Experimental Section

All procedures were carried out under argon. *n*-Pentane and cyclopentane were dried over $LiAlH_4$.

1: *n*BuLi (11.4 mL of a 1.6 M solution in *n*-hexane) was added dropwise to a solution of phenylethyne (1.86 g, 2 mL, 18.2 mmol) in *n*-pentane (15 mL) at 0 °C. The suspension was stirred for 2 h at room temperature, cooled to 0 °C, and treated with Me_2AlCl (1.7 mL, 1.68 g, 18.2 mmol) dissolved in *n*-pentane (15 mL). The mixture was stirred for 16 h at room temperature, filtered, and evaporated. The residue was recrystallized from *n*-pentane (20/ − 30 °C). Yield: 1.64 g (57 %); colorless, extremely air-sensitive crystals. M.p. (sealed capillary): 76– 80 °C. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.32$ (2H, pseudo-d, Ph), 6.89 (1H, pseudo-t, Ph), 6.78 (2H, pseudo-t, Ph), 0.03 (6H, Me); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 135.5$, 133.8, 131.5, and 128.8 (Ph), 119.9 and 96.8 (C≡C), − 6.8 (AlC); IR (Nujol): $\tilde{\nu}$ [cm^{-1}] = 2089 (νC≡C).

2: A mixture of **1** (628 mg, 3.97 mmol) and Me_2AlH[14] (1.214 g, 20.9 mmol) was heated for 48 h to 80 °C without a solvent. After about 2 h, a solid started to precipitate from the red solution. All volatile components were distilled off in vacuo after cooling to room temperature. The residue was treated with cyclopentane, filtered, and recrystallized at − 30 °C. The crystals of **2** included up to 0.9 molecules cyclopentane per formula unit after thorough evacuation. Yield: 445 mg (0.486 mmol, 61 %), colorless, slightly air-sensitive crystals. M.p. (sealed capillary): 175 °C (decomp.). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.5 - 7.0$ (m, Ph), 5.23 (1H, s, AlHAl), 3.52 (2H, s, CH_2 at C14), 3.07 (8H, s, CH_2), − 0.30 and − 0.68 (each 12H, s, AlMe); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 147.9$ (*ipso*-C at C14), 147.5 (*ipso*-C of the other phenyl groups), 129.6, 129.0, 128.7, 126.1 and 125.7 (Ph), 35.5 (CH_2 at C14), 34.2 (CH_2 at C10 to C13), 30.0 (C10 to C13), 24.1 (C14), − 11.7 and − 12.7 (AlMe); assignment on the basis of *j*-modulated and ^{1}H–^{13}C correlated NMR spectra; IR (Nujol, CsBr plates): $\tilde{\nu}$ [cm^{-1}] = 1599 m (Ph), 1462 vs, 1377 vs (Nujol), 1300 m (ν_{Al-H}), 1186 s, 1154 m, 1072 w, 1030 w (ν_{C-C}), 959 s, 930 m, 907 m, 824 m (Ph), 750 vs, 710 vs, 691 vs, 673 vs, 665 vs (δ_{Ph}, ν_{Al-C}), 581 m, 550 m, 525 m, 505 w, 428 m (ν_{Al-C}); UV/Vis (cyclopentane): λ_{max} [nm] (lg ε) = 250 (4.1).

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[1] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, **1984**; A. F. Hollemann, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, **1995**.

[2] D. M. Schubert, M. A. Bandman, W. S. Rees, Jr., C. B. Knobler, P. Lu, W. Nam, M. F. Hawthorne, *Organometallics* **1990**, *9*, 2046; C. A. Morrison, B. A. Smart, P. T. Brain, D. W. H. Rankin, A. J. Downs, *J. Chem. Soc. Dalton Trans.* **1998**, 2155.

[3] B. Wrackmeyer, H.-J. Schanz, M. Hofmann, P. von R. Schleyer, *Angew. Chem.* **1998**, *110*, 1329; *Angew. Chem. Int. Ed.* **1998**, *37*, 1425; B. Wrackmeyer, H.-J. Schanz, M. Hofmann, P. von R. Schleyer, *Eur. J. Inorg. Chem.* **1998**, 633; R. Köster, G. Seidel, B. Wrackmeyer, *Angew. Chem.* **1994**, *106*, 2380; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2294.

[4] W. Uhl, F. Hannemann, W. Saak, R. Wartchow, *Eur. J. Inorg. Chem.* **1998**, 921.

[5] A. V. Kuchin, S. A. Markova, S. I. Lomakina, G. A. Tolstikov, *J. Gen. Chem. USSR* **1988**, *58*, 1395; *Zh. Obshch. Khim.* **1988**, *58*, 1567.

[6] E. Winterfeldt, *Synthesis* **1975**, 617; I. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3241.

[7] Crystal structure of **2**: Single crystals of **2** were obtained from cyclopentane at 0 °C; $C_{48}H_{60}Al_8 \cdot C_5H_{10}$, triclinic, space group $P\bar{1}$, $a =$ 1189.67(8), $b = 1416.02(9)$, $c = 1674.5(1)$ pm, $\alpha = 113.943(7)$, $\beta =$ 91.812(8), $\gamma = 94.609(8)°$, $V = 2563.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} =$ 1.196 g cm^{-3}, crystal dimensions $0.75 \times 0.66 \times 0.34$ mm, Stoe IPDS diffractometer, $Mo_{K\alpha}$ radiation, 193 K, measurement range: $4.2 < 2\Theta < 51.9°$, 238 exposures, $\Delta\varphi = 1.3°$, 9361 independent reflections, 7194 reflections with $F > 4\sigma(F)$, $\mu = 0.194$ mm^{-1}, programs SHELXTL PLUS REL 4.1 and SHELXL-93, 541 parameters; $R1 = 0.044$ and w$R2$ (all data) = 0.139, max./min. residual electron density: 0.96 (near the disordered cyclopentane molecule)/ − 0.53 × 10^{30} e m^{-3}. The position of the hydrogen atom H1 was taken from a difference Fourier map, and refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113238. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] R. G. Vranka, E. L. Amma, *J. Am. Chem. Soc.* **1967**, *89*, 3121; J. C. Huffman, W. E. Streib, *J. Chem. Soc. Chem. Commun.* **1971**, 911.

