Nucleophilic Additions to a Diphosphirenium Salt: Ring Opening and Ring Expansion Reactions

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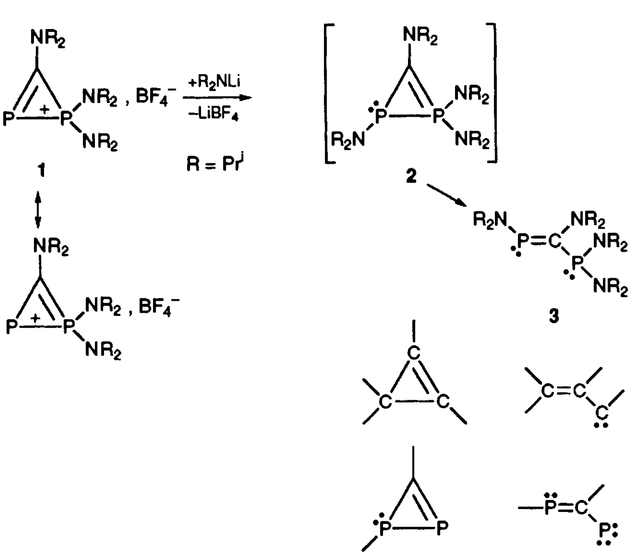
P-Bis(diisopropylamino)-*C*-diisopropylamino diphosphirenium tetrafluoroborate **1** reacts with lithium diisopropylamide and *tert*-butyl isocyanide affording phosphaalkene **3** and the original four-membered heterocycle **5**; **5** is characterized by X-ray diffraction and its chemical reactivity.

It is well known that cyclopropenylium salts are among the most stable carbocations.[1] Recently, we have reported the synthesis of a related diphosphirenium salt **1**.[2] In contrast with cyclopropenylium salts, the stability of **1** cannot be rationalized in terms of 'Hückel aromaticity' owing to the presence of d-orbitals at phosphorus. This dramatic difference induces a very different reactivity concerning nucleophilic addition reactions to **1**.

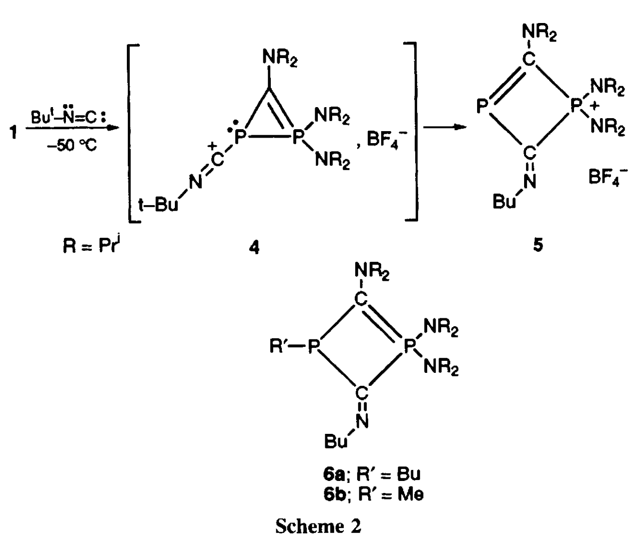
First we have investigated the reaction of a lithium salt with **1**. When a THF solution of the diphosphirenium salt **1**[2] was treated with a stoichiometric amount of LDA at −78 °C, phosphaalkene **3**[3] was isolated in 85% yield. The formation of **3** can be explained by the nucleophilic attack of the lithium salt at the dicoordinated phosphorus atom of **1**, leading to a transient $\lambda^3\sigma^3$, $\lambda^5\sigma^4$-diphosphirene **2**. In contrast with cyclopropenes[4] and $\lambda^3\sigma^3$, $\lambda^3\sigma^2$-diphosphirenes **A**,[5] which are thermodynamnically much more stable than the isomeric vinyl carbenes and phosphaalkenephosphinidenes **B**, respectively, the cyclic 4π-electron ylide **2** is less stable than the opened form **3** (Scheme 1).

