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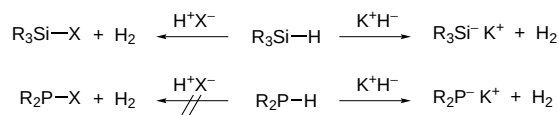
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Umpolung of P–H Bonds**

Dietrich Gudat,* Asadollah Haghighverdi, and Martin Nieger

Dedicated to Professor Gerd Becker
on the occasion of his 60th birthday

Bonds between p-block elements E and hydrogen are employed as versatile synthons in numerous synthetic transformations.^[1] Their reactivity follows a systematic course that is characterized by a change from hydridic (E–H bonds involving elements of Group 13) to protonic (E–H bonds involving elements of Groups 15–17) character of the hydrogen atom. Hydrogen compounds of Group 14 elements are a borderline case: whereas the protonic character of the hydrogen atom dominates for C–H bonds, Si–H bonds may react both as the source of a hydride or of a proton (Scheme 1).^[1, 2]



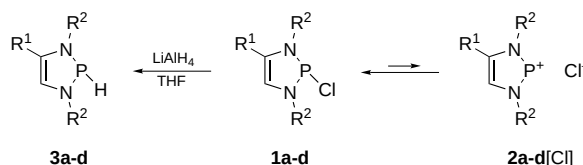
Scheme 1. X = halogen, OR.

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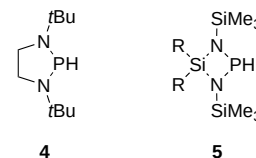
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The reactivity of P–H bonds in phosphane derivatives is generally determined by the protonic character of the hydrogen atom (Scheme 1), even though in view of the similar electronegativities ($\chi^{\text{AR}}(\text{H}) = 2.2$, $\chi^{\text{AR}}(\text{P}) = 2.06$) and resulting low bond polarities it appears conceivable to achieve an umpolung of the reactivity by means of suitable substituent effects.^[3] Taking into account our observation that π -delocalization effects which can be described in terms of σ^* aromaticity^[4] render the P–Cl bonds in *P*-chloro-1,3,2-diazaphospholenes **1** more polar and favor dissociation under formation of the cations **2**,^[5] it appeared of interest to establish if the same effects can also be applied to generate hydridic reactivity of the P–H bonds in *P*-hydrido-1,3,2-diazaphospholenes **3** (Scheme 2).



Scheme 2. R¹ = H, R² = *t*Bu (**1a–3a**), 2,4,6-Me₃C₆H₂ (Mes) (**1c–3c**); R¹ = Cl, R² = *t*Bu (**1b–3b**), Mes (**1d–3d**).

The target compounds **3a–d** are formed in clean reactions upon treatment of **1a–d** with stoichiometric amounts of LiBEt₃H or LiAlH₄ in THF and were isolated as light yellow, air- and moisture-sensitive oils or solids after distillative work-up (**3a, b**) or crystallization (**3d**). The constitution of all products can be deduced unequivocally from their spectroscopic data. The ³¹P NMR signals ($\delta^{31}\text{P} = 57.1$ (**3a**), 71.6 (**3b**), 64.0 (**3c**), 75.8 (**3d**)) appear at slightly lower field than in the 1,3,2-diazaphospholidine **4** ($\delta^{31}\text{P} = 57.9$ ^[6]). The P,H coupling constants display a remarkable substitution dependence: whereas the couplings in the *N*-*tert*-butyl derivatives **3a, b** ($^1J(\text{P,H}) = 181$ (**3a**), 219 (**3b**) Hz) are clearly larger than in **4** ($^1J(\text{P,H}) = 156$ Hz^[6]), those in the *N*-mesityl compounds **3c, d** ($^1J(\text{P,H}) = 139$ (**3c**), 147 (**3d**) Hz) come close to the extremely low values of the four-membered heterocycles **5** (R = Me, Ph; $^1J(\text{P,H}) = 125$ –127 Hz^[7]). Following common concepts, the decrease of $^1J(\text{P,H})$ can be related with decreasing p-character and lengthening of the P–H bond and should thus indicate a bond-weakening effect. This hypothesis is corroborated by the red shift of the P–H stretching vibration frequencies in **3a–d** ($\tilde{\nu}(\text{PH}) = 2120$ –2202 cm⁻¹) as compared to those of known cyclic and acyclic diaminophosphanes ($\tilde{\nu}(\text{PH}) = 2220$ –2340 cm⁻¹^[6, 8]), and by the result of a single-crystal X-ray diffraction study of **3d**.^[9]



