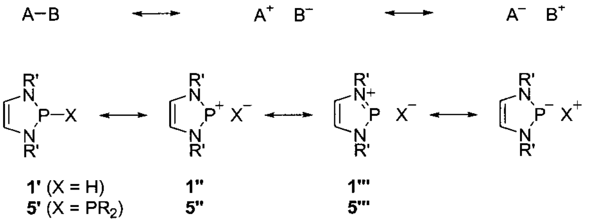
Polarized P–P Bonds

Diphosphanes with Polarized and Highly Reactive P–P Bonds

Sebastian Burck, Dietrich Gudat, and Martin Nieger*

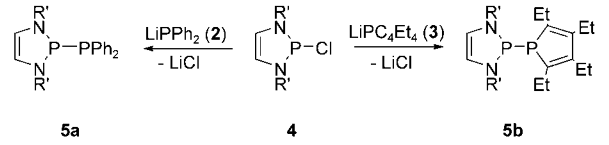
Single bonds are described in the valence-bond (VB) model in terms of resonance between covalent and ionic canonical structures (Scheme 1).[1] Whereas the covalent canonical structure is dominant for homoatomic bonds (A–B), the weight of the appropriately polarized ionic canonical structure prevails for heteroatomic bonds with a large electronegativity difference ($\chi A \ll \chi B$). As a result, this leads to a lower covalent bond order and a substantial bond polarity ($A^{\delta+}$–$B^{\delta-}$).



Scheme 1. R' = Mes, *t*Bu.

We reported in 2000 on the hydride reactivity of 2-hydridodiazaphospholenes **1**, and interpreted this behavior as a consequence of a polarization $P^{\delta+}$–$H^{\delta-}$ of the P–H bond that can be explained in terms of a hyperconjugation between the six π electrons in the C_2N_2 moiety and the σ*(P–H) orbital.[2] In the frame of the VB model, this indicates that ionic canonical structures contribute, regardless of the low electronegativity difference (χ^{AR}(H) 2.2, χ^{AR}(P) 2.06), significantly to the bonding. The cause of this effect lies in the high cation stability of the diazaphospholenium fragment which yields an energetic stabilization of canonical structures such as **1**'' and **1**''', and provides, for example, the driving force for the increased tendency towards dissociation of *P*-halogeno-1,3,2-diazaphospholenes.[3] Following this principle, a combination of a diazaphospholenium with a stable anionic phosphanide fragment should likewise render the polarization of the homoatomic P–P bond of a diphosphane feasible. Herein we describe the synthesis and characterization of such derivatives, and the unusual reactivity of the P–P bond resulting from the polarization will be demonstrated.

First attempts at the synthesis of *P*-phosphanyldiazaphospholenes were made starting from lithium diphenylphosphanide (**2**) or lithium tetraethyl phospholide (**3**),[4] whose high anion stability offer particularly suitable conditions for a dipolar polarization of the P–P bond. The reaction of **2** or **3** with an equivalent of the *P*-chlorodiazaphospholene **4** in THF yielded cleanly the target compounds **5a**,**b**, which were isolated after workup as yellow, crystalline solids that are sensitive to hydrolysis and were characterized by means of spectroscopic and analytical studies (Scheme 2).



Scheme 2. R' = Mes.

Whereas the spectroscopic data are not very unusual,[5] X-ray crystal structural studies[6] furnished clear evidence for a weakening of the P–P bond that is expected as the result of an increased weight of ionic canonical structures such as **5**'''. The P1–P2 bond length in **5a** (2.334(1) Å, Figure 1) is substantially longer than typical P–P distances in diphosphanes (2.217 ± 0.08 Å[8]) and exceeds even the distances in the sterically overcrowded $[\{(Me_3Si)_2CH\}_2P]_2$ (2.310 Å),[9] which dissociates easily under homolytic cleavage of the P–P bond to give two radicals, and in the 1,1-diaminodiphosphane $(i\text{Pr}_2N)_2P$–PPh_2 (2.250 Å),[10] for which, owing to the significantly lower cation stability of $(i\text{Pr}_2N)_2P^+$ as compared to a diazaphospholenium cation,[3] a less pronounced dipolar polarization of the P–P bond is expected.