[9] W. Uhl, *Z. Naturforsch. B.* **1988**, *43*, 1113; R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2983.

[10] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[11] J. Bicerano, D. S. Marynick, W. N. Lipscomb, *Inorg. Chem.* **1978**, *17*, 3443; M. Gielen, *Polyhedron* **1988**, *7*, 363; P. von R. Schleyer, K. Najafian, A. M. Mebel, *Inorg. Chem.* **1998**, *37*, 6765.

[12] J. C. Huffman, D. C. Moody, R. Schaeffer, *Inorg. Chem.* **1976**, *15*, 227.

[13] J. J. Eisch, S. G. Rhee, *Liebigs Ann. Chem.* **1975**, 565, zit. Lit.

[14] H. Lehmkuhl, K. Ziegler in *Methoden der Organischen Chemie (Houben-Weyl) 4th ed., 1952 –*, Vol. XIII/4, **1970**, p. 58.

Stereospecific Migration of P from N to C_{sp^2}: Ring-Expansion Reaction of Chiral Diazaphospholidine Oxides

Olivier Legrand, Jean Michel Brunel, and Gérard Buono*

Many modern synthetic targets, in particular those of interest for pharmaceutical and agrochemical preparations, are either benzenoid or incorporate key aromatic or heteroatomic components.[1, 2] In this context, *ortho*-lithiation has appeared as one of the most important methods for the regiospecific construction of polysubstituted aromatic compounds.[3] When the *ortho*-lithiation directing group contains an electronegative atom attached to a π-unsaturated or coordinatively unsaturated group, the lithiated species may undergo 1,3-migration to the *ortho* position on the aromatic ring. Such metalation-induced 1,3-migration is very common in benzene systems and has been seen for the rearrangement of 1) arenesulfonamides of N-substituted anilines to N-substituted 2-aminoaryl aryl sulfones,[4] 2) aryl *O*-carbamates to salicylamides,[5] 3) *o*-bromophenyl esters to *o*-hydroxyaryl ketones,[6] 4) arylphosphate esters to 2-hydroxyaryl phosphonates,[7] and 5) (triarylsiloxy)benzenes to *o*-(triarylsilyl)phenols.[8]

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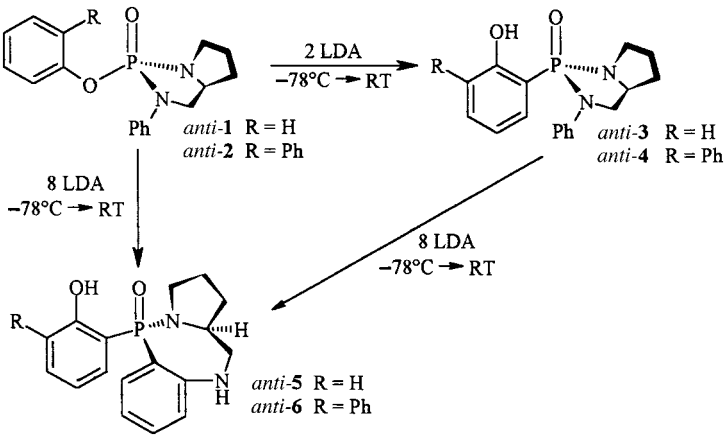
Our group recently reported the synthesis of new chiral *o*-hydroxyarylphosphane oxides involving a stereospecific rearrangement[9] and their use as catalysts in the asymmetric addition of diethylzinc to aromatic aldehydes.[10] Furthermore, aromatic compounds substituted with both amino and phosphanyl or phosphinoyl groups have been prepared by directed *ortho*-lithiation.[11] In this area, Hellwinkel and Modro were the first to describe the preference in the O $\rightarrow C_{sp^2}$ versus N $\rightarrow C_{sp^2}$ migration of the phosphoryl group in *ortho*-lithiated phenyl phosphoramidates or phosphordiamidates.[12] Here we report a new general procedure for the first ring-expansion reaction of diazaphospholidine oxides involving a stereospecific migration of P from N to C.

Reaction of pure diastereomer *anti*-**1** in presence of two equivalents of lithium diisopropylamide (LDA) at $-78\,^{\circ}C$ to room temperature led to the stereospecific formation of the hydroxyphenyldiazaphospholidine oxide *anti*-**3** in 94% yield.[9] However, the new compound *anti*-**5** is formed in 89% yield when the reaction is performed with eight equivalents of LDA and with stirring at room temperature overnight (Scheme 1).



Scheme 1. Diastereoselective synthesis of *anti*-**5** and *anti*-**6**.

In this case, two diastereoselective 1,3-migration rearrangements occurred, and a stereospecific ring expansion is observed. Moreover, treatment of pure *anti*-**3** with eight equivalents of LDA also led to the diastereoselective formation of *anti*-**5**. These results suggest that in the presence of a large excess of LDA, a P–O to P–C_{sp^2} rearrangement occurred followed by a P–N to P–C_{sp^2} rearrangement. On the other hand, treatment of a 55/45 mixture of *anti*-**1** and *syn*-**1** under the same experimental conditions (8 equiv of LDA, $-78\,^{\circ}C$) led to *syn*-**5** in 73% yield (based on *syn*-**1**) besides *anti*-**5** in 81% yield (based on *anti*-**1**).[13] Moreover, in the case of the 1,3-rearrangement of diazaphospholidine oxide *anti*-**2**, single crystals of the product *anti*-**6** suitable for X-ray analysis have been obtained by slow crystallization in ethyl acetate. The proposed boat structure with a phenyl group in an equatorial position was thus proven (Figure 1).[14, 15]

