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Synthetic Utility of Stable Phosphanylcarbenes: Synthesis and Crystal Structure of an α-(Lithiomethylene)phosphorane[**]

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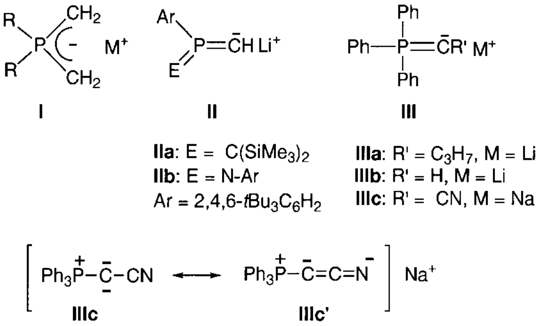
Antoine Baceiredo, and Guy Bertrand[*]

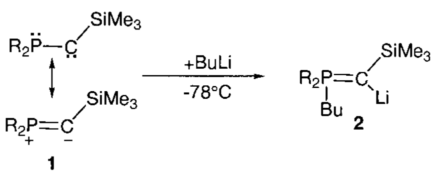
*Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday*

Alkali metal phosphonium diylides **I** are well-characterized compounds and their properties and molecular structures have been thoroughly investigated.[1] In contrast, the phosphonium yldiides **II** and **III**, which formally feature a dicarbanion center, have been poorly studied (Scheme 1). Niecke et al.[2] concluded that the stability of the lithium phosphoranylidene ylides **IIa, b** was due to the incorporation of the metalated carbon atom into the heteroallylic π-electron system. The first synthesis of an α-(lithiomethylene)phosphorane (**IIIa**) was proposed by Schlosser et al.[3] and was based on the reaction of pentaphenylphosphorane with excess n-butyllithium. Later, Corey et al.[4] showed that the phosphonium yldiide **IIIb** can be prepared at low temperature by direct lithiation of the corresponding ylide, and underwent Wittig reactions even with sterically hindered ketones. The (sodiocyanomethylene)phosphorane **IIIc**[5] is the only α-(metallomethylene)phosphorane, which has been isolated so far. However, from IR and NMR data, Bestmann et al.[5] showed that the resonance structure **IIIc′** strongly contributed to the electron distribution in **IIIc** and, therefore, this compound can hardly be considered as a phosphonium yldiide. The instability of derivatives **III** and the difficulties associated with the metalation of the starting phosphonium ylides hampered their promising synthetic application.[6] Here, we propose a new strategy for the one-step synthesis of α-(lithiomethylene)phosphoranes of type **III**, as well as the first single-crystal X-ray diffraction study of such a highly reactive compound.



Scheme 1.

We have already shown that the stable phosphanyl(silyl)carbene **1** undergoes formal 1,2-addition reactions with protic reagents (MeOH, Me_2NH, etc.)[7] as well as with Lewis acids ($MeOB(OMe)_2$, $MeGaMe_2$, etc.)[8] giving rise to the corresponding phosphorus ylides. Thus, we investigated the reaction of **1** with alkyllithium reagents, in the hope of obtaining the corresponding 1,2-adduct, namely the lithium phosphonium yldiide **2** (Scheme 2). Indeed, according to ^{31}P NMR spectroscopic results, addition of one equivalent of nBuLi (1.6 M in hexane) to a solution of carbene **1**[8b] in pentane at $-78\,^\circ C$ instantaneously and quantitatively led to the desired adduct **2**. On warming to room temperature and partial evaporation of the solvent, two equivalents of THF were added. From this solution single crystals, suitable for an X-ray diffraction study,[9] were obtained at $-20\,^\circ C$. The molecular structure of **2** is shown in Figure 1. In the solid state, **2** is monomeric and features a trigonal-planar coordinated lithium atom (sum of the angles: 359.9°), which is complexed by two molecules of THF. The geometry around the ylidic carbon atom is also planar (sum of the angles: 359.8°), whereas in nonstabilized ylides it is slightly pyramidalized.[10] The P–C bond length (1.636 Å) is one of the shortest known for a P–C(ylide) bond;[10a] the Si–C1 bond length is also very short (1.775 Å compared to 1.87–1.91 Å for Si–CH_3), which emphasizes the stabilizing effect of the negative charge by the silyl group.[11] Significantly, the C–Li bond almost eclipses the P–C(Bu) bond (Li-C1-P-C29 dihedral angle: 17.4(1.0)°). All structural data are in agreement with the results of ab initio calculations[12] which also predicted that the deprotonation of $H_3P{=}CH_2$ to give $H_3P{=}CHLi$ would induce a rotation about the P–C bond, causing the C–Li bond to eclipse one of the P–H bonds.