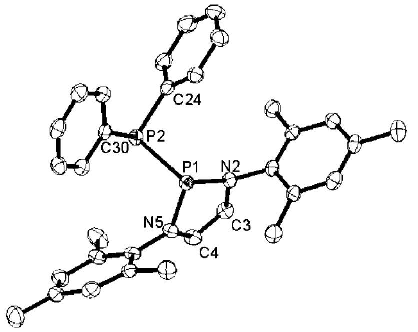


Figure 1. Molecular structure of **5a** in the crystal (H atoms omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-P2 2.334(1), P1-N2 1.710(2), P1-N5 1.734(2), N5-C4 1.402(2), C3-N2 1.419(2), C3-C4 1.325(3); N2-P1-N5 90.3(1), N5-P1-P2 99.5(1), P2-P1-N2 104.0(1), P1-P2-C30 93.6(1), C24-P2-P1 99.6(1), C24-P2-C30 102.5(1).

Compound **5b** (Figure 2a) is notable not only for the further elongation of the P–P bond to 2.484(1) Å, but also for the contraction of the P1-P2-C24(C27) bond angles to 81–82°. As a consequence of this effect, the P1 atom lies above the planar phosphole ring (Figure 2b), and the sum of all bond angles at the phosphanyl P atom decreases from 295.6° (**5a**) to

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[*] Dipl. Chem. S. Burck, Prof. Dr. D. Gudat
Anorganisch-Chemisches Institut
Universität Stuttgart
Pfaffenwaldring 55, 70550 Stuttgart (Germany)
Fax: (+49) 711-685-4241
E-mail: gudat@iac.uni-stuttgart.de
Dr. M. Nieger
Anorganisch-Chemisches Institut
Universität Bonn
Gerhard-Domagk Strasse 1, 53121 Bonn (Germany)

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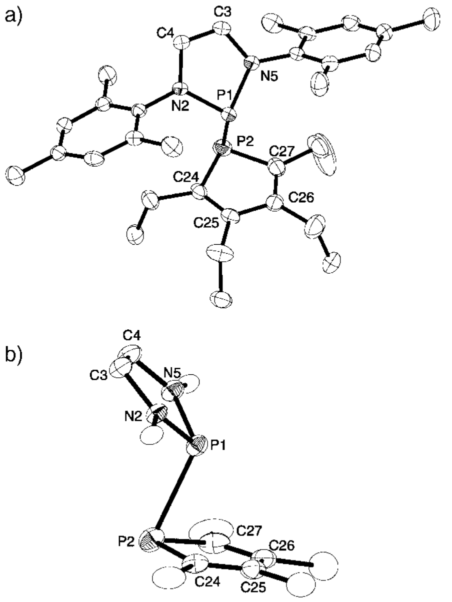
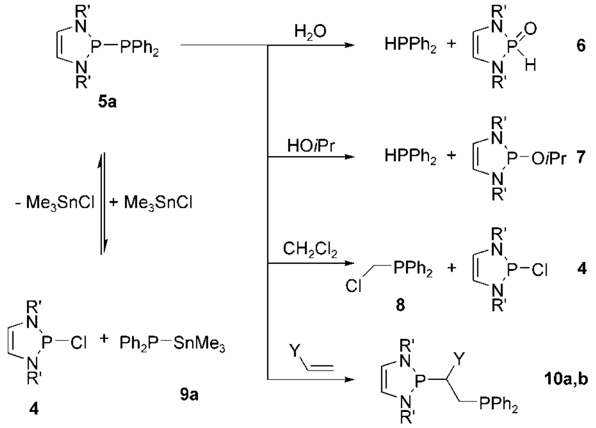


Figure 2. Complete (a) and reduced view (b, all atoms that are not directly adjacent to one of the five-membered rings were omitted) of the molecular structure of **5b** in the crystal (H atoms omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-P2 2.484(1), P1-N5 1.716(2), P1-N2 1.722 (2), N2-C3 1.404(2), C3-C4 1.327(3), C4-N5 1.397(3), P2-C27 1.788(2), P2-C24 1.789(2), C24-C25 1.371(3), C25-C26 1.446(3), C26-C27 1.371(3); N5-P1-N2 87.1(1), N5-P1-P2 110.9(1), N2-P1-P2 109.7(1), C27-P2-C24 90.5(1), C27-P2-P1 81.9(1), C24-P2-P1 81.1(1).