Extension of this reaction to phenyldiazaphospholidine oxides compounds as substrates led to remarkable results (Scheme 2). Precursors **9** were readily synthesized by a substitution reaction between phenylphosphonic dichloride

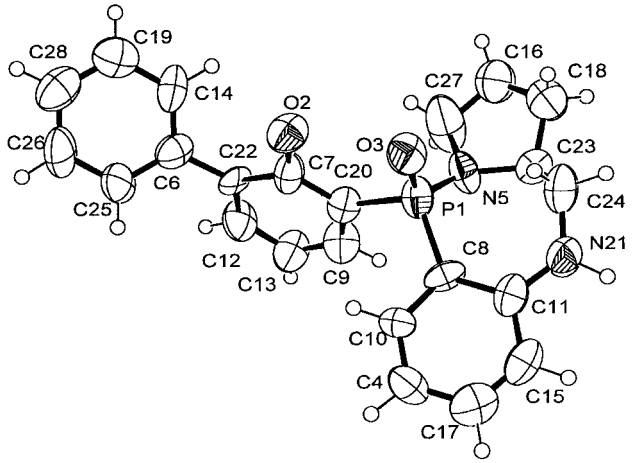
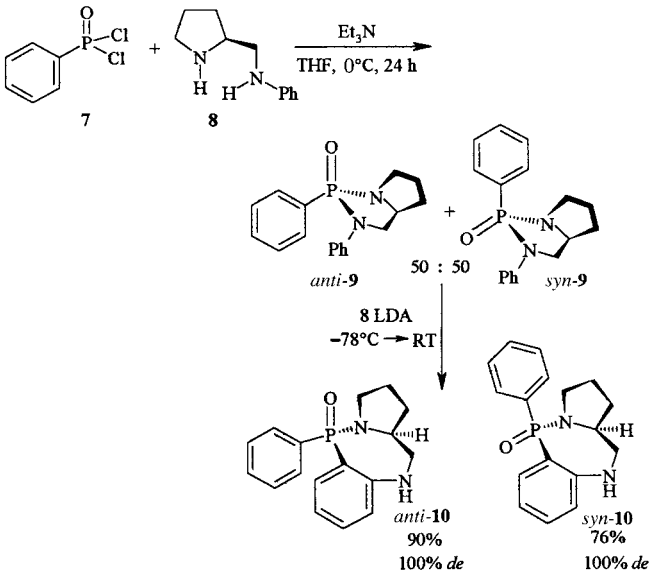


Figure 1. Structure of *anti*-**6**. Selected bond lengths [Å] and angles [°]: P1–O3 1.51(2), P1–C8 1.81(2), P1–N5 1.64(2), P1–C20 1.81(2), C24–N21 1.44(3), C11–N21 1.35(3), C7–O2 1.37(3); O3-P1-N5 117.6(8), O3-P1-C8 112.7(8), O3-P1-C20 108.1(8), N5-P1-C8 107.0(9), N5-P1-C20 102.6(8), C8-P1-C20 108.1(8), P1-N5-C23 123.3(13), P1-N5-C27 121.2(14), C24-N21-C11 123.9(19), P1-C8-C11 125.8(15), C6-C22-C12 121.1(20).



Scheme 2. Diastereoselective synthesis of *anti*-**10** and *syn*-**10**.

(**7**) and (*S*)-(anilinomethyl)pyrrolidine (**8**)[16] in THF at $0\,^{\circ}C$; a separable mixture of *anti*-**9** and *syn*-**9** in a 50/50 diastereomeric ratio was formed. Subsequent treatment of each pure diastereomer with eight equivalents of LDA at $-78\,^{\circ}C$ resulted in the migration of the phosphonyl group from the nitrogen to the *ortho* aromatic carbon atom to produce *anti*-**10** and *syn*-**10** stereoselectively in 90 and 76% yield, respectively. Thus, to our knowledge, a new stereospecific ring-expansion reaction proceeding by a 1,3-migration of P from N to C has been observed, leading to the synthesis of a new class of chiral organophosphorus compounds.

Since it was clearly established that the 1,3-phosphorus migration proceeds with retention of configuration at the phosphorus atom, a mechanism via a trigonal-bipyramidal (TBP) intermediate can be postulated (Scheme 3).[17] Mislow has suggested that if the bond-making or bond-breaking step is rate determining, then apical addition and elimination will

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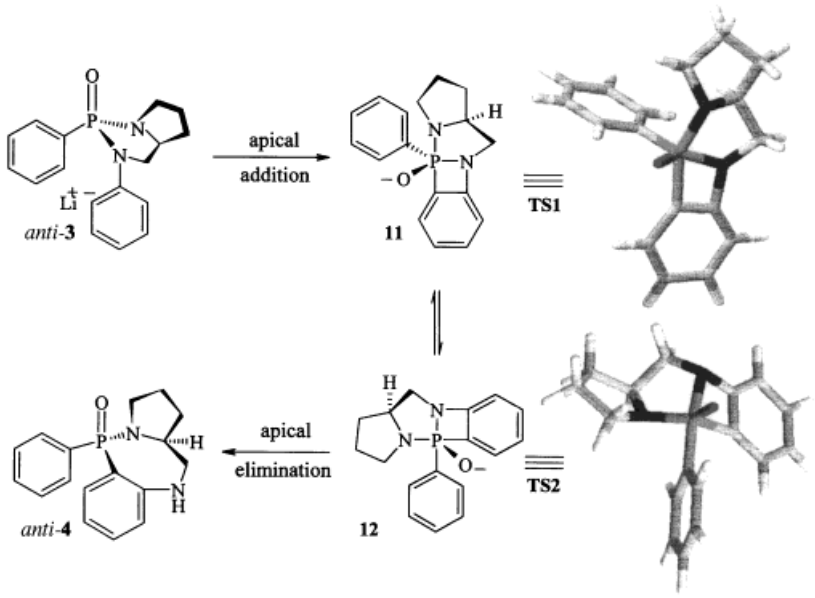