Scheme 2. $R = c\text{Hex}_2N$.

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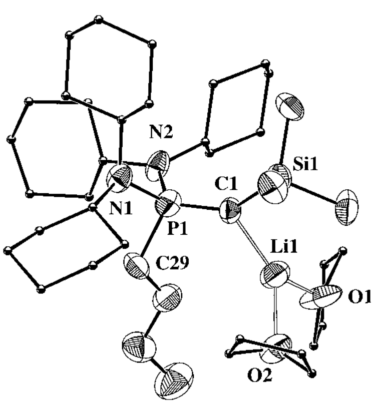
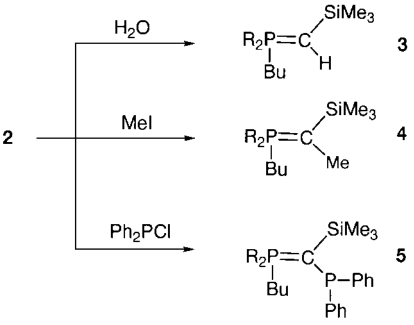


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: C1–P1 1.636(11), C1–Si1 1.775(10), C1–Li1 2.06(2), P1–N1 1.736(8), P1–N2 1.740(8), P1–C29 1.871(10); P1-C1-Si1 139.0(7), P1-C1-Li1 123.7(8), Si1-C1-Li1 97.1(8), C1-P1-N1 124.2(5), C1-P1-N2 115.7(5), N1-P1-N2 99.9(4), C1-P1-C29 112.6(5), N1-P1-C29 100.5(5), N2-P1-C29 100.4(5).

The ^{31}P NMR spectrum of compound **2** at room temperature showed one broad signal at $\delta = +41$ which, on cooling the sample to $-70\,^{\circ}$C, was resolved into two new signals at $\delta = +47$ and $+32$ (6/4 ratio; coalescence temperature of about $-30\,^{\circ}$C). This is in agreement with the presence of two rotamers of **2** at low temperature. The magnitude of the free energy of activation (35.4 kJ mol^{-1}) is of the order found for a restricted rotation about the P–C bond in phosphonium ylides.[11] Even at $-70\,^{\circ}$C, only one broad signal was observed at $\delta = +3.9$ in the ^{6}Li NMR spectrum recorded with a ^{6}Li-doped sample of **2**. However, selective ^{31}P irradiation experiments showed that the ^{6}Li signals corresponding to the two rotamers overlapped, and we estimate the $^{2}J_{\mathrm{P,Li}}$ coupling constants to be 1 Hz.

Compound **2** is highly moisture sensitive and is easily transformed into the corresponding phosphonium ylide **3**. It also reacts at low temperature with electrophiles such as methyl iodide and chlorodiphenylphosphane to give the corresponding ylides **4** and **5**, respectively (Scheme 3).



Scheme 3. R = cHex$_2$N.

Experimental Section

1: In a typical experiment, a solution of the corresponding phosphanyl(silyl)diazomethane[8b] (0.1 g, 0.2 mmol) in pentane (1 mL) was irradiated (300 nm) for 8 h. According to ^{31}P NMR spectroscopy the reaction was quantitative and phosphanyl(silyl)carbene **1** was used without any further purification.

3: Yellow oil (0.09 g, 94 % yield); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 63.5$; ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 5.3$ (d, ^{3}J(P,C) = 3.7 Hz, CH_3Si), 8.0 (d, ^{1}J(P,C) = 125.7 Hz, P=C), 14.6 (s, P$(CH_2)_3$*C*H_3), 25.2 (d, ^{3}J(P,C) = 18.5 Hz, P$(CH_2)_2$*C*H_2), 26.8 (s, NCCC*C*), 28.1 and 28.3 (s, NCC*C*), 31.0 (d, ^{1}J(P,C) = 87.2 Hz, P*C*H_2), 35.6 and 36.4 (s, NC*C*), 56.8 (d, ^{2}J(P,C) = 5.0 Hz, NC); elemental analysis (%) calcd for $C_{32}H_{63}N_2SiP$: C 71.85; H 11.87; N 5.24; found: C 72.25; H 12.07; N 5.04.

