1,1-disubstituted alkene α-methylstyrene, the 1,2-*cis*-disubstituted alkene cyclohexene, and the trisubstituted alkene 1-phenylcyclohexene. In all cases diol selectivities of over 75% are obtained, frequently greater than 90%. Calculations of oxygen consumption show that in all reactions both oxygen atoms are used productively for diol formation and catalyst regeneration. The aryl-substituted diols are formed with good to very good enantioselectivities (80–96% *ee*) which are only slightly lower than those achieved under the optimized Sharpless conditions. This is largely attributable to the higher temperature (50°C compared to 0°C).

In summary, osmium-catalyzed dihydroxylations may be carried out simply and practicably with oxygen at normal pressure in a basic two-phase system. Both oxygen atoms are incorporated into the product in an atom-efficient manner. The diols are obtained in excellent yields, and the catalyst can be recycled. Thus the method described here represents not only an improvement over the versatile Sharpless dihydroxylation, but also opens up new perspectives for by-product-free preparation of diols used on an industrial scale.

Received: June 22, 1999 [Z13598]
German edition: *Angew. Chem.* **1999**, *111*, 3211–3212

Keywords: dihydroxylations · homogeneous catalysis · osmium · oxidations · oxygen

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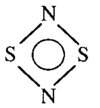
Valence Isomerization of a 1,3-Diphosphacyclobutane-2,4-diyl: Photochemical Ring Closure to 2,4-diphosphabicyclo[1.1.0]butane and Its Thermal Ring Opening to *gauche*-1,4-Diphosphabutadiene[**]

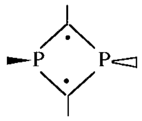
Edgar Niecke,* André Fuchs, and Martin Nieger

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

The disulfur dinitride **I** is generally considered as a prominent example of an electron-rich π-delocalized four-membered ring system.[1] Valence isomerization to a bicyclobutane, butadiene, or cyclobutene analogue is unknown, although polymerization by means of diradical ring opening is known.[2] Recently, we established[3] the existence of a further four-membered ring system, isoelectronic with **I**, in the form of 1,3-diphosphacyclobutane-2,4-diyl **II** (a 2,4-diphosphabicyclo[1.1.0]butane bond stretch isomer[4]) and characterized structurally the first derivatives.[3, 5] Ab initio calculations confirm a substantial diradical contribution to the parent system of **II**[6] which results from the high inversion barrier of the phosphorus atom. Transannular C–C bond formation to the thermodynamically favored 2,4-diphosphabicyclo[1.1.0]butane **III**,[7] however, does not occur.[8] Instead, thermal rearrangements are induced which, similar to **I**, were initiated by ring opening.[3, 5] This includes the valence isomerization of **II** to 1,2-dihydro-1,2-diphosphete **IV** which we recently reported,[9] and which proceeds via a phosphanylcarbene **V**.[10] We report here on the photochemically induced ring closure of **II** to the 1,3-diphosphabicyclo[1.1.0]butane **III** and its thermal ring opening to *gauche*-1,4-diphosphabutadiene **VI**. Previously, phosphabicyclobutanes have only been known with phosphorus in the bridge position;[11] for free phosphabutadienes only the *trans* form has been hitherto established.[12]



I



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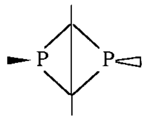

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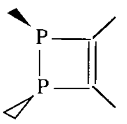

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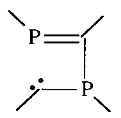
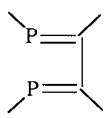


V



VI

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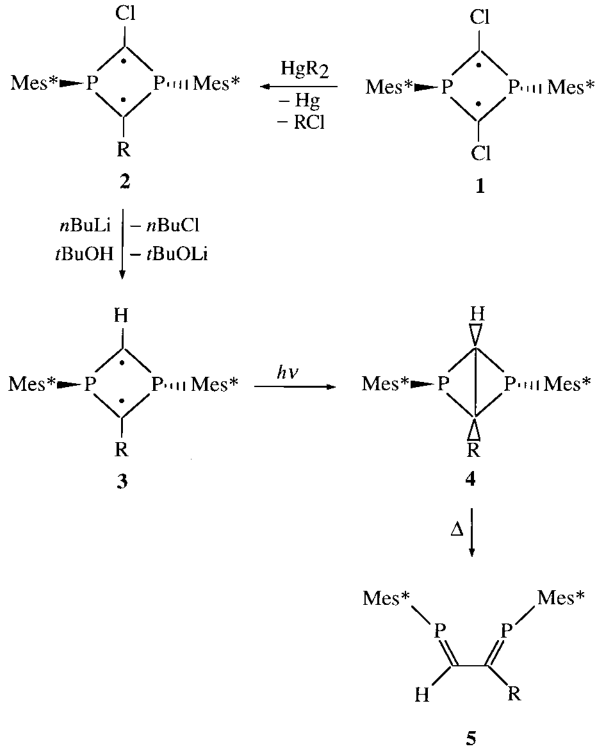
[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie. Published in part at the "XIV International Congress on Phosphorus Chemistry", Cincinnati, **1998**, Abstr. No. LM 2-3.

