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Increasing the Lability of Polarised Phosphorus–Phosphorus Bonds

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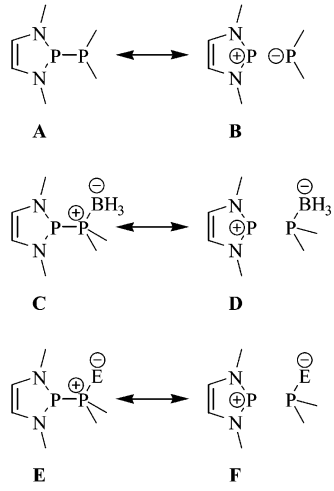
Diphosphanes with polarised P–P bonds react readily with Lewis acids like borane, gallium trichloride, or with elemental selenium, to give products arising from electrophilic attack at the more basic phosphorus atom and consecutive bond cleavage. Spectroscopic studies proved that the initial reaction with borane proceeds under preservation of the P–P bond to give a transient phosphane–borane which rearranged below ambient temperature. The results suggest that Lewis acid coordination decisively enhances the weakening of the polarised P–P bond.

Introduction

Unsymmetrical diphosphanes **A** react easily with electrophiles by heterolytic cleavage of the phosphorus–phosphorus bond.[1] The unusually high degree of reactivity has been attributed to ionic bond polarisation which was expressed in terms of bond/no-bond resonance between two canonical structures **A** and **B** (Scheme 1). The bond polarisation follows in this picture from a significant contribution of resonance structure **B**, which results in the first place from the high stability of the 1,3,2-diazaphospholenium cation[2,3] and may be further enhanced by suitable electronic stabilisation of the anion fragment (e.g. in an aromatic phospholide[1]). Since attachment of an electrophilic borane renders a phosphanide anion likewise less nucleophilic,[4] and thus more stable, it can be assumed that the balance between resonance structures **C** and **D** of a diphosphane–borane adduct is even further shifted to the side of a ionic structure **D**. Similar arguments hold for the resonance structures **E**, **F** of products arising from oxidation of the exocyclic phosphorus atom by a chalcogen (E = O, S, Se). In both cases, the increased weight of the ionic resonance structure implies a further weakening effect on the P–P bond and suggests that the products should even be more prone to undergo bond cleavage reactions than the diphosphane **A**. In a formal sense, the bonding situation in a borane adduct **C**/**D** is comparable to that in P–P-bonded phosphane–phosphenium adducts which are likewise known to react under P–P bond cleavage and ligand exchange.[5]



Scheme 1.

In this contribution we report on studies of the reactions of diphosphanes **A** with selenium, borane, and gallium trichloride, and present evidence which proves that the action of a Lewis acid or the oxidation by a chalcogen renders the P–P bond indeed more prone for activation reactions.

Results and Discussion

The reaction of the diphosphane **1a**[1] with 1 equiv. of elemental selenium yielded a mixture of the starting material and the diselenophosphinate **2** (Scheme 2). Quantitative formation of **2** was accomplished after addition of a second equivalent of selenium.

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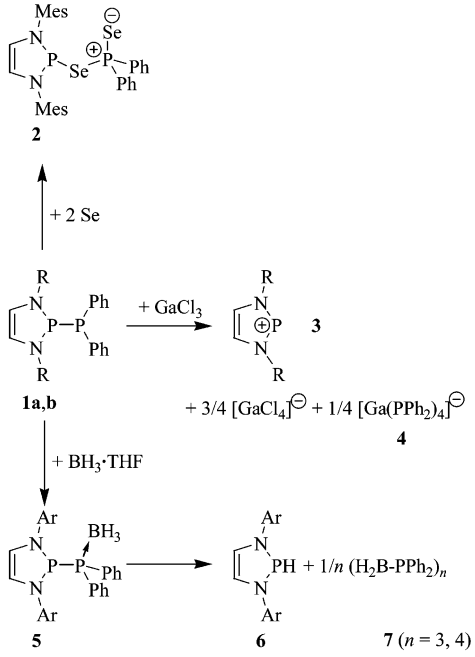

Scheme 2. Reactions of the diphosphanes **1a/b** [**1a**: R = Mes (2,4,6-$Me_3C_6H_2$); **1b**: R = 2,6-$Me_2C_6H_3$; **5**, **6**: Ar = 2,6-$Me_2C_6H_3$].