253.5° (**5b**). The P–C and C–C bonds in the phosphole ring are comparable to the known values (P–C 1.79 ± 0.07 Å, C=C 1.36 ± 0.07 Å, C–C 1.46 ± 0.06 Å[11]) in phospholes and in η^1-phospholyl complexes. The distances within the diazaphospholene rings of **5a**,**b** are similar to the values found for the P-H derivative **1b** (Scheme 1, R′ = Mes).[2]

Both the lengthening of the P–P bonds and the unusual bond angle deformations in **5b** are in principle confirmed by DFT calculations[12] on the model compound **5c** (Scheme 1; **5c**: R′ = H; X = H_4C_4P; P–P 2.522 Å; C-P-P 83.7°; numerical differences between computed and experimental bond lengths of similar magnitude were also observed for **4**[3]). The assumption of significant ionic bonding contributions and a low covalent bond order for **5c** is further emphasized by natural bond order (NBO)/natural resonance theory (NRT) analyses,[13] which attest contributions by ionic canonical structures such as **5**″ or **5**‴, respectively,[14] of 28%, a significant charge transfer of −0.33 electrons from the diazaphospholene to the phosphole ring, and a very low value of 0.56 for the Wiberg bond index of the P–P bond. A detailed inspection of the non-localizable fraction of the electron density in the phospholyl fragment of **5c** suggests further that the bonding situation can be described, in good accordance with the unusual molecular geometry, in terms of a hybrid between a diphosphane with a localized P–P bond and a $\pi(\eta^3)$-phospholyl complex of a diazaphospholenium ion.[15]

That the ionic polarization implied by the elongation of the P–P bond in connection with the theoretical findings leads to a significant chemical activation, as in the case of the hydridodiazaphospholenes **1**,[2] is confirmed by a series of reactions that proceed by metathesis or by insertion into the P–P bond (Scheme 3).



Scheme 3. R′ = Mes; Y = CN (**10a**), CO_2Me (**10b**).

In contrast to white phosphorus, which is, regardless of its high reactivity, chemically inert against pure water, **5a** reacts with H_2O within a few minutes at 20 °C quantitatively under cleavage of the P–P bond to give diphenylphosphane and the 2-oxodiazaphospholene **6**.[16] A slower reaction to yield $HPPh_2$ and the alkoxydiazaphospholene **7**[16] is observed with *i*PrOH.[16] The cleavage of **5a** by CH_2Cl_2 at 40–60 °C to give **4** and (chloromethyl)diphenylphosphane (**8**)[17] follows the known pattern of reactions of diphosphanes with perfluoroalkyl iodides or CCl_4,[18] but is noteworthy because of the mild reaction conditions. Noteworthy is the reaction of **5a** with Me_3SnCl to give an equilibrium mixture that is dynamic on the NMR time scale and contains, beside the starting materials (ca. 10%), the chlorodiazaphospholene **4** and diphenyl(trimethylstannyl)phosphane (**9a**)[17] as main products.[19] The reaction pathway represents in essence a reversal of the dechlorostannylation that has been established as a smooth synthetic route to oligophosphanes,[20] and may be regarded to provide an experimental clue for a comparatively low P–P bond energy in **5a**. Analogous reactions to those for **5a** were also observed for **5b**.

In addition to the metathesis reactions with polar E–H or E–Cl single bonds, the diphosphanes **5** exhibit likewise an interesting reactivity towards olefins, which provides a surprisingly simple route to 1-phosphanyl-2-diazaphospholenylethane derivatives with electronically different donor centers. As first examples we studied the reactions of **5a** with acrylonitrile or methyl acrylate, respectively, which proceed under mild conditions (50 °C) by chemo- and regioselective addition to the C=C double bond to give the products **10a** and **10b**, respectively. Both compounds were isolated in yields of 31% (**5a**) and 63% (**5b**) and were identified by spectroscopy.[16] Unsymmetrical and potentially chiral phosphanes of this type, which are of current interest in catalysis,[21] have as yet not been prepared from diphosphanes.[22] The reaction described here displays close analogies to the recently reported "non-oxidative" insertion of a metal atom into the P–C bond of a phosphenium–carbene adduct.[23]

Remarkably, unlike tetraaminodiphosphanes that may easily decay into two phosphanyl radicals,[24] **5a,b** fail to react with P_4 under addition to a P–P bond even in boiling toluene; possibly, this may indicate a certain complementary nature of reactions involving radical ($R_2P{\cdot\cdot}PR_2$) or ionic ($R_2P^{+-}PR_2$) activation of a P–P bond.