The structure of crystalline **3d** is composed of isolated molecules that display no significant intermolecular interactions (Figure 1).^[11] The five-membered ring features an “envelope” conformation with the phosphorus atom sticking out of the plane formed by the remaining ring atoms, and the attached hydrogen atom adopting a “flagpole” position. The

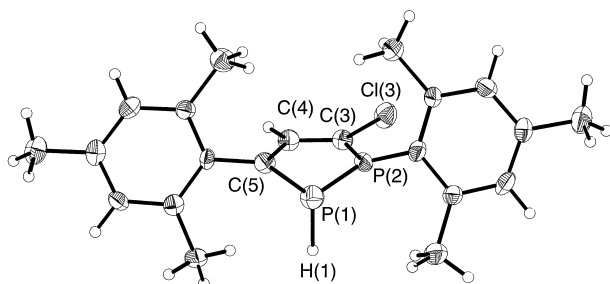


Figure 1. Molecular structure of **3d** in the crystal (50% probability thermal ellipsoids); important distances [Å] and angles [°]: P(1)–H(1) 1.51(4), P(1)–N(5) 1.709(3), P(1)–N(2) 1.722(3), N(2)–C(3) 1.407(5), C(3)–C(4) 1.327(5), C(3)–Cl(3) 1.720(4), C(4)–N(5) 1.410(5), N(5)–P(1)–N(2) 89.92(16), N(5)–P(1)–H(1) 97.8(14), N(2)–P(1)–H(1) 99.3(14).

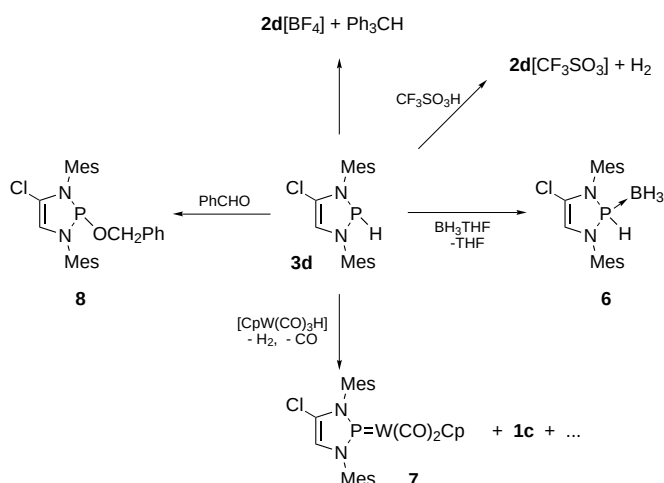
P–H distance (1.51(4) Å) is notably longer than known P–H bond lengths in phosphanes (1.288 ± 0.09 Å^[12]). The endocyclic bond lengths (P–N 1.709(3), 1.722(3), C–N 1.407(5), 1.410(5), C=C 1.327(5) Å) range as in **1a**, **c** and **2a**^[5, 13] between those of genuine single and double bonds, even if the extent of bond length equalization decreases from **2a** over **1a**, **c** to **3d**.

In accord with model calculations^[14] these findings may be interpreted by assuming that hyperconjugative interaction between the six π electrons in the C_2N_2 unit and the $\sigma^*(P-H)$ orbital results (as in the case of **1**^[5]) in partial delocalization of π electrons in the ring. The lower extent of this “ σ^* aromaticity”^[4] in **3d** as compared to that in **1a**, **c** is consistent with the lower acceptor ability of the $\sigma^*(P-H)$ as compared to that of a $\sigma^*(P-Cl)$ orbital. Direct consequences of this π delocalization are a weakening of the P–H bond and a concomitant increase of charge density at the hydrogen atom (i.e. increasing hydridic character), which become immediately evident from comparison of computed P–H distances, $\nu(PH)$ vibrational frequencies, and atomic charges of the model compounds **A–C** (Table 1).

Table 1. Computed (at the MP2/6-31 + g(d,p(P-H))-level)^[14] P–H distances, $\nu(P-H)$ vibrational frequencies, and atomic charges $q(H)$ (from natural bond order (NBO) population analyses) in the model compounds **A–C**.