The ^{31}P NMR spectrum of isolated **2** shows signals at δ = 164.4 and 20.4 ppm attributable to the tri- and the tetracoordinate phosphorus atoms, respectively. The upfield signal displays a single set of ^{77}Se satellites ($^1J_{PSe}$ = 617 Hz) which remains unchanged in the temperature range between 30 and –80 °C and suggests the occurrence of dynamic exchange between terminal and bridging selenium atoms [this view is also in accord with the observation that the magnitude of this coupling is intermediate with respect to the two distinguishable couplings $^1J_{PSe}$ = 368, 762 Hz in tBu$_2$P–Se–P(Se)tBu$_2$[6]]. The observation of coupling between the ^{31}P nuclei ($^2J_{PP}$ = 5.1 Hz) in the spectra of freshly prepared solutions allows to conclude that the exchange is strictly intramolecular. Ageing of the solutions is usually accompanied by some signal broadening which renders the splitting unobservable. This effect can be explained as a consequence of intermolecular exchange processes that are presumably catalysed by trace amounts of decomposition products formed.

An X-ray diffraction study of a single-crystal grown from toluene solution at 4 °C revealed the presence of isolated molecules with a planar diazaphospholene ring (deviation of any atom from mean plane < 0.03 Å). The endocyclic bond lengths are similar to those in *P*-chlorodiazaphospholenes.[7] The P2–Se1/Se2 bond lengths of 2.193(1) and 2.135(1) Å differ perceptibly, but their average comes close to the mean P–Se distance in ionic diselenophosphinates (2.17 ± 0.03 Å[8]), and the asymmetry in the PSe_2 moiety resembles that in the η^1-bound ligands in a complex [Ga(η^2-Se_2P*i*Pr_2)(η^1-Se_2P*i*Pr_2)$_2$].[9] The P1–Se1 bond [2.766(1) Å] clearly exceeds a normal single bond in compounds RR′P–SeR′′ (mean distance 2.26 ± 0.07 Å[8]) but matches the appropriate "inter-ionic" distances (2.64–2.79 Å) in the iminophosphenium diselenophosphinate [Mes*NP][Se_2PPh_2] of Niecke et al.[10] In contrast to this species, the molecular structure of which was deemed to resemble the "frozen transition state" for a [1,3]-sigmatropic shift of an iminophosphenium fragment between the two selenium atoms of a covalent diselenophosphinate,[10] the P1–Se2 distance in **2** [3.391(1) Å] is clearly nonbonding. Altogether, the molecular structure of **2** (Figure 1) is best described as contact ion pair of a 1,3,2-diazaphospholenium cation and a η^1-bound diselenophosphinate anion. A similar view of the bonding situation was recently suggested for *P*-chlorodiazaphospholenes.[7]

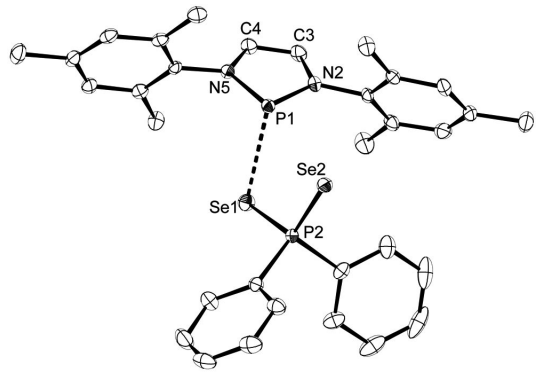

Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn with 50% probability level, and H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N2 1.688(2), P1–N5 1.689(2), P1–Se1 2.766(1), P1–Se2 3.391(1), P2–Se1 2.193(1), P2–Se2 2.135(1), N2–C3 1.402(3), C3–C4 1.343(3), C4–N5 1.398(3); N2–P1–N5 88.5(1), N2–P1–Se1 108.3(1), N5–P1–Se1 102.6(1), N2–P1–Se2 104.9(1), N5–P1–Se2 166.6(1), Se1–P1–Se2 72.60(2), P2–Se1–P1 92.76(2), Se2–P2–Se1 116.48(3), P2–Se2–P1 77.99(2).

The reaction leading to **2** is related to known reactions of diphosphanes R_4P_2 with chalcogens E (E = S, Se) which yield, depending on the nature of reactants and reaction conditions, either diphosphane chalcogenides R_2P–P(E)R_2, chalcogenobis(phosphanes) R_2P–E–PR_2, or phosphanyl dichalcogenophosphinates R_2P–E–P(E)R_2, respectively.[6,11,12] The formation of all products in these reactions can be rationalised by a common mechanism[10] proceeding by initial oxidation of one phosphorus atom, subsequent migratory insertion of the chalcogen atom into the P–P bond, and, finally, oxidation of one phosphorus atom by a second chalcogen atom. Even if the overall conditions during the formation of **2** are similar to those employed for the conversion of sterically congested symmetrical diphosphanes R_4P_2 (R = *t*Bu, *i*Pr_2N) into phosphanyl diselenophosphinates R_2P–Se–P(Se)R_2,[6,12] the present reaction differs as no spectroscopically detectable intermediates could be observed. This finding implies that the first reaction step is in this case rate-determining and suggests thus that the initial selenation of **1** further facilitates the P–P bond-cleavage step.