In summary, we have described the synthesis and characterization of diphosphanes with a polarized P–P bond. The molecules display not only an interesting bonding situation, but also allow a variety of synthetically valuable transformations which are, together with coordination chemical studies, currently under investigation.

Experimental Section

5a,b: A solution of $LiPPh_2$ (10 mmol) in THF (20 mL) or $LiPC_4Et_4$ (10 mmol)[4] in THF (50 mL) was added dropwise to a cooled (−78 °C) solution of **4** (10 mmol) in THF (100 mL). The mixture was then allowed to warm to ambient temperature, and stirred for one additional hour. The solvent was removed in vacuum, the residue extracted with hexane (100 mL), and filtered over Celite. The filtrate was concentrated to 30 mL, and the product crystallized at −20 °C.

5a: M.p. 193 °C, yield 77 %. ^{1}H NMR (C_6D_6): $\delta = 7.22$ (m, 4H, o-H_{Ph}), 6.80–6.77 (m, 6H, m/p-H_{Ph}), 6.61 (br, 4H, m-H_{Mes}), 5.78 (d, 2H, $^3J_{P,H} = 1.5$ Hz, N-CH), 2.40 (br, 12H, o-CH_3), 2.07 ppm (s, 6H, p-CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 136.7$ (dd, $^1J_{P,C} = 25.7$ Hz, $^2J_{P,C} = 12.7$ Hz, i-C_{Ph}), 135.8 (dd, $^2J_{P,C} = 10.4$ Hz, $^3J_{P,C} = 1.3$ Hz, i-C_{Mes}), 133.3 (br, o-C_{Mes}), 133.3 (d, $^5J_{P,C} = 2.0$ Hz, p-C_{Mes}), 132.7 (dd, $^3J_{P,C} = 15.5$ Hz, $^4J_{P,C} = 4.8$ Hz, m-C_{Ph}), 128.2 (br, m-C_{Mes}), 126.4 (d, $^4J_{P,C} = 6.1$ Hz, o-C_{Ph}), 125.6 (s, p-C_{Ph}), 118.4 (dd, $^2J_{P,C} = 7.6$ Hz, $^3J_{P,C} = 1.0$ Hz, N-CH), 19.0 (d, $^6J_{P,C} = 1.0$ Hz, p-CH_3), 18.4 ppm (br s, o-CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K): $\delta = 131.0$ (d, $^2J_{P,P} = 259$ Hz, PN_2), −28.8 ppm (d, $^2J_{P,P=}259$ Hz, PPh_2); MS (EI, 70 eV, 410 K): m/z (%): 508(0.1) $[M]^+$, 323(100) $[PN_2C_{20}H_{24}]^+$, 185(17) $[PPh_2]^+$; correct elemental analysis.