			
	A	B	C
$r(P-H)$ [Å]	1.447	1.426	1.406
$\nu(P-H)$ [cm ^{−1}]	2217	2361	2509
$q(H)$	−0.14	−0.11	−0.08

Chemical studies confirm that the enhancement of the hydridic character of the P–H bond, which has been inferred from spectroscopic and structural criteria, leads in fact to an umpolung of the reactivity. Thus, **3d** reacts with $[Ph_3C]^+[BF_4]^-$ under hydride transfer to give a quantitative yield of triphenylmethane and the phosphonium ion **2d** (Scheme 3).^[15] The same cation is also formed upon treatment of **3d** with trifluoromethanesulfonic acid. The reaction proceeds with gas evolution (H_2) and was found by ³¹P NMR spectroscopic



Scheme 3. Reactions of **3d**.

studies to occur spontaneously and without detectable intermediates even at -78°C in CH_2Cl_2 . Evidence for a quaternization, which is typical for secondary or tertiary phosphanes, was obtained in no case, even if the formation of the stable BH_3 adduct **6** from **3d** and $BH_3 \cdot THF$ suggests a sufficient basicity for the phosphorus atom.

Reaction of **3d** with the transition metal hydride $[CpW(CO)_3H]$ affords as main product (ca. 50%) the phosphonium complex **7**,^[16] which was spectroscopically identified, together with **1c** (ca. 25%) and further as yet not characterized by-products. Whereas the formation of **7** can be explained by condensation of the hydridic P–H and acidic W–H functionalities of **3d** and $[CpW(CO)_3H]$, respectively, which proceeds with cleavage of H_2 and subsequent elimination of CO, **1c** arises presumably from C–Cl/P–H meta-thesis between two molecules of **3d**.^[18]

Beside the observation of H_2 elimination in reactions with compounds containing acidic protons, the umpolung of the P–H bonds in **3** becomes further manifest in an inverse regioselectivity during the addition to carbonyl compounds. Thus, reaction of **3d** with benzaldehyde proceeds not as expected^[19] with formation of a α -hydroxybenzyl phosphane, but yields rather as the only product the benzyloxy derivative **8**, which was isolated as a yellow oil and characterized by spectroscopic techniques.^[16] The regioselectivity of the addition can be deduced unequivocally from the appearance of the signal of a benzylic CH_2 moiety in the $^{13}C\{^1H\}$ DEPT spectrum, and the absence of a characteristic $\nu(OH)$ band in the IR spectrum.

Experimental Section

3a–d: A solution of **1a–d** (10 mmol) in THF (50 mL) was added dropwise at 4°C to a suspension of $LiAlH_4$ (2.5 mmol) in THF (10 mL). Stirring was continued for 1 h, the solvent removed in vacuo, and the oily residue dissolved in hexane (50 mL). The formed precipitate was filtered off over Celite and the solvent removed in vacuo. The crude product was characterized by NMR spectroscopy (**3c**), or purified by means of vacuum distillation (**3a**, **b**) or recrystallization from pentane at -20°C (**3d**). **3a:** b.p. 50°C (1 mbar), yield 65%; ³¹P NMR (121.5 MHz, C_6D_6): $\delta = 57.1$ (d, $^1J(P,H) = 181$ Hz); ¹H NMR (300 MHz, C_6D_6): $\delta = 1.14$ (d, $^4J(P,H) = 0.9$ Hz, 18H), 5.97 (d, $^3J(P,H) = 4.0$ Hz, 2H), 6.07 (d, $^1J(P,H) = 181$ Hz, 1H); MS (16 eV): m/z (%): 200 (10) [M^+], 199 (78) [$M^+ - H$], 143 (28)