Considering that group-13 element halides form stable adducts with phosphanes and diphosphanes,[13] we studied next the reaction of equimolar amounts of **1a** and $GaCl_3$

in the hope to obtain a stable adduct. A ^{31}P NMR spectrum of the reaction mixture showed in addition to the signal of the 1,3,2-diazaphospholenium cation **3**[2] at δ = 205 ppm a further broad signal at δ = –45.5 ppm. The ^{71}Ga NMR spectrum disclosed likewise the formation of two gallium-containing species of which one was easily identified as $[GaCl_4]^-$ ($\delta^{71}Ga$ = 251 ppm).[14] The position of the second signal ($\delta^{71}Ga$ = 266 ppm) is in accord with the reported chemical shift of the anion $[Ga(PPh_2)_4]^-$ (**4**)[15] which accounts also for the remaining ^{31}P NMR signal. The formation of these species is explained if one assumes that the reaction proceeds by coordination of the Lewis acid to the PPh_2 moiety of **1a** and concomitant P–P bond cleavage to give the cation **3** and an anion $[Ph_2PGaCl_3]^-$, which then undergoes redistribution of Ph_2P and Cl substituents.

Detection of the postulated Lewis acid adduct of a diphosphane was finally feasible in the reaction of **1b** with 1 equiv. of BH_3·thf at –10 °C. ^{31}P NMR spectra of reaction mixtures disclosed that the signals of **1b** had been displaced by a new AX-type spin system with chemical shifts of δ = 116.3 and –5 ppm, respectively. The significant increase in the magnitude of $^1J_{PP}$ (409 Hz) and the broadening of the upfield resonance due to partially resolved spin coupling to $^{10/11}B$ nuclei prove the coordination of a BH_3 unit to the Ph_2P moiety of **1b** and lead us to formulate the product as the diphosphane–borane **5**. The product decomposed within several hours at –10 °C, or more rapidly upon warming to room temperature, to give a mixture of the cyclic phosphanylboranes **7** which was identified by the coincidence of the observed ^{31}P and ^{11}B chemical shifts [$\delta^{31}P$ = –19.7 (br.) ppm; $\delta^{11}B$ = –37.2 (br.) ppm] with literature data,[16,17] and the *P*-hydridodiazaphospholene **6**. The identity of the latter was derived from the presence of a doublet ^{31}P NMR signal ($\delta^{31}P$ = 64.1 ppm) with a characteristic splitting of $^1J_{PH}$ = 138 Hz, and was verified by independent synthesis by reduction of the appropriate *P*-chloro-1,3,2-diazaphospholene with $LiAlH_4$ as previously reported.[3] A plausible mechanism for the formation of **6**, **7** involves cleavage of the P–P bond of **5** with concomitant transfer of a hydride ion from the BH_3 moiety to the diazaphospholene phosphorus atom, and trimerisation of the remaining Ph_2P–BH_2 fragment. Such a reaction pattern is highly unusual, as borane adducts of diphosphanes are normally isolable and thermally highly stable species,[18] and has so far only been reported for the polarised diphosphane $(F_3C)_2PPH_2$.[19] The low temperature in the formation of the oligomers **7** is further remarkable, since generation of the same species by rhodium catalysed dehydrocoupling of a phosphane–borane requires temperatures around 120 °C.[16]

Conclusions

It was demonstrated that the diphosphanes **1a**,**b** react with selenium, gallium trichloride, or borane at or below ambient temperature under P–P bond cleavage. This behaviour contrasts with the known reactivity of symmetrical diphosphanes which yield normally thermally very stable adducts with Lewis acids. It appears plausible that all observed reactions of **1a**,**b** are initiated by coordination of the Lewis acid to the Ph_2P moiety, even if the resulting adduct was detected only in one case by NMR spectroscopy. The unusually low reaction temperatures for this type of fragmentation support the hypothesis that Lewis acid coordination facilitates the bond cleavage step by boosting the polarisation in the P–P bond. Considering that this conclusion is likely to hold as well for reactions of diphosphanes like **1a**,**b** with other types of electrophiles, our new findings permit a conclusive understanding of the previously observed diphosphanation of electron-deficient alkenes or alkynes[1] under exceptionally mild conditions.