The crystalline 1,3-diphosphacyclobutane-2,4-diyl **2**, which is readily available from 1,3-diphosphacyclobutane-2,4-diyl $[Mes^*PCCl]_2$ (**1**) ($Mes^* = 2,4,6\text{-}tBu_3C_6H_2$)[3] by selective Cl/$SiMe_3$ exchange (0.5 equiv $Hg(SiMe_3)_2$, can be transformed into the protonated derivative **3** with *n*BuLi and subsequent *t*BuOH addition (Scheme 1). This product can be isolated in the form of a red crystalline solid. Whereas **3** is thermally extremely stable,[13] irradiation (10% solution in *n*-pentane, −30 °C) induced a rapid conversion of **3** into the 1,3-diphosphabicyclo[1.1.0]butane **4**, which was isolated as a yellow solid and can be transformed into the 1,4-diphosphabutadiene **5** by heating (10% solution in mesitylene, 150 °C, 2 h) (Scheme 1; see Experimental Section).



Scheme 1. Synthesis of **2**–**5**. $R = SiMe_3$; $Mes^* = 2,4,6\text{-}tBu_3C_6H_2$.

The ^{31}P and ^{13}C NMR shifts of **2** and **3** correspond to those of the first 1,3-diphosphacyclobutane-2,4-diyls, $[Mes^*PCCl]_2$[3] and $[2,2,6,6\text{-}Me_4C_5H_6NPCCl]_2$.[9] The observed A_2X pattern of the ring carbon atom signals in the $^{13}C\{^1H\}$ NMR spectrum and the ideal 1:2:1 triplet structure of the signal of the ring proton in **3** ($\delta = 4.9$, $^2J(H,P) = 33.8$ Hz) exclude the presence of the thermodynamically favored 1,2-dihydro-1,2-diphosphete **6**.[14] The changes in the NMR spectrum observed during the irradiation of **3** are manifested in a strong deshielding of all ring atoms ($\delta(^{31}P) = -83.4$, -84.2, ($^2J(P,P) = 32.4$ Hz; $\delta(^{13}C) = 28.3$ ($^1J(C,P) = 74.8$, 66.4 Hz), 28.3 ($^1J(C,P) = 58.0$, 47.7 Hz)). The position of the signals and the splitting pattern indicate the presence of the bicyclic valence isomer **4**. The chemical nonequivalence of the two phosphorus atoms confirm the axial/equatorial arrangement of the aryl residues, required for a stereoselective reaction course **3**→**4**.

The structures of **3** and **4** derived from the NMR data are proved by X-ray structural analysis[15] (Figures 1a and 1b). This confirms the presence of a planar P_2C_2 ring for **3** with the phosphorus atoms in the 1,3 position and *trans* aryl substituents (C_i symmetry). The pyramidalization at the phosphorus atoms in **3** (sum of the valence angle 337° and 341°) is similar to that in $[Mes^*PCCl]_2$ (**3a**) (338°).[3] Unlike in **3a**, the carbon atoms in **3** are trigonal-planar coordinated. This geometry causes comparatively shorter P−C distances (mean value: 173 pm; cf. 175 pm in **3a**),[3] indicating a reinforcement of the cyclic electron delocalization (weakening of the diradical character) in comparison to **3a**. The transannular C−C linkage **3**→**4** (**3**: C1···C2 247, **4**: C1−C2 152 pm) is associated with a folding of the P_2C_2 four-membered ring (folding angle P1-C1-C2-P2 117°). The aryl substituents are thus forced into the axial/equatorial position, an indication of the retention of the configuration at the phosphorus atoms. The folding is associated with a loss of π-electron delocalization, which is expressed by an increase in the P−C distances to typical values for single bonds (mean value 184 pm).

