P-Substituted Carbenes

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Cyclic Carbodiphosphorane–Diphosphinocarbene Thermal Interconversion**

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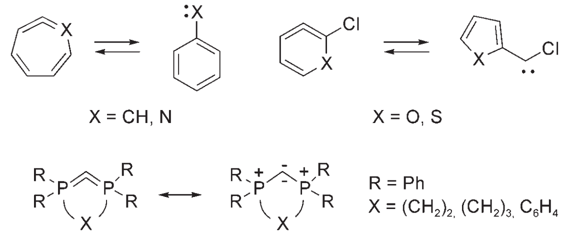
Ring constraints that are caused by bending and twisting of the normally linear allene group engender substantial strain and resultant kinetic reactivity.[1] The small cyclic cumulenes are extremely short-lived intermediates, and their unique electronic properties and reactivities are of particular interest.[1–3] These highly strained cyclic allenes lie close in energy to corresponding aryl carbenes[4] or aryl nitrenes,[5] for which photochemical or thermal interconversions have been well-studied experimentally and computationally (Scheme 1).[4–7]



Scheme 1.

Cyclic carbodiphosphoranes can also be considered as heterocyclic allenes, but their ring strain should be much smaller owing to the polarized ylidic P–C double bonds.[8] Whereas the reduced ring size destabilizes these compounds, the critical ring size for stability seems to be five atoms.[9] Recently, we synthesized five-membered carbodiphosphorane **1a**, which exhibits unusual stability.[10] Herein, we report the unprecedented thermal ring contraction of the five-membered cyclic carbodiphosphorane **1a** into a four-π-electron four-membered 1,2λ^5-azaphosphete **2a** (Figure 1).[11] This rearrangement possibly takes place by an

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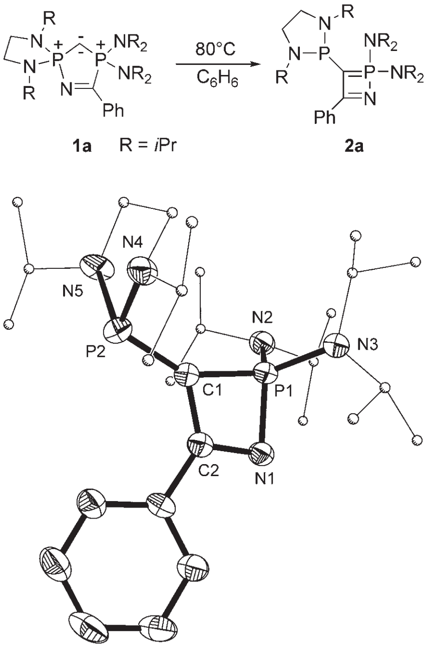


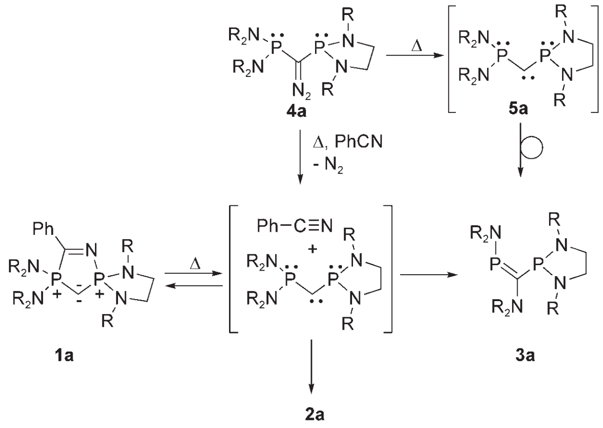
Figure 1. Ring contraction of **1a** and molecular structure of **2a**. Carbon atoms of substituents on the amino groups are simplified in the structure for clarity. Selected bond lengths [Å]: C1-C2 1.428(3), C2-N1 1.384(3), N1-P1 1.661(2), C1-P1 1.789(3). The mean deviation from the best C1-C2-N1-P1 plane is 0.005 Å.

interconversion between cyclic carbodiphosphorane **1a** and acyclic diphosphinocarbene **5a**.