Scheme 3. The rearrangement mechanism of the stereospecific migration of P from N to C_{sp^2}.

be more favorable than either equatorial addition and apical elimination or apical addition and equatorial elimination.[18] Formation of a pentacoordinate intermediate with the entering nucleophile in an apical position of the trigonal bipyramid may occur by nucleophilic attack of the tetrahedral phosphorus center. Owing to the constrained diazaphospholidine ring, *ortho*-phenyl anion attack would lead to a TBP intermediate **11**, in which the four-membered azaphosphetane and the five-membered diazaphospholane rings adopt axial–equatorial positions[19–22] and the electron-donating oxygen anion ligand adopts an equatorial position.[23–25] Considering a low-energy Berry pseudorotation[26] (**11** $\rightleftharpoons$ **12**), the more apicophilic nitrogen atom of the azaphosphetane ring may adopt an apical position. At the same time, the exocyclic oxygen anion group tends to remain equatorial throughout the pseudorotation process by serving as a pivot.[27] Moreover, the inversion of configuration at the phosphorus atom is energetically unfavorable since it involves the epimerization of the phosphorus(v) atom in the TBP intermediates, implying improbable intermediates in which either the azaphosphetane or diazaphospholane rings are forced to adopt a diequatorial position with the oxygen anion group in an apical position.[28]

In conclusion, we have described the first totally stereospecific ring-expansion reaction of diazaphospholidine oxides by a 1,3-migration rearrangement. A mechanistic rationale involving an addition–pseudorotation–elimination pathway has been proposed in agreement with the experimental results.

Experimental Section

General procedure for the preparation of the new ring-expansion compounds: To a stirred solution of the corresponding precursor (1.0 mmol) in dry THF (15 mL) under argon atmosphere was slowly added at $-78\,^{\circ}C$ a solution of LDA (4 mmol (for *anti*-**10** and *syn*-**10**) or 8 mmol (for *anti*-**5**, *syn*-**5**, and *anti*-**6**), 2 M in THF). The mixture was allowed to warm to room temperature and stirred overnight. Then the reaction was quenched by addition of a saturated solution of NH_4Cl (20 mL). The product was extracted with ethyl acetate (3×10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography on a silica gel column.

anti-**5**: Purification by column chromatography (silica gel; ethyl acetate) afforded *anti*-**5** as a pale yellow solid (280 mg (89 %) from pure *anti*-**1**; 140 mg (81 % based on *anti*-**1**) from a 55/45 mixture of *anti*-**1** and *syn*-**1**). M.p. 202 °C; ^{1}H NMR (200 MHz): $\delta = 1.67-2.08$ (m, 4H), 3.01–3.05 (m, 1H), 3.48–3.69 (m, 4H), 3.40–4.20 (br s, 1H), 6.68 (d, $J = 8.8$ Hz, 1H), 6.71 (d, $J = 7.7$ Hz, 1H), 6.82 (td, $J = 7.5$, 2.5 Hz, 1H), 6.96 (dd, $J = 8.2$, 5.3 Hz, 1H), 7.17–7.31 (m, 3H), 7.38 (dd, $J = 8.3$, 7.3 Hz, 1H), 11.60 (s, 1H); ^{13}C NMR (50 MHz): $\delta = 24.6$ (d, $J = 6.8$ Hz), 32.1 (d, $J = 5.8$ Hz), 48.5 (d, $J = 2.3$ Hz), 51.8 (d, $J = 2.3$ Hz), 62.9 (d, $J = 2.5$ Hz), 112.1 (d, $J = 130.4$ Hz), 116.7 (d, $J = 128.2$ Hz), 118.0 (d, $J = 8.9$ Hz), 118.5 (d, $J = 10.1$ Hz), 118.7 (d, $J = 14.3$ Hz), 119.1 (d, $J = 12.0$ Hz), 132.3 (d, $J = 7.9$ Hz), 132.5, 133.9 (d, $J = 11.6$ Hz), 134.2, 149.9 (d, $J = 4.2$ Hz), 163.8 (d, $J = 5.5$ Hz); ^{31}P NMR (40.5 MHz) $\delta = 39.5$; elemental analysis calcd for $C_{17}H_{19}N_2O_2P$ (314.3): C 65.0, H 6.1, N 8.9, P 9.9; found: C 65.2, H 6.0, N 9.0, P 9.9.

syn-**5**: Purification by column chromatography (silica gel; ethyl acetate) afforded *syn*-**5** as a pale yellow solid (105 mg (73 % based on *syn*-**1**) from a 55/45 mixture of *anti*-**1** and *syn*-**1**). M.p. 196 °C; ^{1}H NMR (200 MHz): $\delta = 1.68-2.14$ (m, 4H), 2.94–3.35 (m, 3H), 3.40–3.75 (very br s, 1H), 3.50 (dd, $J = 12.0$, 4.0 Hz, 1H), 3.85–3.95 (m, 1H), 6.75–6.84 (m, 2H), 6.88 (dd, $J = 8.3$, 5.5 Hz, 1H), 6.96 (tdd, $J = 7.6$, 2.2, 1.0 Hz, 1H), 7.24–7.36 (m, 2H), 7.59 (ddd, $J = 14.2$, 7.7, 1.5 Hz, 1H), 7.75 (ddd, $J = 14.4$, 7.7, 1.6 Hz, 1H), 11.58 (s, 1H); ^{13}C NMR (50 MHz): $\delta = 25.3$ (d, $J = 8.7$ Hz), 30.6 (d, $J = 7.4$ Hz), 46.7 (d, $J = 2.9$ Hz), 54.0, 57.1 (d, $J = 4.3$ Hz), 114.0 (d, $J = 132.2$ Hz), 117.7 (d, $J = 9.0$ Hz), 118.9 (d, $J = 13.0$ Hz), 120.9 (d, $J = 9.9$ Hz), 121.5 (d, $J = 127.6$ Hz), 121.8 (d, $J = 13.0$ Hz), 133.0 (d, $J = 4.3$ Hz), 133.2, 134.1, 134.9 (d, $J = 10.1$ Hz), 149.4 (d, $J = 5.6$ Hz), 162.5 (d, $J = 5.6$ Hz); ^{31}P NMR (40.5 MHz): $\delta = 31.3$; elemental analysis calcd for $C_{17}H_{19}N_2O_2P$ (314.3): C 65.0, H 6.1, N 8.9, P 9.9; found: C 64.9, H 6.2, N 8.8, P 10.0.

