of the framework within a six-membered ring.

Experimental

All manupulations were carried out in dry glassware under nitrogen or argon. Solvents were dried by standard procedures and kept under nitrogen. All precautions necessary for the safe handling of $LiP(SiMe_3)_2$[13] and $R_2BP(SiMe_3)_2$ were taken[4]. − NMR: Jeol X 270, Jeol 400, Bruker AP 200 with C_6D_6, $SiMe_3$, $BF_3 \cdot OEt$, and 85% H_3PO_4 as standards; all NMR spectra were recorded in C_6D_6 solutions. − IR: Perkin-Elmer 325.

3a: To a solution of 9-BBN-P(SiMe₃)₂ (**1**, 2.0 ml, 5.9 mmol) in 10 ml of hexane was added with stirring a hexane solution (5 ml) of 0.83 ml of CH₃C(O)Cl (**2a**, 11.6 mmol). The colorless precipitate that formed immediately dissolved within 23 min. All volatile products were removed after 14 h in vacuo yielding 0.95 g of **3a** as an orange-red oil which solidified within four days. − ¹H NMR: δ = 1.8−2.3 (m, 9-BBN, 14H); 1.80 [d, ³J(PH) = 10.4 Hz, CH₃, 6H]. − ¹¹B NMR: δ = 14.6. − ¹³C NMR: δ = 31.7, 22.5, 21.0 (9-BBN), 30.3 (C*Me*), 128.7 [d, ¹J(PC) = 23.1 Hz, P=C]. − IR (Nujol, Hostaflon): ṽ = 1520 cm⁻¹. − MS (70 eV), *m/z* (%): 238 (98) [M⁺], 223 (10.6) [M − Me⁺], 210 (20) [M − C₂H₄], 43 (100) [MeCO⁺]. − UV/Vis (hexane): λ_max = 258, 407 nm. − C₁₂H₂₀BOP₂ (238.1): calcd. C 60.54, H 8.47; found C 59.24, H 8.89.

3b: A solution of 2.0 ml (5.9 mmol) of **1** in 10 ml of pentane was cooled with dry ice and stirred. Then a solution of 0.69 ml of C₆H₅C(O)Cl (**2b**, 5.9 mmol) in 5 ml of pentane was added. The resulting colorless precipitate dissolved on warming with the formation of a red solution. Removal of all volatile material in vacuo gave a highly viscous oil which could be crystallized from ether and purified by recrystallization from toluene. Yield: 0.56 g of **3b** as black-violet crystals (26.3%), m.p. 203°C. − ¹H-NMR: δ = 1.8−2.4 (m, 9-BBN, 14H), 6.93 (t), 7.06 (t), 8.17 [d, ³J(HH) = 7.3 Hz]. − ¹¹B NMR: δ = 13.5. − ¹³C NMR: δ = 32.4, 25.6, 21.2 (broad), 127.7 [d, ³J(PC) = 16.7 Hz, *ipso*-C], 129.2, 130.6, 135.3 [d, ⁵J(PC) = 2.3 Hz, *p*-C], 139.3 [d, ¹J(PC) = 26.2 Hz, P=C]. − ³¹P NMR: δ = 60.4. − IR (Nujol): ṽ = 1478 cm⁻¹ (CO). − MS (70 eV), *m/z* (%): 362 (15.6) [M⁺], 165 (100) [(9-BBN)OCO⁺], 105 (34.4) [PhCO⁺]. − C₂₂H₂₄BO₂P (362.2): calcd. 72.95, H 6.68; found C 73.12, H 6.64.

Crystal Structure Analyses: Siemens P4 four circle-automated diffractometer, Mo-$K_α$ radiation, graphite monochromator. The programmes SHELXTL-PLUS and SHELX 93 were used for all calculations. − *Crystallographic Data:* Size of single crystal: 0.22 × 0.32 × 0.60 mm³, blackred pillars, C₂₂H₂₄BO₂P, M_r = 362.2; a = 10.222(2), b = 18.960(3), c = 19.722(4) Å; V = 3822(2) Å³, orthorhombic crystal system, space group *Pbca*; d_calc. = 1.259 Mg/m³, μ = 1.57 cm⁻¹, F(000) = 1536. − *Data Collection:* 2Θ-range = 3−48° measured in ±*h*, −1 to *k*, −1 to *l*; scan speed = 2−60°/min depending on signal intensity, scan width = 0.90°; reflections measured = 5467, unique reflections = 3351, reflections considered as observed [$I \geq 4\sigma(I)$] = 2396. − *Structure Solution and Refinement:* Direct methods, positions of nonhydrogen atoms found and refined anisotropically. The difference Fourier synthesis revealed all positions of hydrogen atoms which were refined with fixed isotropic U_i. 235 variables refined, reflections:variables = 10.2, R = 0.0478, R_w = 0.0489, R = 0.069 (all data), GOOF = 1.52; largest residual peak = 0.20 e/Å³.

*2-(Di-tert-butylboryloxy)-2-phenyl-1-(trimethylsilyl)-1-phosphaethene (*5*):* 2.0 ml of *t*Bu₂B−P(SiMe₃)₂ (**4**) was dissolved in 5 ml

of pentane, and a solution of 0.64 ml of $C_6H_5C(O)Cl$ (5.5 mmol) in 5 ml of pentane was added at $-50°C$ with stirring. After the solution had attained ambient temp. within ≈ 1 h the now deep red solution was freed from a solid by filtration, and then all volatile material was evaporated in a vacuo at 100 Torr (Me_3SiCl detected in the condensate, $\delta^1H = 0.33$). Distillation of the residue at $95-100°C/0.2$ Torr yielded about ≈ 1 g of **5** ($\approx 50\%$) as a colorless oil. – ^1H NMR (C_6D_6): $\delta = 0.48$ [d, $^3J(PH) = 4.4$ Hz, $SiMe_2$] 1.21 (s, CMe_3), $7.0-8.3$ (m, C_6H_5). – ^{11}B NMR: $\delta = 49.4$. – ^{13}C NMR: $\delta = 4.2$ [d, $^2J(PC) = 11.5$ Hz, $SiMe_3$], 28.8 (s, CMe_3), 167.4 [d, $^1J(PC) = 174$ Hz, P=C], 127.8, 127.9, 128.4, 130.5 (C_6H_5), $\delta(BC)$ not detected. – ^{31}P NMR: $\delta = 134.2$. – MS (70 eV), m/z (%): no $M^{+\cdot}$, 278 (55) $[M^+ - C_4H_8]$, 105 (93) $[PhCO^+]$, 73 (100) $[SiMe_3^+]$. – $C_{18}H_3BOPSi$ (334.3): calcd. C 64.67, H 9.65; found C 59.13, H 8.88, correct ratio C:H = 6.7:1 (compound oxidized during weighing).

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