The cyclic carbodiphosphorane **1a** transforms almost quantitatively and regioselectively to 1,2λ^5-azaphosphete **2a** when a solution of **1a** in benzene is heated at 80°C for 60 hours. The ^{31}P and ^{13}C NMR spectroscopic data of **2a** are very similar to those of previously reported azaphosphetes.[11] This result is surprising because the thermal ring contraction of relatively small rings is quite rare.[12,13] It is important to note that the imine nitrogen atom in **2a** is now bonded to the bis(diisopropylamino)phosphino fragment, thus indicating that the ring contraction does not proceed by a simple P→C 1,2-migration of the imine carbon atom. The position of the nitrogen atom was spectroscopically confirmed by the chemical shift in the ^{31}P NMR spectrum ($\delta = 57.1$ ppm) and the large P,H coupling constant ($^3J_{PH} = 15$ Hz) typical for a tetravalent phosphorus atom.[14] The structure of **2a** was undoubtedly confirmed by a single-crystal X-ray diffraction analysis (Figure 1).[15]

In the course of careful analysis, we also observed a small amount (ca. 1%) of *C*-phosphino phosphaalkene **3a** (^{31}P NMR: $\delta = 206.3$ and 105.3 ppm, $^2J_{PP} = 265$ Hz), which suggests the transient formation of diphosphinocarbene **5a** during the [3+2] retrocycloaddition (Scheme 2).[16]

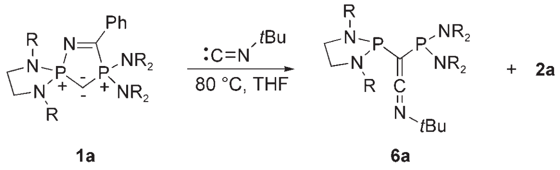
To prove our hypothesis, diphosphinocarbene **5a** was generated from the corresponding diphosphinodiazomethane **4a** by thermolysis in toluene solution at 80°C. As expected, in the absence of any trapping agent, phosphaalkene **3a** was isolated in nearly quantitative yield. In contrast, when the reaction was performed in the presence of benzonitrile (one equivalent), a mixture of **3a** (75%), four-membered



Scheme 2. Thermal interconversion between carbodiphosphorane **1a** and diphosphinocarbene **5a**.

heterocycle **2a** (20%), and carbodiphosphorane **1a** (5%) was obtained. As observed in the transformation of **1a**, only one regioisomer was detected for **2a**.[17] These observations are in agreement with the formation of carbene **5a** during the thermolysis of carbodiphosphorane **1a**, and their interconversion.

To confirm the transient formation of diphosphinocarbene **5a**, the thermal decomposition of **1a** was performed in the presence of one equivalent of *tert*-butyl isocyanide , which is known to react with phosphinocarbenes.[18] In this case, the reaction gave a mixture of the expected keteneimine **6a** (5%) and four-membered ring **2a** (95%; Scheme 3). In the presence of an excess of *tert*-butyl isocyanide, the reaction was not clean.



Scheme 3. Trapping reaction of diphosphinocarbene **5a** with *tert*-butyl isocyanide.

Density functional theory (DFT) calculations[19] were carried out to gain insight into the nature of the conversion of compound **1a** into **2a** (Scheme 1). Model compound **1b** (R = Me) was chosen to explore computationally its transformation into **2b**. The geometric and electronic properties of **1b** were calculated first. Our results indicate that **1b** exhibits the electronic properties that would be expected for an sp^2-hybridized singlet carbene possessing two additional electrons, as shown in Figure 2. In this figure it is shown that the usual frontier molecular orbitals of a singlet carbene become the HOMO−1 and HOMO in **1b**. Thus, the main atomic contributions to the HOMO−1 and HOMO in **1b** are similar to those of the carbon atom in the a$_1$-symmetric HOMO and b$_2$-symmetric LUMO of the sp^2-hybridized singlet methylene group, respectively. Moreover, the electrostatic potential that is projected onto the electron density of **1b** reveals a strong

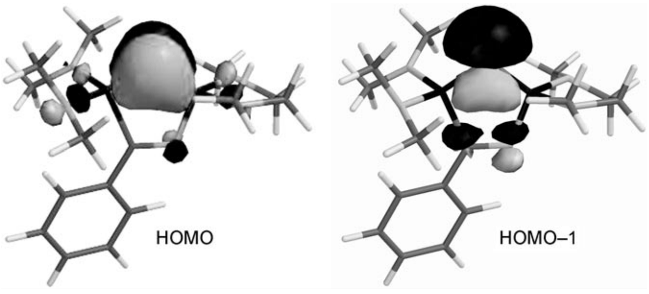


Figure 2. HOMO and HOMO−1 of **1b**.

negative potential around the central carbon atom of carbodiphosphorane **1**.