$[M^+ - C_4H_8]$, 87 (100) $[M^+ - 2C_4H_8]$; IR (gas): $\tilde{\nu} = 2176\text{ cm}^{-1}$ (P–H). **3b**: b.p. 55 °C (1 mbar), yield 78%; ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 71.6$ (d, $^1J(\text{P,H}) = 219\text{ Hz}$); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.99$ (d, $^4J(\text{P,H}) = 0.7\text{ Hz}$, 9H), 1.33 (d, $^4J(\text{P,H}) = 1.7\text{ Hz}$, 9H), 6.16 (d, $^3J(\text{P,H}) = 3.3\text{ Hz}$, 1H), 6.23 (d, $^1J(\text{P,H}) = 219\text{ Hz}$, 1H); IR (Nujol): $\tilde{\nu} = 2202\text{ cm}^{-1}$ (P–H). **3c**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 64.0$ (d, $^1J(\text{P,H}) = 139\text{ Hz}$); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.44$ (s, 6H), 2.48 (s, 6H), 2.56 (s, 3H), 2.59 (s, 3H), 6.16 (d, $^3J(\text{P,H}) = 1.8\text{ Hz}$, 2H), 7.04 (br, 4H), 7.13 (d, $^1J(\text{P,H}) = 139\text{ Hz}$, 1H); **3d**: m.p. 87–89 °C, yield 72%; ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 75.8$ (d, $^1J(\text{P,H}) = 147\text{ Hz}$); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.09$ (s, 6H), 2.23 (s, 6H), 2.23 (s, 3H), 2.37 (s, 3H), 5.87 (d, $^3J(\text{P,H}) = 0.9\text{ Hz}$, 1H), 6.67 (s, 2H), 6.70 (s, 1H), 6.72 (s, 1H), 7.17 (d, $^1J(\text{P,H}) = 147\text{ Hz}$, 1H); MS (16 eV): m/z (%): 358(43) $[M^+]$, 357(100) $[M^+ - H]$; IR (gas): $\tilde{\nu} = 2120\text{ cm}^{-1}$ (P–H).

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- [15] All products were identified by comparison of their ^1H and ^{31}P NMR data with those of authentic samples.
- [16] Characteristic spectroscopic data: **6**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 85.9$ (br d, $^1J(\text{P,H}) = 353\text{ Hz}$); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.29$ (br, 3H; BH_3), 2.03 (s, 9H), 2.13 (s, 3H), 2.38 (s, 3H), 2.43 (s, 3H), 5.32 (d, $^3J(\text{P,H}) = 10.3\text{ Hz}$, 1H), 6.62 (s, 1H), 6.67 (s, 1H), 6.70 (s, 2H), 8.01 (d, $^1J(\text{P,H}) = 353\text{ Hz}$, 1H); $^{11}\text{B}\{^1\text{H}\}$ NMR (96.2 MHz, C_6D_6): $\delta = -34.3$ (d, $^1J(\text{P,B}) = 52\text{ Hz}$); **7**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 173$ (d, $^3J(\text{P,H}) = 8\text{ Hz}$, $^1J(\text{W,P}) = 765\text{ Hz}$); ^1H NMR (300 MHz, C_6D_6): $\delta = 2.05$ (s, 3H), 2.06 (s, 3H), 2.27 (s, 6H), 2.29 (s, 6H), 4.52 (s, 5H; C_5H_5), 5.93 (d, $^3J(\text{P,H}) = 7.4\text{ Hz}$, 1H), 6.78 (s, 2H), 6.79 (s, 2H); IR (CH_2Cl_2): $\tilde{\nu} = 1841, 1959\text{ cm}^{-1}$ (CO); **8**: ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 121.3$ (t, $^3J(\text{P,H}) = 9\text{ Hz}$); ^1H NMR (300 MHz, C_6D_6): 2.12 (s, 6H), 2.27 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 2.45 (s, 3H), 4.50 (d, $^3J(\text{P,H}) = 9.0\text{ Hz}$, 2H; OCH_2), 5.83 (d, $^3J(\text{P,H}) = 0.7\text{ Hz}$, 1H; 5-H), 6.7–7.0 (m, 9H; $m\text{-H}$ and Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6): $\delta = 66.9$ (d, $^2J(\text{PC}) = 25.6\text{ Hz}$; OCH_2); MS (16 eV, 100 °C): m/z (%): 464(12) $[M^+]$, 357(14) $[M^+ - \text{OCH}_2\text{Ph}]$.
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Stereoselective Synthesis and Palladium-Catalyzed Transformations of 2-Alkylidene-5-vinyltetrahydrofurans**

Peter Langer* and Edith Holtz

Domino and sequential reactions are of interest in modern organic chemistry since they enable the rapid assembly of complex products.^[1] In the course of our studies on the development of domino reactions of dianions and dianion equivalents,^[2] we have recently reported the first cyclizations of dilithiated 1,3-dicarbonyl compounds with oxalic acid dielectrophiles.^[3] These reactions allow an efficient, regio- and stereoselective synthesis of the pharmacologically relevant substance class of γ -alkylidenebutenolides. Although a variety of simple condensation reactions of dianions with monofunctional alkyl halides are known, only a few domino dialkylation reactions of dianions with difunctional alkyl

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