anti-**6**: Purification by column chromatography (silica gel; ethyl acetate/methanol 80/20) afforded *anti*-**6** as a pale yellow solid (330 mg, 84 %). M.p. 208 °C; $[\alpha]_D^{20} = +168$ ($c = 0.44$, CH_2Cl_2); ^{1}H NMR (200 MHz): $\delta = 1.64-2.09$ (m, 4H), 3.03–3.17 (m, 1H), 3.50–3.75 (m, 4H), 4.55 (br s, 1H), 6.68–6.82 (m, 2H), 6.88 (td, $J = 7.6$, 2.9 Hz, 1H), 7.19–7.48 (m, 7H), 7.63–7.68 (m, 2H), 11.97 (s, 1H); ^{13}C NMR (50 MHz): $\delta = 24.7$ (d, $J = 6.7$ Hz), 32.0 (d, $J = 6.0$ Hz), 48.4 (d, $J = 2.2$ Hz), 52.1, 62.7 (d, $J = 2.5$ Hz), 112.7 (d, $J = 129.4$ Hz), 117.2 (d, $J = 126.9$ Hz), 118.6 (d, $J = 9.9$ Hz), 119.0 (d, $J = 13.2$ Hz, 2C), 127.1, 128.1 (s, 2C), 129.5 (s, 2C), 130.4 (d, $J = 9.9$ Hz), 131.7 (d, $J = 8.5$ Hz), 132.6, 134.1 (d, $J = 11.5$ Hz), 135.0, 137.9, 149.9 (d, $J = 4.4$ Hz), 160.8 (d, $J = 5.6$ Hz); ^{31}P NMR (40.5 MHz): $\delta = 39.7$; elemental analysis calcd for $C_{23}H_{23}N_2O_2P$ (390.42): C 70.8, H 5.9, N 7.2, P 7.9; found: C 70.7, H 5.9, N 7.3, P 8.0.

anti-**10**: Purification by column chromatography (silica gel; ethyl acetate/methanol 80/20) afforded *anti*-**10** as a pale yellow solid (270 mg, 90 %). M.p. 174 °C; $[\alpha]_D^{20} = +113$ ($c = 0.40$, CH_2Cl_2); ^{1}H NMR (200 MHz): $\delta = 1.67-2.04$ (m, 4H), 3.10 (dd, $J = 14.4$, 6.0 Hz, 1H), 3.22–3.33 (m, 2H), 3.36–3.52 (m, 2H), 4.37 (br s, 1H), 6.72 (dd, $J = 8.0$, 5.5 Hz, 1H), 6.88 (tdd, $J = 7.5$, 2.0, 1.0 Hz, 1H), 7.26 (tt, $J = 7.7$, 1.3 Hz, 1H), 7.38–7.45 (m, 3H), 7.60–7.68 (m, 2H), 7.72 (ddd, $J = 13.3$, 7.7, 1.5 Hz, 1H); ^{13}C NMR (50 MHz): $\delta = 24.9$ (d, $J = 8.6$ Hz), 30.6 (d, $J = 7.4$ Hz), 47.2, 51.3, 60.9 (d, $J = 3.8$ Hz), 115.9 (d, $J = 117.7$ Hz), 118.1 (d, $J = 9.3$ Hz), 118.4 (d, $J = 11.9$ Hz), 128.2 (d, $J = 12.9$ Hz, 2C), 131.0 (d, $J = 10.5$ Hz, 2C), 131.2, 132.0 (d, $J = 1.9$ Hz), 134.8 (d, $J = 7.4$ Hz), 134.8 (d, $J = 126.3$ Hz), 152.1 (d, $J = 5.8$ Hz); ^{31}P NMR (40.5 MHz): $\delta = 29.0$; elemental analysis calcd for $C_{17}H_{19}N_2OP$ 298.32: C 68.4, H 6.4, N 9.4, P 10.4; found: C 68.5, H 6.3, N 9.4, P 10.4.

syn-**10**: Purification by column chromatography (silica gel; ethyl acetate/methanol 80/20) afforded *syn*-**10** as a pale yellow solid (230 mg, 76 %). M.p. 186 °C; $[\alpha]_D^{20} = +20$ ($c = 0.40$, CH_2Cl_2); ^{1}H NMR (200 MHz): $\delta = 1.74-2.06$ (m, 4H), 2.93–3.10 (m, 2H), 3.29 (dd, $J = 13.2$, 5.7 Hz, 1H), 3.78 (dd,

$J = 13.2$, 3.5 Hz, 1H), 3.89 – 3.94 (m, 1H), 4.32 (br s, 1H), 6.73 (ddd, $J = 8.0$, 5.3, 0.8 Hz, 1H), 6.83 (tdd, $J = 7.7$, 2.2, 1.1 Hz, 1H), 7.22 (tt, $J = 7.7$, 1.4 Hz, 1H), 7.34 – 7.50 (m, 4H), 7.81 (ddd, $J = 12.2$, 7.7, 1.6 Hz, 2H); ^{13}C NMR (50 MHz): $\delta = 25.3$ (d, $J = 8.7$ Hz), 30.5 (d, $J = 7.5$ Hz), 48.2 (d, $J = 3.2$ Hz), 52.6, 58.8 (d, $J = 4.2$ Hz), 114.1 (d, $J = 174.0$ Hz), 119.1 (d, $J = 8.8$ Hz), 119.7 (d, $J = 13.0$ Hz), 119.8 (d, $J = 125.1$ Hz), 128.0 (d, $J = 12.9$ Hz, 2C), 132.3 (2C), 134.5 (d, $J = 10.1$ Hz), 151.8 (d, $J = 4.4$ Hz); ^{31}P NMR (40.5 MHz): $\delta = 26.0$; elemental analysis calcd for $C_{17}H_{19}N_2OP$ 298.32: C 68.4, H 6.4, N 9.4, P 10.4; found: C 68.4, H 6.5, N 9.3, P 10.4.