5b: m.p. 97 °C, yield 65 %. ^{1}H NMR (C_6D_6): $\delta = 6.77$ (s, 4H, m-CH), 5.85 (d, 2H, $^3J_{P,H} = 0.5$ Hz, N-CH), 2.45 (s, 12H, o-CH_3), 2.34 (q, 4H, $^3J_{H,H} = 7.5$ Hz, CH_2), 2.12 (s, 6H, p-CH_3), 1.73 (br dq, 4H, $^3J_{H,H} = 7.5$ Hz, $J_{P,H} = 9.3$ Hz, CH_2), 1.07 (t, 6H, $^3J_{H,H} = 7.5$ Hz, CH_3), 1.06 ppm (t, 6H, $^3J_{H,H} = 7.5$ Hz, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 152.2$ (dd, $^2J_{P,C} = 8.9$ Hz, $^3J_{P,C} = 2.6$ Hz, PCC), 143.4 (dd, $^1J_{P,C} = 22.4$ Hz, $^2J_{P,C} = 14.6$ Hz, PC), 136.9 (dd, $^2J_{P,C} = 7.4$ Hz, $^3J_{P,C} = 1.7$ Hz, i-C), 136.1 (d, $^5J_{P,C} = 2.0$ Hz, p-C), 135.5 (dd, $^3J_{P,C} = 3.3$ Hz, $^4J_{P,C} = 1.6$ Hz, o-C), 129.5 (d, $^4J_{P,C} = 1.1$ Hz, m-C), 120.9 (dd, $^2J_{P,C} = 8.8$ Hz, $^3J_{P,C} = 1.2$ Hz, N-CH), 21.0 (dd, $J_{P,C} = 22.5$, 0.9 Hz, CH_2), 20.9 (d, $J_{P,C} = 1.6$ Hz, CH_2), 20.5 (d, $^6J_{P,C} = 0.8$ Hz, p-CH_3), 19.7 (dd, $^4J_{P,C} = 6.2$ Hz, $^5J_{P,C} = 3.2$ Hz, o-CH_3), 18.3 (dd, $^3J_{P,C} = 5.7$ Hz, $^4J_{P,C} = 2.4$ Hz, CH_3), 16.6 ppm (d, $^4J_{P,C} = 1.1$ Hz, CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K): $\delta = 147.1$ (d, $^1J_{P,P} = 188$ Hz, PN_2), 23.1 ppm (d, $^1J_{P,P} = 188$ Hz, $P_{phosphole}$); MS (EI, 70 eV, 380 K): m/z (%): 518(0.1) $[M]^+$, 323(100) $[PN_2C_{20}H_{24}]^+$, 196(14) $[PC_{12}H_{20}]^+$; correct elemental analysis.

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[1] G. A. Gallup , *Valence Bond Methods—Theory and Applications*, Cambridge University Press, Cambridge, **2002**.

[2] D. Gudat, A. Haghverdi, M. Nieger, *Angew. Chem.* **2000**, *112*, 3211; *Angew. Chem. Int. Ed.* **2000**, *39*, 3084.

[3] D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, *Chem. Eur. J.* **2000**, *6*, 3414.

[4] X. Sava, L. Ricard, F. Mathey, P. Le Floch, *Inorg. Chim. Acta* **2003**, *350*, 182.

[5] A VT-NMR study showed a significant temperature dependence of the values of $^1J_{P,P}$ in **5a,b** (**5a**: $^1J_{P,P} = 255$ Hz (203 K) to 264 Hz (363 K); **5b**: $^1J_{P,P} = 177$ Hz (203 K) to 204 Hz (363 K)). The precise origin of this effect, which is likewise known for other diphosphanes and has been explained by temperature-dependent equilibria between conformers (cf. J. G. Verkade, L. D. Quin, *P-31 NMR-Spectroscopy in Stereochemical Analysis*, VCH, Deerfield Beach, **1987**, p. 450f), is currently being intensively investigated.

[6] Crystal structure analyses: Nonius KappaCCD diffractometer, $T = 123(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), SHELX97 program package[7] for structure solution (direct methods) and refinement (full-matrix, least-squares refined against F^2). The positions of the hydrogen atoms were refined with a riding model. **5a**: yellow crystals, $C_{32}H_{34}N_2P_2$, $M_r = 508.6$, crystal size $0.45 \times 0.30 \times 0.20$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.1758(2)$, $b = 10.6220(3)$, $c = 17.1208(7)$ Å, $\alpha = 96.601(2)$, $\beta = 100.350(2)$, $\gamma = 106.349(2)°$, $V = 1381.75(8)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.181$ mm^{-1}, $T = 123(2)$ K, $F(000) = 540$, $\theta_{max} = 25°$, 10884 reflections, of which 4866 were independent ($R_{int} = 0.043$), $R_1 = 0.039$ (for $I > 2\sigma(I)$), $wR_2 = 0.089$ (all data). **5b**: yellow crystals, $C_{32}H_{44}N_2P_2$, $M_r = 518.6$, crystal size $0.50 \times 0.40 \times 0.30$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.1305(2)$, $b = 8.9507(2)$, $c = 20.5590(5)$ Å, $\alpha = 96.269(1)$, $\beta = 90.165(1)$, $\gamma = 94.510(1)°$, $V = 1482.50(6)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.169$ mm^{-1}, $F(000) = 560$, $\theta_{max} = 25°$; 13028 reflections, of which 5220 were independent ($R_{int} = 0.034$); $R_1 = 0.044$ (for $I > 2\sigma(I)$), $wR_2 = 0.125$ (all data). CCDC-232847 (**5a**) and CCDC-232848 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467; b) G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**.

