

N-Heterocyclic Carbenes as Promoters for the Rearrangement of Phosphaketenes to Phosphaheteroallenes: A Case Study for OCP to OPC Constitutional Isomerism

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Abstract: The concept of isomerism is essential to chemistry and allows defining molecules with an identical composition but different connectivity (bonds) between their atoms (constitutional isomers) and/or a different arrangement in space (stereoisomers). The reaction of phosphanyl ketenes, (NHP)–P=C=O (NHP = N-heterocyclic phosphonium) with N-heterocyclic carbenes (NHCs) leads to phosphaheteroallenes (NHP)–O–P=C=NHC in which the PCO unit has been isomerized to OPC. Based on the isolation of several intermediates and DFT calculations, a mechanism for this fundamental isomerisation process is proposed.

Constitutional isomerism has been detected almost 200 years ago by Liebig and Wöhler who debated on the composition and chemical reactivity of silver fulminate, Ag(C≡N–O), and silver cyanate, Ag(N=C=O).^[1] This truly ground-breaking discovery changed the dogma that only compounds of different chemical composition can show different chemical reactivity. The interconversion of both isomers in their protonated forms, on one hand either as H–N=C=O (isocyanic acid) or cyanic acid (N≡C–OH) and on the other hand as isofulminic acid (H–O–N=C:) or fulminic acid (O=N–C–H) has been studied computationally.^[2] These investigations show that fulminic acid is thermodynamically less stable by 80 kcal mol^{–1} than cyanic acid. Nevertheless, the conversion of fulminic acid to cyanic acid is hampered by intermediates and activated complexes at high energies

making fulminic acid derivatives kinetically stable. In contrast to the isomerization of nitrile oxides to isocyanates (R–C≡N→O → R–N=C=O),^[3] the interconversion R–O–C≡N⇌R–O–N=C: has never been observed experimentally. For the phosphorus analogues, namely phosphacyanate (O–C≡P)[–] and phosphafulminate (O–P=C:)[–], similar energy differences as for the nitrogen analogues were calculated.^[4] With respect to H–P=C=O, the isomer H–O–P=C: is again about 80 kcal mol^{–1} less stable, and on the calculated minimum energy reaction path (MERP) for the isomerisation, energetically high-lying transition states have to be overcome.^[4c]

Natural population analyses (NPA) and natural resonance theory (NRT)^[5] were used to compare the anions OCP[–] and OPC[–] (for details see Figure S51 in the Supporting Information). For OPC[–], the calculated Wiberg bond index (WBI) for the CP bond (2.828) and PO bond (1.135) in combination with the bond distances (CP: 1.610 Å; PO: 1.541 Å), NPA charges (O: –1.03 e, P: +1.10 e, C: –1.07 e), and molecular electrostatic potential (MEP) indicate C≡P triple bond and P–O single bond character and a charge alternation O[–], P⁺, C[–]. The electronic ground state of the OPC[–] anion is best described by one main resonance structure with a positively charged phosphorus center to which other resonance forms contribute with rather little weight (< 10 %). This is in marked contrast to its OCP[–] isomer, which is best described by two resonance forms of almost equal importance and negatively charged phosphorus and oxygen centers.^[6]

Sodium phosphoethynolate Na(OCP) (**1**) is remarkably stable^[7,8] but so far HO–C≡P has neither been prepared nor observed. However, the phosphanyl phosphaketenone [(HC)₂(NR)₂P]–P=C=O (**3b**; see Scheme 1) is easily accessible and stable (R = Dipp = 2,6-diisopropylphenyl).^[9] This compound contains a long P–P bond (2.441 Å) and is best described as a very intimate ion pair between a cyclic 1,2,3-diazaphospholenium cation [(HC)₂(NR)₂P]⁺ (NHP⁺) with a delocalized 6π-electron ring skeleton and the OCP[–] anion. The (NHP⁺) cation may be viewed as a sterically protecting group which, like a proton, is tightly bound but mobile and allows rearrangements to occur.^[9] In an assumed (NHP)–O–P=C: isomer the carbene-like divalent terminal carbon center may be too reactive to allow isolation. As a suitable stabilizing agent, a stable N-heterocyclic carbene (NHC) like **IPr**, **IMes** or **IPr^H** (see Scheme 2) deemed especially suited. Indeed, NHCs have been proven to allow for the isolation of highly reactive main group fragments.^[10] A calculation of the stabilizing energy given by the hypothetical reaction