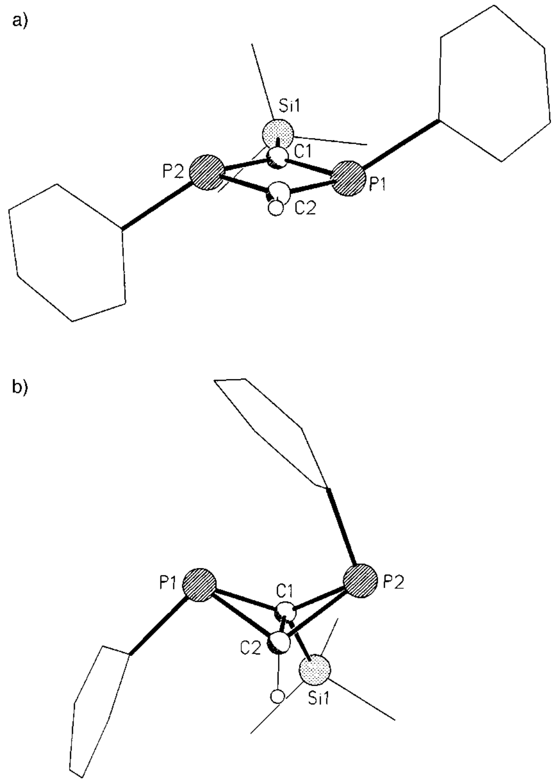


Figure 1. a) Simplified representation of the crystal structure of **3** (an independent molecule; without hydrogen atoms). Selected bond lengths [pm], bond angles [°], and torsion angles [°]: P1−C1 172.8(3), P1−C2 172.3(3), P2−C1 174.3(3), P2−C2 171.9(3); C1-P1-C2 91.5(1), P1-C1-P2 88.2(1), C1-P2-C2 91.1(1), P1-C2-P2 89.2(1); P1-C1···C2-P2 179.6(2). Sum of angles Σ at C1 360°, at C2 360°; P1, P2, C1 and C2 lie in one plane (deviation from the mean plane 0.2 pm). b) Simplified representation of the crystal structure of **4** (without hydrogen atoms). Selected bond lengths [pm], bond angles [°], and torsion angles [°]: P1−C1 187.0(3), P1−C2 182.0(3), P2−C1 186.1(3), P2−C2 181.2(3), C1−C2 151.6(4); C1-P1-C2 48.5(1), P1-C1-P2 100.3(1), P1-C1-C2 64.0(1), P1-C2-P2 104.1(1), C1-C2-P1 67.5(1), C1-P2-C2 48.7(1), P2-C1-C2 63.9(1), C1-C2-P2 67.3(1); P1-C1-C2-P2 −117.3(1).

The thermolysis of **4** (1,2-dimethoxyethane (DME), 150 °C, 2 h) proceeds smoothly to give a product which exhibited a strong deshielding of the phosphorus atoms in the ^{31}P NMR spectrum ($\delta = 298.2$, 280.0). The changes in the ^{13}C NMR shifts of the ring carbon atoms on transformation of **3** to **4** correlate with the $\delta(^{31}\mathrm{P})$ values ($\delta = 184.3$, 177.4) and suggest the formation of a butadiene-like system with phosphorus atoms in the 1,4 positions. This constitution is supported by the low-field position and the multiplet structure of the ^{1}H NMR signal ($\delta = 7.46$, $J(\mathrm{H,P}) = 4.6$, 28.7 Hz). The large contribution of the P–P coupling constant of 167.8 Hz, which would be in agreement with neighboring lone pairs of electrons on the phosphorus atoms, is conspicuous.

Figure 2 shows the molecular structure of **5** in the crystal.[15] Unlike the previously known, *trans*-configured 1,4-diphosphabutadienes,[18] **5** exists in the *gauche*-(*cis,anti*) form (torsion angle P1-C1-P2-C2 41°). This conformation, in which the two methylene carbon fragments, unlike a *cis* form,[19] are transposed in opposite directions, leads to a reduction in the repulsive interactions between the lone pairs of electrons on the phosphorus atoms. The peripheral aryl substituents are located in the *exo,exo* position, which is to be expected for a contrarotatory ring opening **4**→**5**.[5] Ab initio calculations also favor a contrarotatory process in the ring opening of the bicyclobutane to the *gauche* butadiene.[20] The large value of the $^{3}J(\mathrm{P,P})$ coupling constant is equally compatible with the *gauche* conformation of **5**. The P–C distances (P1–C1 168.2(2), P2–C2 169.7(2) pm) and the C–C bond lengths (146.4 (2) pm) confirm the formation of a conjugated π-electron system. Steric factors impose the almost orthogonal alignment of the aryl moieties to the P_2C_2 fragment. The remaining bond lengths and angles show nothing conspicuous.