Experimental Section

General: All manipulations were carried out under a protective gas (argon) in flame-dried glassware. Solvents were dried by using common procedures. **1a**,**b** were prepared as described previously.[1] NMR spectra: Bruker Avance 400 (^1H: 400.13 MHz; ^{31}P: 161.9 MHz; ^{13}C: 100.4 MHz; ^{71}Ga: 122.0 MHz) at 30 °C; chemical shifts refer to ext. TMS (^1H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), $Ga(NO_3)_3$ (Ξ = 30.496576 MHz, ^{71}Ga). MS: Varian MAT 711, EI, 70 eV. Elemental analysis: Perkin–Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries.

Synthesis of 2: 1a (2 mmol, 1.06 g) and elemental selenium (4 mmol, 0.32 g) were dissolved in toluene (50 mL), and the mixture was heated to 110 °C for 4 h. After cooling to room temperature, the solvent was reduced to half the volume. Storage at 4 °C afforded yellow needles that were filtered off and dried in vacuo to give 1.28 g (93%) of **2** of m.p. 165 °C. ^1H NMR (C_6D_6): δ = 8.12–7.95 (m, 4 H, Ph), 6.93–6.83 (m, 6 H, Ph), 6.71 (s, 4 H, *m*-C*H*), 5.87 (d, $^3J_{PH}$ = 0.8 Hz, 2 H, NC*H*), 2.31 (s, 12 H, *o*-CH_3), 2.10 (s, 6 H, *p*-CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 132.6 (d, $^2J_{PC}$ = 2.2 Hz, *i*-*C*), 130.6 (d, $^2J_{PC}$ = 4.3 Hz, *o*-*C*H), 130.2 (s, *o*-*C*), 127.2 (d, $^1J_{PC}$ = 11.6 Hz, *i*-*C*), 125.3 (d, $^3J_{PC}$ = 0.9 Hz, *m*-*C*H), 125.0 (s, *m*-*C*H), 124.4 (s, *p*-*C*), 123.6 (s, *p*-*C*H), 117.7 (d, $^2J_{PC}$ = 9.8 Hz, N*C*H), 16.0 (d, $^6J_{PC}$ = 0.8 Hz, *p*-*C*H_3), 14.5 (d, $^4J_{PC}$ = 3.2 Hz, *o*-*C*H_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 164.4 (d, $^2J_{PP}$ = 5.1 Hz, N_2P), 20.4 (d, $^2J_{PP}$ = 5.1, $^1J_{PSe}$ = 617 Hz, $P$$Ph_2$) ppm. Attempts to record a ^{77}Se NMR spectrum were unsuccessful, presumably as detection of a signal was precluded by extensive exchange-induced line broadening. (+)-FAB MS (3-nitrobenzyl alcohol): *m*/*z* (%) = 323.2 (50.8) $[M]^+$, 133.0 (50.0) $[M - C_{11}H_{13}NP]^+$, 119.1 (17.2) $[M - C_{11}H_{13}N_2P]^+$, 73.0 (100.0) $[M - C_{13}H_{22}]^+$. $C_{32}H_{34}N_2P_2Se_2$ (666.50): calcd. C 57.67, H 5.14, N 4.20; found C 57.69, H 5.28, N 4.27.

Reaction of 1a and $GaCl_3$: 1a (0.15 mmol, 76 mg) and $GaCl_3$ (0.15 mmol, 26 mg) were dissolved in CD_3CN (1 mL). Quantitative formation of **3**, **4** was confirmed by ^1H and ^{31}P NMR spectroscopy. ^1H NMR (CD_3CN): δ = 8.02 (s, 4 H, *m*-C*H*), 7.47 (m, 4 H, *o*-C*H*), 7.30–7.15 (m, 6 H, *m*/*p*-C*H*), 5.41 (d, $^3J_{PH}$ = 1.0 Hz, 2 H, NC*H*), 2.36 (s, 6 H, *p*-CH_3), 2.14 (s, 12 H, *o*-CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN): δ = 206.0 (N_2P), –45.4 [br. s, Ga($P$$Ph_2$)$_4$] ppm. ^{71}Ga NMR (CD_3CN): δ = 266 [br. s, *Ga*(PPh_2)$_4$], 251 (s, *Ga*Cl_4) ppm.