The reaction path that was found on the B3LYP/6-31 + G* potential-energy surface associated with the conversion of **1b** into **2b** is displayed in Figure 3. We have located the saddle point **TS1**, which is associated with a thermal [3+2] retrocycloaddition. This [3+2] retrocycloaddition step leads to one equivalent of benzonitrile and to carbene **5b** (R = Me). It is interesting to note that carbene **5b** and benzonitrile lie about 15 kcal mol^{-1} above **1b**, a result compatible with the observation of the formation of a small amount of **1a** when **5a** is allowed to react with one equivalent of PhCN (see above).

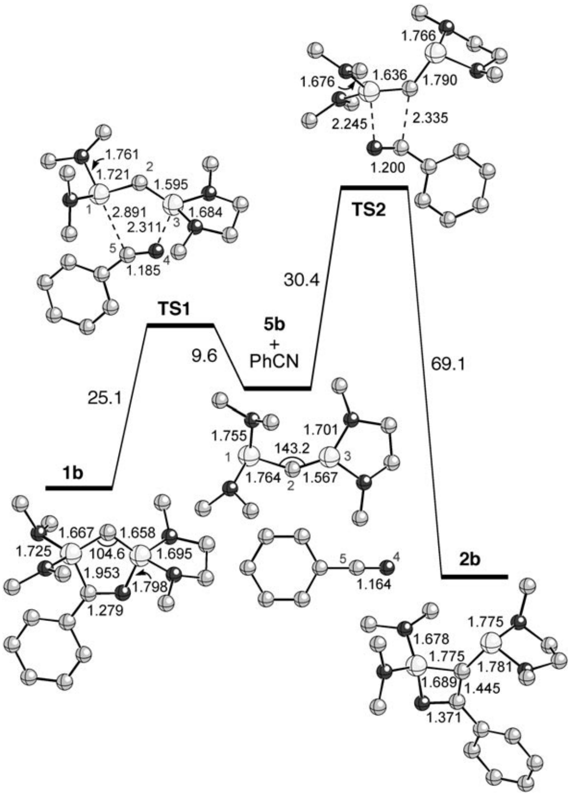


Figure 3. Chief geometric features of fully optimized (B3LYP/6-31 + G* level) structures involved in the conversion of **1b** into **2b**. Bond lengths and angles are given in Å and degrees, respectively. C gray, N black, P white. Hydrogen atoms have been omitted for clarity. Relative energies (B3LYP/6-31 + G* + ΔZPVE level) are given in kcal mol^{-1}.

Carbene **5b** can react in a formally [2+2] fashion via saddle point **TS2** to yield **2b**.[20] In this transition state, reactants interact in a suprafacial manner with a quite synchronous development of the C2–C5 and N4–P1 bonds. Natural bond orbital (NBO)[9] analysis of **TS2** reveals, however, a pseudopericyclic character for **TS2**, in which lone pairs, π bonds, and σ bonds interchange roles.[21]

In summary, our calculations are compatible with a retro-[3+2]/pseudo-[2+2] sequence in which carbenes of type **5** are involved, the whole process being exothermic by about 13 kcal mol^{-1}. As expected, the barrier in energy of the retro-[3+2] transformation is relatively small and even smaller than that of the subsequent cycloaddition. These theoretical results support our first hypothesis that the effect of high ring strain in **1** can be the driving force for this transformation to give a transient carbene **5**. Interestingly, the close energies between **1** and **5** and the small barrier also strongly support the unprecedented interconversion between two different types of divalent carbon species (dianionic and carbene): carbodiphosphorane **1a** and diphosphinocarbene **5a.** Further studies of the nature of this interconversion as well as the application of this new process for the preparation of original carbenes are in progress.

Experimental Section

Details of the experimental procedures are provided in the Supporting Information.