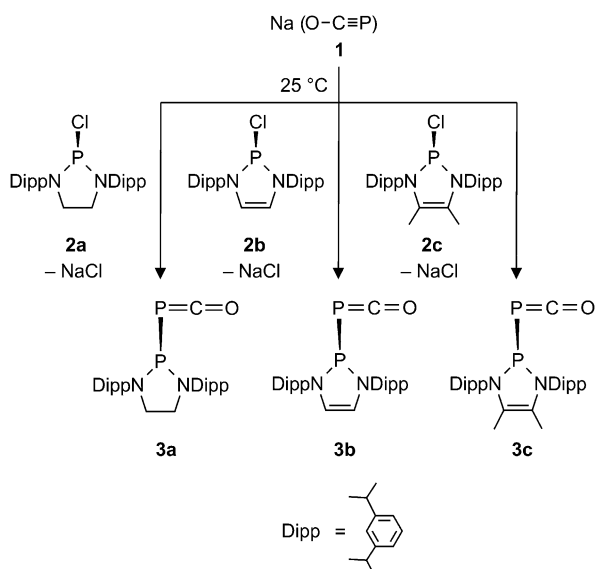
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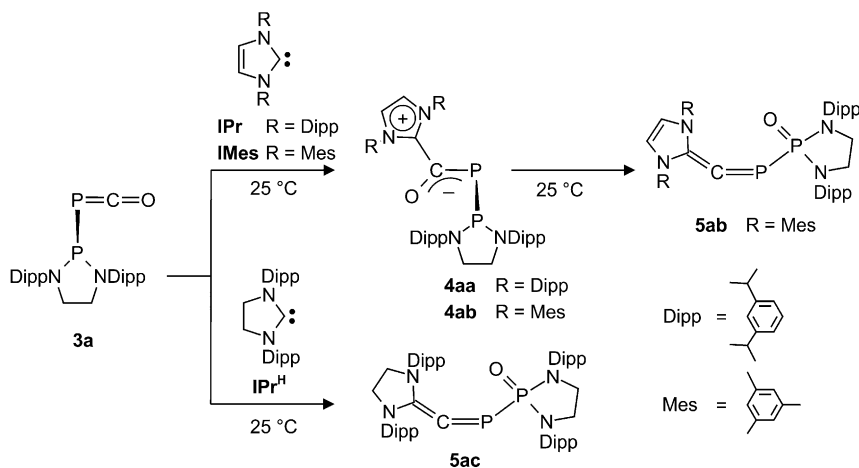
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Scheme 1. Synthesis of phosphanyl phosphaketenes **3a–3c**.



Scheme 2. Reactions between **3a** and unsaturated NHCs (**IPr**, **IMes**) and saturated **IPr^H**.

$\text{H}-\text{O}-\text{P}=\text{C}+\text{NHC} \rightarrow \text{H}-\text{O}-\text{P}=\text{C}=\text{NHC}$ amounts to $\Delta E = -106.1 \text{ kcal mol}^{-1}$ which should be more than sufficient to overcome the intrinsic instability of $\text{R}-\text{O}-\text{P}=\text{C}$ derivatives. Here we report that $\text{R}-\text{P}=\text{C}=\text{O}$ can indeed be isomerized to $\text{R}-\text{O}-\text{P}=\text{C}$ with the help of an NHC.

The reaction of $\text{Na}(\text{OCP})$ (**1**) in the form of its dioxane adduct, $[\text{Na}(\text{OCP})\cdot(\text{dioxane})_{2.5}]$,^[8a,d] and the NHP chlorides **2a–c**^[11] with the bulky Dipp substituent led to the desired phosphanyl phosphaketenes **3a–3c** (Scheme 1).