4: Yellow oil (0.09 g, 92 % yield); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 69.7$; ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 3.5$ (d, ^{3}J(P,C) = 2.6 Hz, CH_3Si), 9.2 (d, ^{1}J(P,C) = 127.6 Hz, P=C), 14.6 (s, P$(CH_2)_3$*C*H_3), 16.2 (d, ^{2}J(P,C) = 1.8 Hz, =C*C*H_3), 25.7 (d, ^{3}J(P,C) = 16.2 Hz, P$(CH_2)_2$*C*H_2), 27.1 (s, NCCC*C*), 27.7 (d, ^{2}J(P,C) = 4.1 Hz, PCH_2*C*H_2), 28.5 and 28.6 (s, NCC*C*), 33.1 (d, ^{1}J(P,C) = 84.1 Hz, PCH_2), 36.9 (d, ^{3}J(P,C) = 3.8 Hz, NC*C*), 37.3 (d, ^{3}J(P,C) = 1.0 Hz, NC*C*), 57.2 (d, ^{2}J(P,C) = 5.5 Hz, N*C*); elemental analysis (%) calcd for $C_{33}H_{65}N_2SiP$: C 72.20; H 11.93; N 5.10; found: C 71.95; H 11.65; N 5.24.

5: White crystals (0.12 g, 93 % yield); m.p. 185–186 °C; ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 88.6$ {d, ^{2}J(P,P) = 183.5 Hz, $(R_2N)_2P$}, 5.3 (d, Ph_2P); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 5.7$ (d, $^{3}J_{\mathrm{PC}} = 2.9$ Hz, CH_3Si), 12.0 (dd, ^{1}J(P,C) = 105.0 and 21.9 Hz, P=C), 15.8 (s, P$(CH_2)_3$*C*H_3), 26.6 and 26.8 (s, NCCC*C*), 27.5, 27.7, 27.8 and 28.1 (s, NCC*C*), 28.9 (d, ^{3}J(P,C) = 24.7 Hz, P$(CH_2)_2$*C*H_2), 35.6 (d, ^{3}J(P,C) = 6.2 Hz, NC*C*), 36.2 (d, ^{3}J(P,C) = 6.9 Hz, NC*C*), 36.7 and 37.2 (s, NC*C*), 38.0 (d, ^{1}J(P,C) = 93.1 Hz, P*C*H_2), 57.0 (d, ^{2}J(P,C) = 4.1 Hz, N*C*), 57.3 (d, ^{2}J(P,C) = 8.0 Hz, N*C*), 126.8 (s, C_p), 133.9 (d, ^{2}J(P,C) = 18.9 Hz, C_o), 137.8 (s, C_m), 145.9 (dd, ^{1}J(P,C) or ^{3}J(P,C) = 12.2 and 8.8 Hz, C_i); elemental analysis (%) calcd for $C_{44}H_{72}N_2SiP_2$: C 73.49; H 10.09; N 3.90; found: C 73.60; H 10.18; N 4.05.

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[9] Crystal data for **2**: $C_{40}H_{78}LiN_2O_2PSi$, $M_r = 685.04$, triclinic, space group $P\bar{1}$, $a = 10.789(2)$, $b = 13.336(3)$, $c = 15.667(3)$ Å, $\alpha = 88.88(2)$, $\beta = 89.79(2)$, $\gamma = 69.95(2)^{\circ}$, $V = 2117.2(7)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.075$ Mg m^{-3}, $F(000) = 760$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(\mathrm{Mo}_{\mathrm{K}\alpha}) = 0.126$ mm^{-1}. Data were collected on a STOE-IPDS diffractometer using an oil-coated, rapidly cooled crystal of dimensions ($0.3 \times 0.2 \times 0.05$ mm) by the φ-scan method ($4^{\circ} \leq 2\theta \leq 43^{\circ}$). Of a total of 17411 collected reflections, 4506 were independent ($R_{\mathrm{int}} = 0.2344$) and were used to refine 518 parameters by using 288 distance and ADP restraints, maximum and minimum of the final difference Fourrier synthesis: 257 and -334 e nm^{-3}, $R1(F > 2\sigma(F)) = 0.0704$ and $wR2 = 0.2353$ (all data) with $R1 = \Sigma||F_o - F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. The structure was solved by direct methods (SHELXS-97)[13] and refined by full-matrix least-squares procedures on F^2 (SHELXL-97).[14] The hydrogen atom positions were geometrically idealized and refined by using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this

paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103076. 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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Opposite Orientation of Backbone Inclination in Pyranosyl-RNA and Homo-DNA Correlates with Opposite Directionality of Duplex Properties**