Carbenium ions undergo a nucleophilic attack by the carbon atom of isocyanides giving nitrilium intermediates.[6] **1** reacts with *tert*-butyl isocyanide in dichloromethane at −50 °C to give **5**, which was isolated as yellow crystals (70% mp 191–192 °C). The ^{31}P NMR spectrum showed a doublet of quintets at 78.2 (J_{PP} 20.8 Hz, J_{PH} 14.8 Hz), and a doublet at 183.7 (J_{PP} 20.8 Hz), arguing for a $-P{=}C{-}P(NR_2)_2$ sequence. The cyclic structure was obvious from the ^{13}C NMR spectrum, which features two doublets of doublets for the ring carbons at 173.5 (J_{PC} 92.9 and 69.5 Hz) and 193.7 (J_{PC} 66.8 and 40.7 Hz). Definite proof for the structure of **5** has been obtained by an X-ray diffraction study (Fig. 1).† As expected the ring is planar with the two nitrogen bounded to the ring-carbon atoms in the same plane. Although the P(2)–C(1) bond distance [1.743(4) Å] is rather long for a phosphorus–carbon double bond, it is comparable to the values observed for C-amino substituted phosphaalkenes.[7] Since the values of the P(2)–C(2) [1.828(4) Å] and the C(2)–N(4) bond lengths [1.259(5) Å] are usual for P–C single bond and imine, respectively, and the geometric parameters around P(1) are typical of a phosphonium salt, it is clear that almost no delocalization of the positive charge occurs.

From a mechanistic point of view, it is quite reasonable to postulate the transient formation of nitrilium salt **4**, followed by a ring expansion reaction; the transfer of the positive



Scheme 1



Scheme 2

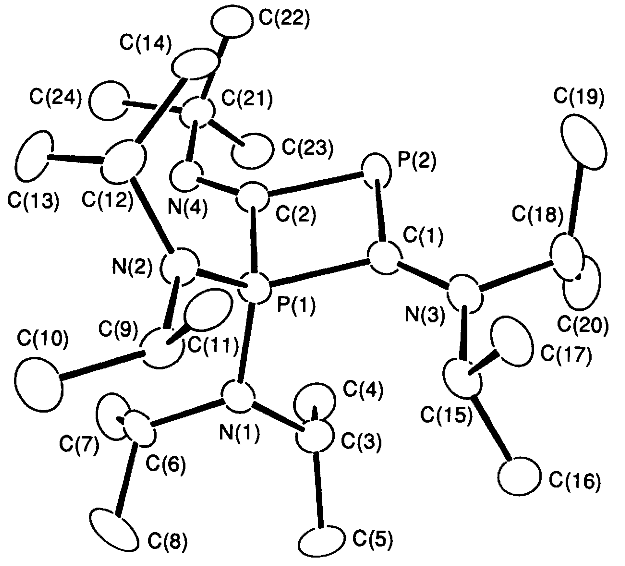


Fig. 1 ORTEP diagram of **5**, showing 35% probability ellipsoids. Some metric data include: P(1)–C(1) 1.830(4); P(1)–C(2) 1.813(3); P(1)–N(1) 1.637(3); P(1)–N(2) 1.619(3); P(2)–C(1) 1.743(4); P(2)–C(2) 1.828(4); C(1)–N(3) 1.319(5); C(2)–N(4) 1.259(5) Å; N(1)–P(1)–N(2) 109.4(1); N(1)–P(1)–C(1) 110.7(2); N(1)–P(1)–C(2) 116.6(1); N(2)–P(1)–C(1) 121.4(2); C(1)–P(1)–C(2) 82.8(2); C(1)–P(2)–C(2) 84.9(2); P(1)–C(1)–P(2) 97.3(2); P(1)–C(2)–P(2) 95.0(2)°.

charge from carbon to phosphorus being the driving force (Scheme 2).

The derivative **5** (one of the very rare four-membered heterocycles featuring a $\lambda^3\sigma^2$-phosphorus-carbon double bond[8]) smoothly reacts with nucleophiles such as butyl- or methyl-lithium leading to a new family of phosphorus heterocycles **6** in nearly quantitative yields.

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Footnote

Crystal data for **5**: $C_{24}H_{51}N_4P_2{\cdot}BF_4$, M = 544.4, monoclinic, space group $P2_1/c$, a = 14.771(2), b = 9.8345(9), c = 21.769(2) Å, β = 95.68(1)°, V = 3146.8(5) Å^3, Z = 4, D_c = 1.149 g cm^{-3}, μ = 1.8 cm^{-1}. Measurements: CAD4, radiation: Mo-Kα (λ = 0.71073 Å); solution: SHELX programs. 5132 collected data, 4930 unique reflections, 3061 observed [$F_o{}^2 > 3\sigma(F_o{}^2)$], number of variables: 343 (3 F atoms disordered, all non-H atoms anisotropic). R = 0.046, R_w = 0.046. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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