These compounds were isolated as yellow solids in high yield and fully characterized including single crystal X-ray diffraction studies. As an example, the structure of **3a** is displayed in Figure 1A (for **3c** see Figure S43 in the Supporting Information). Like in the previously reported **3b**^[9] these NHP-substituted phosphaketenes show very long P–P distances. For **3a** the P–P bond is slightly shorter (2.379 Å; versus **3b**: 2.441 Å, **3c**: 2.481 Å) indicating a stronger interaction between the OCP^- anion and the non-

aromatic 1,2,3-diazaphospholidinenium cation. The bond lengths in the $\text{P}=\text{C}=\text{O}$ units in **3a–c** are almost identical within the experimental error (average: $\text{P}-\text{C} = 1.634 \text{ Å}$; $\text{C}-\text{O} = 1.167 \text{ Å}$). Small $^1J_{\text{PP}}$ coupling constants in the ^{31}P spectra of about 250 Hz are consistent with the long P–P bonds.

Each of the phosphaketenes **3a–c** was reacted with the stable NHCs 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**IPr**), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**IMes**), and 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene (**IPr^H**).^[12] The reactions between the unsaturated NHCs (**IPr**, **IMes**) and **3a** give the imidazolium adducts **4aa** and **4ab** as first products of which **4aa** could be isolated in pure form as yellow crystals (Scheme 2).

A large $^1J_{\text{PP}} = 325.1 \text{ Hz}$ indicates that the P–P bond is retained. This was confirmed by a single crystal X-ray diffraction analysis (Figure 1B). The C2–C1 distance [1.516(2) Å] indicates a single bond. The P–C [1.761(2) Å] and C–O bonds [1.249(2) Å] are significantly elongated with respect to **3a**. Consequently, **4aa** is best described as a zwitterion (Scheme 2).^[13]

With the sterically less congested **IMes** the corresponding adduct **4ab** could be characterized by NMR spectroscopy (see Supporting Information) but not isolated in pure form. Longer reaction times led to the quantitative rearrangement of **4ab** to **5ab**. The NMR data of the resulting blue solution indicate that **5ab** contains a P–P bond ($^1J_{\text{PP}} = 589.5 \text{ Hz}$) and an unsaturated $\text{P}=\text{C}$ bond ($\delta^{13}\text{C} = 297.1 \text{ ppm}$, $^1J_{\text{CP}} = 79.2 \text{ Hz}$), which is confirmed by single crystal X-ray diffraction analysis (Figure 1C). The P2–P1 bond [2.266(1) Å] is slightly longer than typical P–P single bonds.^[14] Both the C2–C1 [1.377(2) Å] and C1–P1 [1.622(2) Å] bonds are short indicative of a multiple bond character. With respect to the central C1–P1 unit, the C- and P-bound substituent point to the same side

so that **5ab** is best described as a bent $\text{C}=\text{C}=\text{P}$ heteroallene with rather acute C2–C1–P1 (148.1°) and C1–P1–P2 (107.8°) angles.^[15]

The same type of compound, **5ac** is obtained in form of pink-violet crystals when **3a** is reacted with the saturated carbene **IPr^H** (for a plot of the structure see Figure S46 in the Supporting Information).

The reactions between the phosphaketenes **3b,c** with the unsaturated 1,3,2-diazaphospholenium units and the three carbenes **IPr**, **IMes**, and **IPr^H** are summarized in Scheme 3. The reactions with the unsaturated carbenes **IPr** and **IMes**, led to the zwitterionic intermediates **4ba**, **4bb**, **4ca**, and **4cb** which were detected after short reaction times at room temperature by their typical ^{31}P spectra (see Supporting Information). When the solutions of **4ba–4cb** are kept for some hours at room temperature, a clean rearrangement to a new set of products **6ba–6cb** (Scheme 3) is observed. The rather small J_{PP} coupling constant of about 13 Hz indicates