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[1] a) D. Lednicer, L. A. Mitscher, *The Organic Chemistry of Drug Design*, *Vol. 1 – 3*, Wiley-Interscience, New York, **1977**; b) D. Lednicer, *Strategies for Organic Drug Synthesis and Design*, Wiley-Interscience, New York, **1998**.

[2] W. Sneader, *Drug Discovery: The Evolution of Modern Medicines*, Wiley, Chichester, **1985**.

[3] Review: a) H. W. Gswend, H. Rodriguez, *Org. React. (N.Y.)* **1979**, *26*, 1; b) P. Beak, V. Snieckus, *Acc. Chem. Res.* **1982**, *15*, 306; c) N. S. Narasimhan, R. S. Mali, *Synthesis* **1983**, 957; d) N. S. Narasimham, R. S. Mali, *Top. Curr. Chem.* **1986**, *138*, 63; e) V. Snieckus, *Bull. Soc. Chim. Fr.* **1988**, 67; f) V. Snieckus, *Heterocycles* **1980**, *14*, 1649; g) V. Snieckus, *Chem. Rev.* **1990**, *90*, 879.

[4] a) D. Hellwinkel, M. Supp, *Chem. Ber.* **1985**, *118*, 66; b) D. Hellwinkel, M. Supp, *Chem. Ber.* **1976**, *109*, 3749; c) S. J. Shafer, W. D. Closson, *J. Org. Chem.* **1975**, *40*, 889.

[5] a) M. P. Sibi, V. Snieckus, *J. Org. Chem.* **1983**, *48*, 1937; b) M. Skowronska-Ptasinska, W. Verboom, D. N. Reinhoudt, *J. Org. Chem.* **1985**, *50*, 2690; c) R. J. Mills, R. F. Horwath, M. P. Sibi, V. Snieckus, *Tetrahedron Lett.* **1985**, 1145.

[6] a) J. A. Miller, *J. Org. Chem.* **1987**, *52*, 323; b) D. Hellwinkel, F. Lammerzahl, G. Hofmann, *Chem. Ber.* **1983**, 3375.

[7] a) L. S. Melvin, *Tetrahedron Lett.* **1981**, *22*, 3375; b) B. Dhawan, D. Redmore, *J. Org. Chem.* **1984**, *49*, 4018; c) B. Dhawan, D. Redmore, *J. Org. Chem.* **1986**, *51*, 179; d) B. Dhawan, D. Redmore, *J. Org. Chem.* **1991**, *56*, 833; e) B. Dhawan, D. Redmore, *Synth. Commun.* **1985**, *15*, 411; f) B. Dhawan, D. Redmore, *Synth. Commun.* **1987**, *17*, 465; g) B. Dhawan, D. Redmore, *J. Chem. Res.* **1988**, 222; h) T. Calogeropoulou, G. B. Hammond, D. F. Wiemer, *J. Org. Chem.* **1987**, *52*, 4185; i) S. Li, G. Wang, *Phosphorus Sulfur Silicon Relat. Elem.* **1991**, *61*, 119; j) J. Heinicke, I. Bohle, A. Tzachach, *J. Organomet. Chem.* **1986**, *317*, 11; k) J. Heinicke, R. Kadyrov, K. Kellner, E. Nietzschmann, A. Tzachach, *Phosphorus Sulfur Silicon Relat. Elem.* **1989**, *44*, 209; l) B. Dhawan, D. Redmore, *J. Org. Chem.* **1991**, *56*, 833.

[8] a) J. L. Speier, *J. Am. Chem. Soc.* **1952**, *74*, 1003; b) J. Heinicke, E. Nietzschmann, A. Tzachach, *J. Organomet. Chem.* **1983**, *232*, 1; c) I. Arai, K. H. Park, G. D. Daves, *J. Organomet. Chem.* **1976**, *121*, 25; d) G. Simchen, J. Pflestschinger, *Angew. Chem.* **1976**, *88*, 444; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 428.

[9] O. Legrand, J. M. Brunel, T. Constantieux, G. Buono, *Chem. Eur. J.* **1998**, *4*, 1061.

[10] a) J. M. Brunel, T. Constantieux, O. Legrand, G. Buono, *Tetrahedron Lett.* **1998**, *39*, 2961; b) O. Legrand, J. M. Brunel, G. Buono, *Tetrahedron Lett.* **1998**, *39*, 9419.

[11] H. G. Franck, J. W. Stadelhofer, *Industrial Aromatic Chemistry*, Springer, Berlin, **1987**.

[12] a) A. M. Jardine, S. M. Vather, T. A. Modro, *J. Org. Chem.* **1988**, *53*, 3983; b) D. Hellwinkel, G. Hofmann, F. Lammerzahl, *Tetrahedron Lett.* **1977**, *37*, 3241. In these cases, the migrations occur at the phenol *N*-methylaniline ring upon use of a large excess of LDA. It clearly appears that the N→C migrations occur only after the O→C migrations have been completed.