[8] Average value ±3 standard deviations as result of a query in the CCSD data base for P–P distances in diphosphanes $R_2P{-}PR_2$ (R = nonmetal substituent).

[9] S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. Voigt, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne, P. P. Power, *J. Am. Chem. Soc.* **2001**, *123*, 9045.

[10] H. R. G. Bender, E. Niecke, M. Nieger, H. Westermann, *Z. Anorg. Allg. Chem.* **1994**, *620*,1194.

[11] Average ±3 standard deviations as result of a query in the CCSD data base for P–C and C–C distances in phospholes.

[12] All computations were carried out at the B3LYP/6-31g(d)-level with the Gaussian program package: Gaussian 98 (Rev. A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B.Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

[13] NBO 5.0: E. D. Glendening, J.K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theo-

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retical Chemistry Institute, Univ. of Wisconsin, Madison, WI, **2001**; http://www.chem.wisc.edu/~nbo5.

[14] In addition to **5**″ and **5**‴, further ionic canonical structures were found which feature delocalization of the negative charge within the phospholyl fragment.

[15] A quite similar bonding situation was established for cyclopentadienyl phosphenium or arsenium ions, respectively; see: D. Gudat, M. Nieger, E. Niecke, *J. Chem. Soc. Dalton Trans.* **1989**, 693; P. Jutzi, T. Wippermann, C. Krüger, H.-J. Kraus, *Angew. Chem.* **1983**, *95*, 244; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 250.