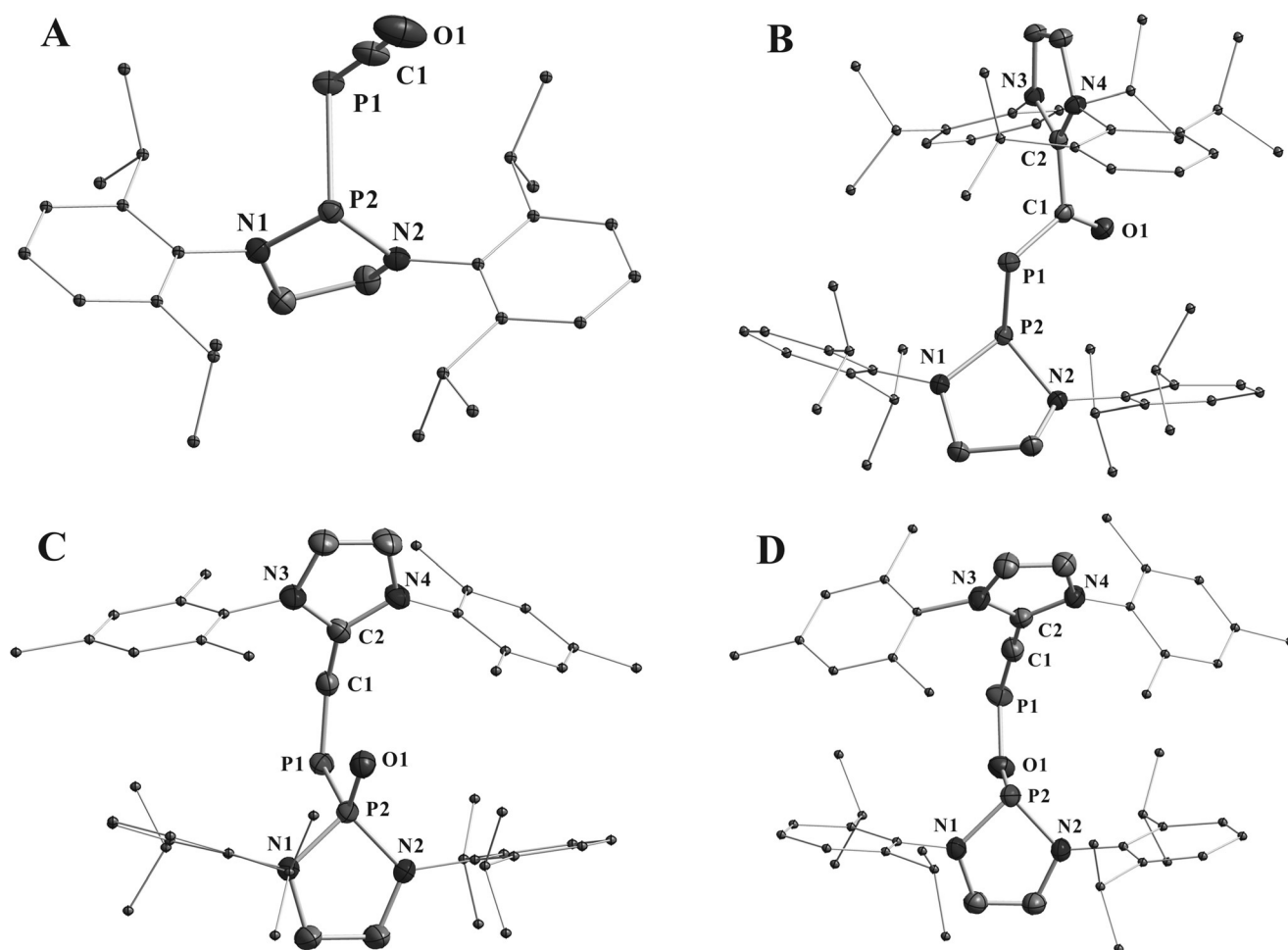
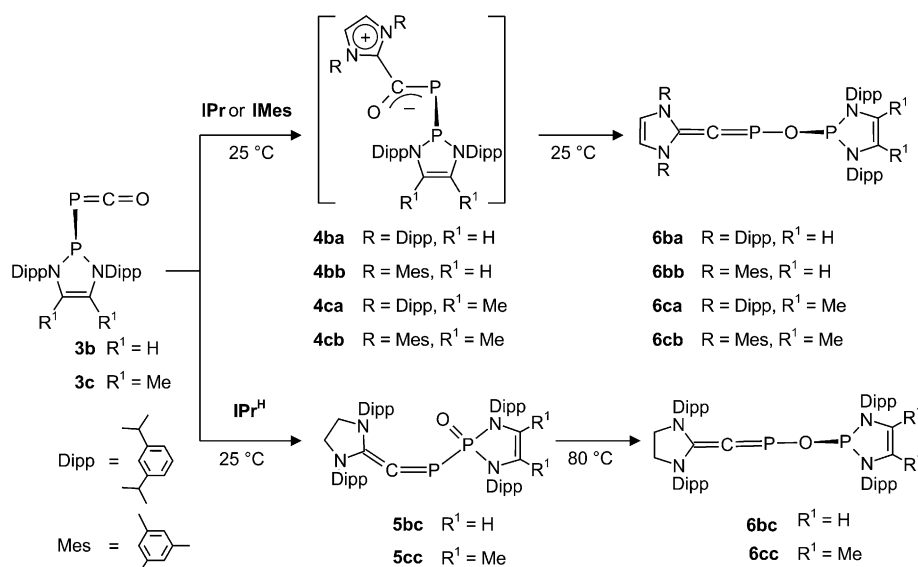