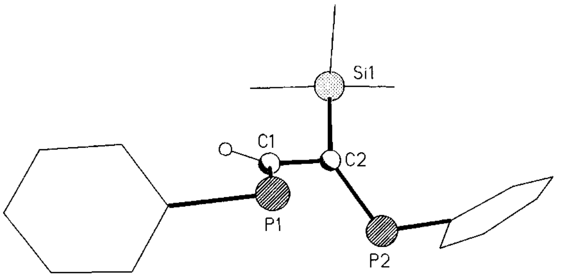


Figure 2. Simplified representation of the crystal structure of **5** (without hydrogen atoms). Selected bond lengths [pm], bond angles [°], and torsion angles [°]: P1–C1 168.5(2), C1–C2 146.4(2), C2–P2 169.7(2), C2–Si1 189.7(2), C1–H1 95; P1-C1-C2 123.2(1), C1-P1-C6 100.0(1), C1-C2-P2 110.8(1), C1-C2-Si1, 114.2(1), C2-P2-C24 108.0(1), P2-C2-Si1 134.9(1); P1-C1-C2-Si1 −142.3(1), P1-C1-C2-P2 41.0(2). Sum of angles Σ at C2 359.9°.

Experimental Section

2: A solution of **1** (1.30 g, 2 mmol) in THF (40 mL) was treated dropwise with a solution of $\mathrm{Hg(SiMe_3)_2}$ in *n*-hexane (0.66 м, 3.2 mL) at 25 °C. The mixture was stirred for 2 h and the red solution was then withdrawn from the resulting mercury with a syringe. Cooling the reaction solution to 2 °C resulted in the crystallization of **2**. Yield 0.96 g (71 %); m.p. 140–142 °C; NMR spectra (25 °C, without signals of the aryl residues): $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CH_2Cl_2}$): $\delta = 2.2$ (s); ^{1}H NMR ($\mathrm{CH_2Cl_2}$): $\delta = -0.49$ (s, $\mathrm{SiMe_3}$); ^{13}C NMR ($\mathrm{CH_2Cl_2}$): $\delta = 1.71$ (t, $^{3}J(\mathrm{C,P}) = 3.4$ Hz, $\mathrm{P_2SiC_3}$), 93.9 (t, $^{1}J(\mathrm{C,P}) = 27.9$ Hz, $\mathrm{P_2CSi}$), 104.5 (t, $^{1}J(\mathrm{C,P}) = 23.1$ Hz, $\mathrm{P_2CCl}$)); UV/Vis (pentane, $c = 2.60 \times 10^{-5}$ mol L^{-1}, 25 °C): λ [nm] (ε) = 205 (77000), 252 (36000), 321 (28000), 458 (2600); MS (70 eV): *m/z* (%): 684 (2) [M^+], 439 (100) [M^+ – Mes*].

3: Compound **2** (0.45 g, 0.66 mmol) was dissolved in THF (3 mL) and metalated at −78 °C within 10 min by stirring with *n*BuLi (0.2 mL, 0.33 mmol) in *n*-hexane ($c = 1.6$ mol L^{-1}). Product **3** crystallized from the solution as yellow crystals after two days at +2 °C. Yield 97 %; m.p. 164–166 °C; NMR spectra (25 °C, without signals from the aryl residues): ^{31}P NMR (ext.): $\delta = 11.3$; ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 5.7$ (t, $^{2}J(\mathrm{H,P}) = 11.4$ Hz, $\mathrm{P_2CHCl}$); ^{13}C NMR ($\mathrm{C_6D_6}$): $\delta = 3.8$ (t, $^{4}J(\mathrm{C,P}) = 4.6$ Hz, $\mathrm{PCSi}C_3$), 104.0 (t, $^{2}J(\mathrm{C,P}) = 4.8$ Hz, $\mathrm{P_2CH}$), 111.0 (t, $^{2}J(\mathrm{C,P}) = 20.2$ Hz, $\mathrm{P_2CSi}$); MS (70 eV): *m/z* (%): 482 (6) [M^+], 73 (100) [$\mathrm{SiMe_3}$].