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In preceding publications on pyranosyl-RNA ("p-RNA")[1a–f] we have emphasized the special importance of interstrand (as opposed to intrastrand) base stacking for the properties of this oligonucleotide base pairing system. Among the properties concerned are the sequence dependence of p-RNA duplex stability,[1a,e,f] the regioselectivity of the influence of dangling bases on duplex stability,[1d] and the sequence dependence of the efficiency and selectivity of template-controlled ligation reactions in replication[1f] and autocatalytic oligomerization.[1e] The dominance of interstrand over intrastrand base stacking in this pairing system is a consequence of the pronounced inclination between the (approximated) backbone axes relative to the axes of Watson–Crick base pairs in p-RNA duplexes. The orientation and approximate degree of this inclination can be easily inferred from a p-RNA strand's (idealized) pairing conformation (Figure 1 a, b). This conformation has been derived by conformational analysis on the basis of steric repulsion criteria[1a] and confirmed in a NMR structure determination of the p-RNA duplex $[pr(CGAATTCG)]_2$.[1c] In accordance with this analysis, molecular mechanics based modeling of the same duplex shows[1c] that interstrand base stacking is expected to be effective between purines and purines as well as between purines and pyrimidines, but not between pyrimidines and pyrimidines (Figure 1 c).

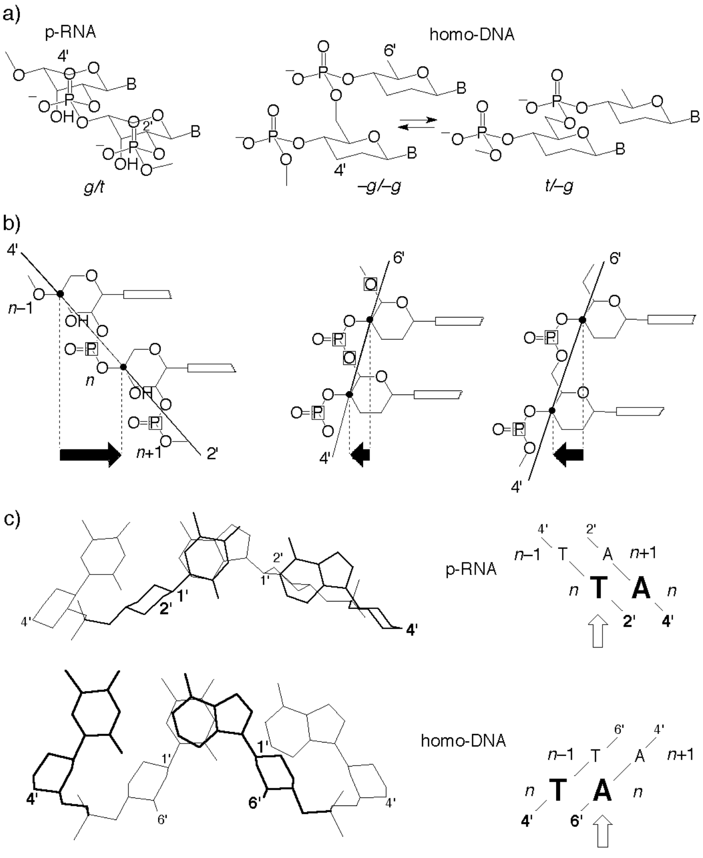

Figure 1. a) Idealized pairing conformations of p-RNA[1a,c] and homo-DNA.[2a,c,d] b) Projections of pairing conformations along an axis perpendicular to the mean planes of pyranose chairs, indicating sense and approximate degree of backbone inclination; nucleosidic torsion angle −120°. c) Projections perpendicular to the plane of a selected base pair of the p-RNA duplex $[pr(CGAATTCG)]_2$[1c] and the homo-DNA duplex $[ddGlc(A_5T_5)]_2$[2d] showing upstream interstrand stacking between a pyrimidine and a purine in p-RNA and corresponding downstream interstrand stacking in homo-DNA (taken from references [1c] and [2d]).

The previously studied homo-DNA[2] is another pairing system with a pronounced backbone inclination. Compared to p-RNA, however, the inclination in homo-DNA is of opposite orientation, as can be deduced from homo-DNA's two (idealized) pairing conformations[2a,c] (Figure 1 a, b). The NMR structure analysis of the homo-DNA duplex $[ddGlc(A_5T_5)]_2$ by Otting et al.[2d] indicates that in at least one of the two pairing conformations, namely $t/-g$, interstrand base stacking should dominate over intrastrand stacking to the same extent as it does in p-RNA (Figure 1c). Whereas in p-RNA interstrand stacking acts in the upstream direction (base n stacks with base $n+1$ of the complementary strand), in homo-DNA it does so in the downstream direction

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