2a: White crystals. M.p. 71–73 °C; ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): $\delta = 57.1$, 76.3 ppm (AX system, $J_{PP} = 11.2$ Hz); ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 22.2$ (d, $J_{CP} = 8.4$ Hz, CH_3), 22.7 (s, CH_3), 23.1 (d, $J_{CP} = 12.2$ Hz, CH_3), 23.6 (d, $J_{CP} = 2.4$ Hz, CH_3), 43.3 (d, $J_{CP} = 5.5$ Hz, NCH), 48.7 (d, $J_{CP} = 5.7$ Hz, NCH_2), 50.9 (d, $J_{CP} = 29.8$ Hz, NCH), 95.9 (dd, $J_{CP} = 40.0$ and 31.0 Hz, PCP), 127.6 (s, CH_{arom}), 130.0 (dd, $J_{PC} = 3.3$ and less than 1 Hz, CH_{arom}), 131.7 (dd, $J_{PC} = 3.3$ and less than 1 Hz, CH_{arom}), 137.8 (dd, $J_{CP} = 3.0$ and 49.8 Hz, C_{ipso}), 190.6 ppm (dd, $J_{CP} = 24.8$ and 33.2 Hz, C=N).

3a: Orange oil. ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): $\delta = 105.4$, 206.4 ppm (AX system, $J_{PP} = 264$ Hz); ^{13}C NMR (C_6D_6, 25 °C, 75 MHz): $\delta = 21.5$ (d, $J_{CP} = 6.8$ Hz, CH_3), 21.9 (d, $J_{CP} = 10.5$ Hz, CH_3), 24.1 (dd, $J_{CP} < 1$ Hz, CH_3), 24.1 (d, $J_{CP} = 7.6$ Hz, CH_3), 45.3 (dd, $J_{CP} = 3.2$ and 6.77 Hz, NCH_2), 46.7 (d, $J_{CP} = 5.1$ Hz, NCH), 50.0 (m, NCH), 168.1 ppm (d, $J_{CP} = 65.6$ and 82.6 Hz, PCP).

4a: Red oil. IR (THF): 2007 cm^{-1}; ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): $\delta = 53.2$, 106.2 ppm (AX system, $J_{PP} = 189$ Hz); ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 22.3$ (dd, $J_{CP} = 8.6$ and less than 1 Hz, CH_3), 22.6 (dd, $J_{CP} = 8.6$ and 2.7 Hz, CH_3), 23.9 (d, $J_{CP} = 6.6$ Hz, CH_3), 24.6 (dd, $J_{CP} = 7.8$ and 2.64 Hz, CH_3), 46.4 (d, $J_{CP} = 7.9$ Hz, NCH_2), 47.7 (d, $J_{CP} = 12.2$ Hz, NCH), 48.6 ppm (d, $J_{CP} = 21.0$ Hz, NCH), signal for PCP was not observed.

6a: Orange oil. ^{31}P {1H} NMR (C_6D_6, 121 MHz): $\delta = 52.8$, 106.1 ppm (AX system, $J_{PP} = 249$ Hz); ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 22.5$ (d, $J_{CP} = 11$ Hz, CH_3), 23.0 (dd, $J_{CP} = 2.8$ and 8.8 Hz, CH_3), 23.8 (d, $J_{CP} = 6.5$ Hz, CH_3), 24.8 (dd, $J_{CP} = 2.2$ and 7.6 Hz, CH_3), 30.5 (s, *t*Bu), 47.5 (s, CH), 47.6 (s, CH_2), 47.7 (s, CH), 50.1 (dd, $J_{CP} = 1.5$ and 22.2 Hz, CH), 56.8 (t, $J_{CP} = 1.9$ Hz, CH_3*C*), 60.4 (dd, $J_{CP} = 42.9$ and 70.1 Hz, PCP), 171.4 ppm (s, *t*BuNC).

Density functional theory (DFT)[22] calculations: All studies were performed at the B3LYP[23] level of theory as implemented in the Gaussian package[24] by using the 6-31 + G(d,f) basis set[25] to describe properly the significant negative charges present along the possible reaction coordinates. All stationary points were subjected to harmonic analysis. Transition structures showed only one imaginary frequency associated with nuclear motion along the reaction coordinate under study as verified by intrinsic reaction coordinate (IRC) computations. Total energies were computed, including zero-point vibrational energy (ZPVE) terms.[26] Bond orders and charges were computed by mean of the NBO method.[27]

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[19] See the Supporting Information for additional details.

[20] We have found a regioisomeric saddle point **TS2′** that lies 0.6 kcal mol^{-1} above **TS2** in the gas phase and in benzene solution (see the Supporting Information). This difference in energy corresponds to a kinetic formation of 71 % of **2b** with respect to its regioisomeric four-membered cycloadduct, which in turn lies 3.9 kcal mol^{-1} above **2b** in the gas phase. It is expected that when R = *i*Pr the regioselectivity will be higher.

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