4: A solution of **3** (198 mg, 305 mmol) in DMF (5 mL) was irradiated at −25 °C with a Hg lamp for 2 h during which time the color of the reaction solution changed from red to yellow. In addition to an as yet unidentified species, **4** was formed as the main product (>90 % by ^{31}P NMR). The reaction solution was evaporated in vacuo and stored at −30°C. Compound **4** crystallized after two days. Yield 1.21 g (67 %); m.p. 164–166 °C; NMR spectra (THF, 25 °C, without signals from the aryl residues): ^{31}P NMR (ext.): $\delta = -83.4$, −84.2 ($^{2}J(\mathrm{P,P}) = 32.4$ Hz); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 2.73$ (dd, $^{2}J(\mathrm{H,P}) = 4.6$, 28.7 Hz); ^{13}C NMR ($\mathrm{C_6D_6}$): $\delta = 28.3$ (dd, $^{1}J(\mathrm{C,P}) = 74.8$, 66.4 Hz), 28.3 ($^{1}J(\mathrm{C,P}) = 58.0$, 47.7 Hz); MS (70 eV): *m/z* (%): 482 (6) [M^+], 73 (100) [$\mathrm{SiMe_3}$].

5: A solution of **4** (155 mg, 162 mmol) in mesitylene (20 mL) was stirred for 2 h at 150 °C. The solvent was then evaporated in vacuo and the residue was dissolved in a little DMF. After one day at 3 °C, yellow crystals of **5** were deposited. Yield 105 mg (68 %); m.p, 188–190 °C; NMR (THF, 25 °C; without signals from the aryl residues): ^{31}P NMR (ext.): $\delta = 298.2$, 280.0 ($^{3}J(\mathrm{P,P}) = 167.8$ Hz); ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = -7.46$ (dd, $J(\mathrm{H,P}) = 15.5$, 20.4 Hz, C(H)CP); ^{13}C NMR ($\mathrm{C_6D_6}$): $\delta = 177.4$ (dd, $J(\mathrm{C,P}) = 23.7$, 40.1 Hz, *C*(H)CP), 184.3 (dd, $J(\mathrm{C,P}) = 16.8$, 79.0 Hz, P*C*(Si)CP); MS (70 eV): *m/z* (%): 482 (6) [M^+], 73 (100) [$\mathrm{SiMe_3}$].

Received December 17, 1998 [Z12792IE]
German version: *Angew. Chem.* **1999**, 3213–3216

Keywords: bond stretch isomers • phosphaalkenes • phosphorus heterocycles • valence isomerization