[13] The notations of the *syn* and *anti* diastereomers are according to the methylene substituent of the pyrrolidine ring with respect to the exocyclic aryl group. If they are at the same side of the five-membered phosphorus-containing ring, we call it a *syn* diastereomer; otherwise, it is an *anti* diastereomer. a) P. Cros, G. Buono, G. Peiffer, D. Denis, A. Mortreux, F. Petit, *New. J. Chem.* **1987**, *11*, 573; b) H. Arzoumanian, G. Buono, M'B. Choukrad, J. F. Petrignani, *Organometallics* **1988**, *7*, 59; c) J. M. Brunel, O. Chiodi, B. Faure, F. Fotiadu, G. Buono, *J. Organomet. Chem.* **1997**, *529*, 285.

[14] X-ray analysis of *anti*-**6**: A colorless plate single crystal of $C_{23}H_{22}N_2PO_2$, obtained by recrystallization in ethyl acetate, with approximate dimensions $0.4 \times 0.3 \times 0.2$ mm was mounted on a glass capillary. All the measurements were made on a Rigaku diffractometer with $Cu_{K\alpha}$ radiation. Cell constants and the orientation matrix for data collection were obtained from a least-square refinement using setting angles of 30 reflections in the range $1 < \theta < 25°$, which corresponded to an orthorhombic cell with dimensions $a = 8.181(1)$, $b = 8.308(1)$, $c = 15.183(1)$ Å; $Z = 2$, $M_r = 389.41$, $\rho_{calcd} = 1.25$ g cm^{-3}. A total of 2155 reflections were collected at $T = 298$ K. The standards were measured after every 655 reflections. Among the first 20 pairs of reflections, the signs of the corresponding calculated differences established that the molecule is described with the correct absolute configuration. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112627. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] a) R. S. Glass, *Conformational Analysis Medium-Sized Heterocycles*, VCH, Weinheim, **1988**, chap. 5, p. 181; b) W. Winter, *Chem. Ber.* **1976**, *109*, 2405; c) W. Winter, *Chem. Ber.* **1978**, *111*, 2942.

[16] a) S. Iriiuchijima, *Synthesis* **1978**, 684; b) U. Schmidt, R. Schölm, *Synthesis* **1978**, 752.

[17] Owing to the stability of some pentacoordinate square-pyramidal (SP) phosphorus species, it is also possible to consider mechanistic pathways proceeding via SP intermediates with the four-membered oxaphosphetane ring and the five-membered diazaphospholane ring in basal positions and the oxygen anion group in an axial position. The stereochemistry of the migration derives from a *cis* basal interaction of the entering/leaving group; see also G. R. J. Thatcher, R. Kluger, *Mechanism and Catalysis of Nucleophilic Substitution in Phosphate Esters* in *Advances in Physical Organic Chemistry*, *Vol. 25* (Ed.: D. Betheil), Academic Press, New York, **1989**, pp. 99 – 265.

[18] K. Mislow, *Acc. Chem. Res.* **1970**, *3*, 321.

[19] Such phosphetane intermediates have played an important role in the elucidation of factors that influence the stereochemistry of the Wittig reaction: a) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863; b) E. Vedejs, C. F. Marth, R. Ruggieri, *J. Am. Chem. Soc.* **1988**, *110*, 3940; c) B. E. Maryanoff, A. B. Reitz, *Phosphorus Sulfur Relat. Elem.* **1986**, *27*, 167; d) B. E. Maryanoff, A. B. Reitz, M. S. Mutter, R. R. Inners, H. R. Almond, Jr., R. R. Whittle, R. A. Olofson, *J. Am. Chem. Soc.* **1986**, *108*, 7664; e) A. B. Reitz, S. O. Nortey, A. D. Jordan, Jr., M. S. Mutter, B. E. Maryanoff, *J. Org. Chem.* **1986**, *51*, 3302.

[20] Isolable 1,2-oxaphosphetanes were synthesized, and X-ray crystallographic analysis was performed to determinate the structure of such compounds. a) T. Kawashima, K. Kato, R. Okazaki, *Angew. Chem.* **1993**, *105*, 941; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 869; b) T. Kawashima, K. Kato, R. Okazaki, *J. Am. Chem. Soc.* **1992**, *114*, 4008.

[21] E. Vedejs, T. J. Fleck, *J. Am. Chem. Soc.* **1989**, *111*, 5861.

[22] For oxaphosphetane pseudorotation, see E. Vedejs, C. F. Marth, *J. Am. Chem. Soc.* **1989**, *111*, 1519.

[23] R. R. Holmes, *Pentacoordinated Phosphorus*, *Vol. 2*, ACS Monograph 176, American Chemical Society, Washington, DC, **1980**.

[24] S. Mc Dowell, A. Streitwieser, *J. Am. Chem. Soc.* **1985**, *107*, 5849.

[25] S. J. Tripett, *Pure Appl. Chem.* **1974**, *40*, 585.

[26] R. S. Berry, *J. Chem. Phys.* **1960**, *32*, 933. In any case turnstile rotation must be taken into consideration as a mechanistic alternative: a) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquading, S. Pfohl, F. Ramirez, E. A. Tsolis, I. Ugi, *Angew. Chem.* **1971**, *83*, 691; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 687; b) F. Ramirez, *Bull. Soc. Chim. Fr.* **1970**, 3491.

  1433-7851/99/3810-1482 $ 17.50+.50/0

[27] AM1 calculations (AMPAC version 2.20) also clearly indicate the favored formation of intermediate TS2 (heat of formation 18.46 kcal) over TS1 (heat of formation 140.22 kcal).

[28] Previous investigations have been carried out on the sterochemical behavior of the four-membered oxyphosphoranes (1,2-oxaphosphetanes) having three P–C bonds: a) F. Ramirez, J. F. Pilot, O. P. Madan, C. P. Smith, *J. Am. Chem. Soc.* **1968**, *90*, 1275; b) F. Ramirez, C. P. Smith, J. F. Pilot, *J. Am. Chem. Soc.* **1968**, *90*, 6726; c) D. B. Denney, D. Z. Denney, C. D. Hall, K. L. Marsi, *J. Am. Chem. Soc.* **1972**, *94*, 245.