Reaction of 1b and BH_3·thf: 1b (0.1 mmol, 48 mg) and BH_3·thf (0.1 mmol, 0.1 mL of 1 M solution in thf) were dissolved in [D_6]-benzene (0.6 mL), and the mixture was immediately cooled to –10 °C. Quantitative formation of **5** was proven by NMR spec-

troscopy. ^{1}H NMR (thf/C_6D_6): δ = 7.47 (m, 4 H, *o*-Ph), 6.88–6.77 (m, 12 H, *m*/*p*-Ph, *m*/*p*-C_6H_3), 5.79 (dd, J_{PH} = 1.1, 1.8 Hz, 2 H, NC*H*), 2.45 (s, 6 H, *o*-CH_3), 2.32 (s, 6 H, *o*-CH_3), 1.4 (v. br., 3 H, BH_3) ppm. ^{31}P{^{1}H} NMR (thf/C_6D_6): δ = 116.2 (d, $^1J_{PP}$ = 409 Hz, N_2P), –5.0 (d, $^1J_{PP}$ = 409 Hz, Ph_2P) ppm. ^{11}B{^{1}H} NMR (thf/C_6D_6): δ = –35.5 (br.) ppm. Upon warming to ambient temperature, the signals of **5** were replaced by those of **6**, **7**. ^{31}P NMR (thf/C_6D_6): δ = 64.1 (d, $^1J_{PH}$ = 137 Hz, **6**), –20.2 (br. s, **7**) ppm. ^{11}B{^{1}H} NMR (thf/C_6D_6): δ = –37.2 (br.) ppm. Repetition of the reaction on a larger scale (1 mmol each of **1b** and BH_3·thf in 20 mL of hexane) afforded after warming to ambient temperature a product mixture which gave a similar ^{31}P NMR spectrum. Attempts to isolate the products formed in pure form remained unsuccessful. The identity of **6** was proven by independent synthesis according to a literature procedure.[3] Yield 62%, m.p. 38 °C. ^{1}H NMR (C_6D_6): δ = 7.12 (d, $^1J_{PH}$ = 138 Hz, 1 H, P*H*), 6.92 (s, 6 H, *m*/*p*-C*H*), 5.74 (d, $^3J_{PH}$ = 2.0 Hz, 2 H, NC*H*), 2.29 (br. s, 18 H, *o*-CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 140.6 (d, $^2J_{PC}$ = 13.8 Hz, *i*-*C*), 137.3 (br. s, *o*-*C*), 128.8 (d, $^5J_{PC}$ = 1.0 Hz, *p*-*C*H), 126.3 (d, $^4J_{PC}$ = 1.8 Hz, *m*-*C*H), 121.3 (d, $^2J_{PC}$ = 6.3 Hz, N*C*H), 19.2 (br. s, *o*-*C*H_3) ppm. ^{31}P NMR (C_6D_6): δ = 64.3 (d, $^1J_{PH}$ = 138 Hz) ppm. $C_{18}H_{21}N_2P$ (296.35): calcd. C 72.95, H 7.14, N 9.45; found C 72.86, H 7.31, N 9.41.

Crystal Structure Study: The single-crystal X-ray diffraction study of **2** was carried out with a Bruker–Nonius Kappa-CCD diffractometer at 123(2) K using Mo-K_α radiation (λ = 0.71073 Å). Direct methods (SHELXS-97[20]) were used for structure solution, and full-matrix least-squares refinement on F^2 (SHELXL-97[21]). H atoms were localised by difference Fourier synthesis and refined using a riding model. An empirical absorption correction from equivalent reflections was applied (min./max. transmission 0.4915/0.6279). The absolute structure was determined by refinement of Flack's parameter, x = 0.079(5).[22] Crystal data: orange crystals, $C_{32}H_{34}N_2P_2Se_2$, M = 666.47, crystal size 0.40 × 0.30 × 0.20 mm, orthorhombic, space group $Pna2_1$ (no. 33), a = 22.938(1), b = 11.153(1), c = 11.863(1) Å, V = 3034.9(4) Å^3, Z = 4, ρ(calcd.) = 1.459 Mg m^{-3}, F(000) = 1352, μ = 2.566 mm^{-1}, 53036 reflexions ($2\theta_{max}$ = 55.0°), 6883 unique (R_{int} = 0.029), 349 parameters, 1 restraint, $R1$ [$I > 2\sigma(I)$] = 0.022, $wR2$ (all data) = 0.057, largest diff. peak/hole 1.326/–0.296 e Å^{-3}. CCDC-660525 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.

Acknowledgments

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