[16] Characteristic spectroscopic data: ^{31}P NMR (161.9 MHz, C_6D_6): $\delta = 0.4$ ppm (dt, $^1J_{P,H} = 650$ Hz, $^3J_{P,H} = 16.4$ Hz); ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 8.72$ (dt, 1H, $^1J_{P,H} = 650$ Hz, $^4J_{H,H} = 1.5$ Hz, P(O)H), 6.94 (m, 2H, *m*-CH), 6.91 (m, 2H, *m*-CH), 5.89 (dd, $^3J_{P,H} = 16.4$ Hz, $^4J_{H,H} = 1.5$ Hz, N-CH), 2.47 (s, 6H, *p*-CH_3), 2.28 (s, 6H, *o*-CH_3), 2.26 ppm (s, 6H, *o*-CH_3). **7**: ^{31}P{^{1}H} NMR: $\delta = 113.3$ ppm (s) ; ^{1}H-NMR (C_6D_6): $\delta = 6.87$ (m, 2H, *m*-CH), 6.83 (m, 2H, *m*-CH), 5.80 (d, 2H, $^3J_{P,H} = 2.1$ Hz, N-CH), 3.96 (dsept, 1H, $^3J_{P,H} = 7.6$ Hz, $^3J_{H,H} = 6.2$ Hz, POCH), 2.51 (s, 6H, *o*-CH_3), 2.44 (s, 6H, *o*-CH_3), 2.15 (s, 6H, *p*-CH_3), 0.82 ppm (d, 6H, $^3J_{H,H} = 6.2$ Hz, $CH(CH_3)_2$). **10a**: ^{31}P{^{1}H} NMR: $\delta = 99.5$ (d, $^3J_{P,P} = 17.9$ Hz, PN_2), -15.5 ppm (d, $^3J_{P,P} = 17.9$ Hz, PPh_2); ^{1}H NMR (C_6D_6): $\delta = 7.20$–7.13 (m, 4H, H_{Ph}), 6.95–6.85 (m, 6H, H_{Ph}), 6.71 (s, 2H, *m*-CH), 6.63 (s, 2H, *m*-CH), 5.61 (dd, 1H, $^3J_{H,H} = 2.5$ Hz, $^3J_{P,H} = 2.4$ Hz, N-CH), 5.56 (dd, 1H, $^3J_{H,H} = 2.5$ Hz, $^3J_{P,H} = 2.5$ Hz, N-CH), 2.50 (s, br, 6H, *o*-CH_3), 2.35 (dddd, 1H, $^3J_{H,H} = 11.1$ und 4.9 Hz, $^{2/3}J_{P,H} = 7.8$ und 7.8 Hz, CN-CH), 2.28 (s, 6H, *o*-CH_3), 2.04 (6H, *p*-CH_3), 1.98 (dddd, 1H, $^2J_{H,H} = 13.7$ Hz, $^3J_{H,H} = 11.1$ Hz, $^{2/3}J_{P,H} = 2.0$ and 6.6 Hz, CH_2), 1.86 ppm (ddd, 1H, $^2J_{H,H} = 13.7$ Hz, $^2J_{H,H} = 4.9$ Hz, $^nJ_{P,H} = 7.0$ Hz, CH_2). **10b**: ^{31}P{^{1}H} NMR: $\delta = 102.6$ (d, $^3J_{P,P} = 11.8$ Hz, PN_2), -13.4 ppm (d, $^3J_{P,P} = 11.8$ Hz, PPh_2); ^{1}H NMR (C_6D_6): $\delta = 7.35$ (m, 2H, H_{Ph}), 7.18 (m, 2H, H_{Ph}), 7.05–6.90 (m, 6H, H_{Ph}), 6.73 (s, 4H, *m*-CH), 5.73 (dd, 1H, $^3J_{H,H} = 2.9$ Hz, $^3J_{P,H} = 2.0$ Hz, N-CH), 5.57 (dd, 1H, $^3J_{H,H} = 2.9$ Hz, $^3J_{P,H} = 2.1$ Hz, N-CH), 3.57 (dddd, 1H, $^3J_{H,H} = 12.3$ and 8.5 Hz, $^{2/3}J_{P,H} = 2.6$ and 0.8 Hz, C(O)-CH), 3.26 (s, 3H, *o*-CH_3), 2.49 (dddd, 1H, $^2J_{H,H} = 13.6$ Hz, $^3J_{H,H} = 12.3$ Hz, $^{2/3}J_{P,H} = 5.2$ and 1.9 Hz, CH_2), 2.49 (s, 6H, *o*-CH_3), 2.36 (s, 6H, *o*-CH_3), 2.13 (s, 3H, *p*-CH_3), 2.08 (s, 3H, *p*-CH_3), 1.91 ppm (dddd, 1H, $^2J_{H,H} = 13.6$ Hz, $^3J_{H,H} = 8.5$ Hz, $^{2/3}J_{P,H} = 2.5$ and 0.3 Hz, CH_2). The regiochemistry in **10a,b** was unequivocally established from 2D-NOESY spectra.

[17] Identified by comparison of ^{31}P and ^{1}H NMR data with those of authentic samples.

[18] G. Elsner, *Methoden Org. Chem. (Houben-Weyl) 4th ed.*, *Vol. 13/E1*, **1980**, 129 ff.

[19] In the analogous reaction of **5a** with Me_3SiCl, formation of traces $\leqslant 1\%$ of the silylphosphane **9b** was likewise established from ^{31}P{^{1}H} and ^{1}H,^{31}P HMQC NMR spectra.

[20] M. Baudler, B. Makowka, *Angew. Chem.* **1984**, *96*, 976; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 987; M. Baudler, L. De Riese-Meyer, *Z. Naturforsch. B* **1986**, *41*, 399.

[21] G. Fries, J. Wolf, M. Pfeiffer, D. Stalke, H. Werner, *Angew. Chem.* **2000**, *112*, 575; *Angew. Chem. Int. Ed.* **2000**, *39*, 564.

[22] Additions of symmetrical diphosphanes to olefins are possible under drastic conditions, but have hardly gained any relevance (cf. ref. [18]).

[23] N. J. Hardman, M. B. Abrams, M. A. Pribisko, T. M. Gilbert, R. L. Martin, G. J. Kubas, R. T. Baker, *Angew. Chem.* **2004**, *116*, 1989; *Angew. Chem. Int. Ed.* **2004**, *43*, 1955.

[24] J. P. Bezombes, P. B. Hitchcock, M. F. Lappert, J. E. Nycz, *J. Chem. Soc. Dalton Trans.* **2004**, 499.