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[15] X-ray crystal analysis: **3**: $C_{41}H_{68}P_2Si$, red crystals, crystal dimensions $0.25 \times 0.40 \times 0.47$ mm; $M_r = 650.98$; triclinic, space group $P\bar{1}$ (no. 2), $a = 14.140(1)$, $b = 18.037(1)$, $c = 20.006(2)$ Å, $\alpha = 113.30(1)$, $\beta = 96.76(1)$, $\gamma = 109.82(1)^\circ$, $V = 4217.3(6)$ Å^3, $Z = 4$, $\mu(\mathrm{Cu_{K\alpha}}) = 1.37$ mm^{-1}, $T = 200(2)$ K, $F(000) = 1432$; $2\Theta_{max} = 135^\circ$; 15743 reflections, of which 15209 were independent and used for all calculations, were measured on a Nonius MACH3 diffractometer with $\mathrm{Cu_{K\alpha}}$ radiation. The structure was determined by direct methods and refined anisotropically on F^2 with the H atoms included with a riding model (programs: SHELXS-97,[16] SHELXL-97[17]). The final quality factor $wR2(F^2)$ was 0.193 with a conventional $R(F) = 0.065$ for 816 parameters and 190 restraints. An extinction correction and an empirical absorption correction was carried out on the basis of Ψ scans (min. and max. transmission 0.430 and 0.916, respectively). In the second molecule, the phosphorus atoms and the trimethylsilyl group are disordered. **4**: $C_{41}H_{68}P_2Si$, yellow crystals, crystal dimensions $0.08 \times 0.10 \times 0.30$ mm; $M_r = 650.98$; monoclinic, space group $P2_1/c$ (no. 14), $a = 11.2020(3)$, $b = 20.5400(3)$, $c = 18.0230(5)$ Å, $\beta = 96.111(4)^\circ$, $V = 4123.3(2)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.16$ mm^{-1}, $T = 123(2)$ K, $F(000) = 1432$; $2\Theta_{max} = 50^\circ$; 23102 reflections, of which 6554 were independent and used for all calculations, were measured on a Nonius-Kappa CCD diffractometer with $\mathrm{Mo_{K\alpha}}$ radiation. The structure was determined by direct methods and refined anisotropically on F^2 with the H atoms included with a riding model (programs: SHELXS-97,[16] SHELXL-97[17]). The final quality factor $wR2(F^2)$ was 0.147 with a conventional $R(F) = 0.050$ for 400 parameters and one restraint. **5**: $C_{41}H_{68}P_2Si$, yellow crystals, crystal dimensions $0.10 \times 0.10 \times 0.25$ mm; $M_r = 650.98$; monoclinic, space group $P2_1/n$ (no. 14), $a = 14.9030(3)$, $b = 10.3010(2)$, $c = 26.6390(8)$ Å, $\beta = 90.992(5)^\circ$, $V = 4088.9(2)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.16$ mm^{-1}, $T = 123(2)$ K, $F(000) = 1432$; $2\Theta_{max} = 55^\circ$; 25234 reflections, of which 7884 were independent and used for all calculations, were measured on a Nonius Kappa CCD diffractometer with $\mathrm{Mo_{K\alpha}}$ radiation. The final quality factor $wR2(F^2)$ was 0.107 with a conventional $R(F) = 0.039$ for 397 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-112271 (**3**), 112272 (**4**), and 112273 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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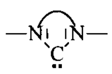
1,3-Diphosphacyclobutane-2,4-diyl-2-ylidenide: A Unique Carbene and Its Trimethylalane Complex**

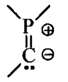
Edgar Niecke,* André Fuchs, Martin Nieger, Olaf Schmidt, and Wolfgang W. Schoeller

Dedicated to Professor Konrad Sandhoff on the occasion of his 60th birthday

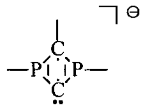
The chemistry of N-heterocyclic carbenes **I** has, through the synthesis of stabilized derivatives by Arduengo et al.,[1] experienced an unexpected renaissance.[2] Heterocycles, in which the position neighboring the carbene atom is not occupied by nitrogen atoms, are not known in free form. On the other hand "push/pull" substituted λ^5-phosphaacetylenes **II** ("kryptocarbenes"[3]) are stable and reveal a carbene-analogous reactivity.[4] In connection with our work on four-membered π-delocalized phosphorus heterocycles (1,3-diphosphacyclobutane-2,4-diyls), which, owing to the pyramidalized carbon and[5]/or[6] phosphorus atoms, are ascribed more or less pronounced diradical character, we became interested in the corresponding isoelectronic anions **III** (1,3-diphosphacyclobutane-2,4-diyl-2-ylidenides). Here we report on the synthesis and bonding analysis of the first representative of this type as well as on the structure of its trimethylalane adduct.



I



II



III

Deprotonation of 1,3-diphosphacyclobutane-2,4-diyl[6] **1** with one equivalent of lithium diisopropylamide (LDA) led to the formation of a deep red solution from which $\mathbf{2}\cdot[\mathrm{Li(thf)}_n]^+$ can be isolated as a dark red, amorphous solid[7] (Scheme 1). In the pure state $\mathbf{2}\cdot[\mathrm{Li(thf)}_n]^+$ can be stored under an inert atmosphere without decomposition; in solution (25°C, THF) **1** is re-formed within one day (ca. 60% according to ^{31}P NMR control). With the Lewis acid trimethylalane, **2** can easily be transformed into the adduct $\mathbf{2}\cdot\mathrm{AlMe_3}$ (**3**), and isolated as the lithium salt $\mathbf{3}\cdot[\mathrm{Li(thf)}_4]^+$ in the form of red, hydrolysis-sensitive crystals (Scheme 1).

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (SSB 334) and the Fonds der Chemischen Industrie. Partly presented at the International Conference on Phosphorus Chemistry, Cincinatti, USA, July 12–17, 1998.