$[Ph_2P(NSiMe_3)]_2CLi_2$: A Dilithium Dianionic Methanide Salt with an Unusual Li_4C_2 Cluster Structure**

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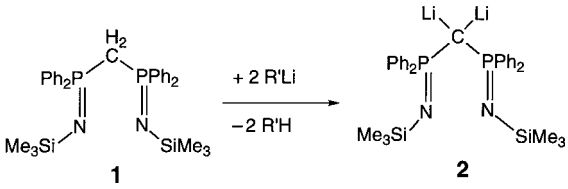
Bis(phosphane) ligands and their oxidized derivatives of the form $CH_2(R_2P{=}E)_2$ (E = O, S, NR′) have been widely used to form stable mono- and polymetallic complexes with both early and late transition metals.[1, 2] Generally the ligand retains its neutral character, and the methylene bridge between the two phosphorus atoms is preserved. However, these backbone protons are moderately acidic, and the ligand may be deprotonated by strong bases such as $LiN(SiMe_3)_2$, NaH, and alkyllithium reagents to generate monoanionic species. Many metal compounds have been derived from these monoanionic ligand precursors, and typically M–C bonds stabilized by additional coordination of the ligand are formed.[3–9] A few unexpected complexes have been reported in which double deprotonation of the P-CH_2-P backbone has been structurally established—namely, $[\{Pd(\mu\text{-}Cl)_2Pt[C(PPh_2)_2]\}_n]$,[10] $[Pt_2\{C(Ph_2P{=}S)_2\}(MeOcod)_2]$[11] (MeOcod = 8-methoxycyclooct-4-ene-1-yl), $[(AlR)\{C(Ph_2P{=}O)_2\}_2(AlR_2)_2]$ (R = Me,[12] Et[13]), and $[\{Al(C_4H_9)\}_2\{Ph_2P(=S)CP(Ph)_2(S)_2\}\{Al(C_4H_9)_2\}_2]$[14]—but to date there has been no rational synthesis of a species with the doubly deprotonated P-C-P methanide moiety. Herein we report the first synthesis and crystal structure of a complex containing such a ligand formed by the double deprotonation of $CH_2(Ph_2P{=}NR)_2$. This represents the first example of a structurally characterized Group 1 metal complex of the $CH_2(R_2P{=}E)_2$ (E = O, S, NR′) ligand systems. In addition the structure is an unusual, highly symmetric dimer cluster of lithium and carbon.

Reaction of $CH_2(Ph_2P{=}NSiMe_3)_2$ (**1**) with two moles of PhLi or MeLi in toluene leads smoothly to the dilithium complex **2** as colorless air- and moisture-sensitive crystals [Eq. (1)].[15]



(1)

The ^{31}P NMR spectrum of the final reaction mixtures showed quantitative conversion of **1** into one single phosphorus-containing product. Complex **2** was isolated in only moderate yield due to its high solubility, and it was fully characterized by elemental analysis and spectroscopic methods. The ^{31}P NMR spectrum of **2** consists of one sharp singlet, indicating that the two phosphorus nuclei are equivalent. The ^{31}P resonance is shifted downfield by 19.1 ppm compared to that of the starting compound **1**. The ^1H NMR spectrum showed the absence of the methylene resonance of the P-CH_2-P backbone, indicating that the ligand has been doubly deprotonated. No $^{13}C\{^1H\}$ NMR signal was observed for the quaternary P-C-P carbon atom despite trials with long acquisition periods, possibly because the signal is very broad due to coupling with the lithium nuclei. However, the lack of suitable protons proximate to the methine carbon atoms provides minimal $^1H \rightarrow {}^{13}C$ magnetization transfer, so it is perhaps not too surprising that this signal is not observed.

The molecular structure of **2**,[16] determined by X-ray diffraction, is unusual and interesting. Figure 1 shows an ORTEP[17] plot of the central cluster structure. The complex is a dimer, with four lithium atoms forming a square plane which is capped above and below by carbon atoms C(1) and C(2) of the two P-C-P frames. The bridging atoms C(1) and C(2) lie 1.67 Å above and below the Li_4 square plane to form a near perfect octahedron of atoms in the center of the cluster, which deviates only slightly from a regular octahedron because of the presence of the different axial atoms. The ligand N-P-C-P-N units are approximately planar, and there is only a small displacement (0.16 – 0.30 Å) of the Si atoms from the P-N-C planes. The N-P-C-P-N ligand planes are orthogonal to each other (the dihedral angle between the two planes is 88.12(11)°) and in turn

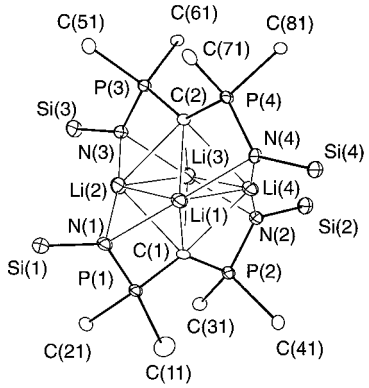


Figure 1. ORTEP[17] view of the central core of **2** showing the atom labeling scheme. All of the hydrogen atoms, the methyl carbon atoms on the silicon atoms, and all phenyl-ring carbon atoms (except the *ipso*-carbon atoms) have been removed for clarity. The atoms are represented by Gaussian ellipsoids at the 20% probability level. The thin lines serve to emphasize the geometrical relationship between the carbon and lithium atoms and are not to be considered normal bonds. Selected interatomic distances [Å] and angles [°]: P(1)–N(1) 1.619(4), P(1)–C(1) 1.695(5), P(2)–C(1) 1.681(5), C(1)–Li 2.33(1) – 2.42(1), C(2)–Li 2.312(9) – 2.45(1), N(1)–Li(2) 2.128(9), N(2)–Li(4) 2.108(9); P(1)-C(1)-P(2) 132.6(3), N(1)-P(1)-C(1) 104.4(2), N(2)-P(2)-C(1) 103.9(2).

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