Figure 1. Molecular structure of **3a**, **4aa**, **5ab** and **6bb** in the solid state (H atoms are omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°] (see the Supporting Information for details): A) **3a**: P1–P2 2.3790(7), P1–C1 1.643(2), C1–O1 1.164(3); O1–C1–P1 178.8(3), C1–P1–P2 88.15(9). B) **4aa**: P1–P2 2.2270(5), P1–C1 1.7611(15), C1–O1 1.2494(17), C1–C2 1.5158(18); C2–C1–O1 114.76(12), C2–C1–P1 114.27(10), O1–C1–P1 130.53(11), C1–P1–P2 90.28(5). C) **5ab**: P2–P1 2.2658(6), P2–O1 1.4793(13), P1–C1 1.6215(18), C1–C2 1.377(2); P2–P1–C1 107.80(7), P1–C1–C2 148.11(16). D) **6bb**: P2–O1 1.6580(19), O1–P1 1.6894(17), P1–C1 1.581(3), C1–C2 1.360(4); P2–O1–P1 130.44(11), O1–P1–C1 113.48(13), P1–C1–C2 169.8(2).

that the P–P bond has been broken in this process. In the reactions of **3b**, **c** with the saturated carbene **IPr^H**, compounds **5bc** and **5cc** were isolated as pale blue powders in high yield (> 80%). After heating toluene solutions of **5bc** and **5cc** to 80 °C for 4 hours, clear yellow solutions were obtained from which the rearranged products **6bc** and **6cc** were isolated in almost quantitative yield. Compounds **5ab** and **5ac** could not be cleanly isomerized under heating.

The structures of **6bb**, **6ca**, and **6bc** were determined by single crystal X-ray diffraction analyses. As an example the structure of **6bb** is shown in Figure 1D. These molecules contain a bent O1–P1–C1 unit (average angle at P1 is 112°) with a C–P bond length of 1.604 Å (average) which is shorter than in the phosphaketenes **3a–c** and close to the calculated one in OPC[−] (1.610 Å, Figure 1). However, the P1–O1 bond (average 1.660 Å) is longer than the calculated one for the OPC anion. Both the bent form and the long P–O bond are caused by the tight interaction of the carbon center C1 with C2 of the NHC moiety (C1–C2_{av} = 1.342 Å indicating a C–C double bond). The C2–C1–P1 angle varies between 169.8° in

6bb and about 148° in **6ca** or **6bc** as was also observed in the C=C=P heteroallene fragments of **5ab** and **5ac**. We calculated the NPA charges and WBI (B3LYP/6-31 + G*) for the model compound **VI** with methyl groups instead of the bulky substituents in **6bb**. The alternating NPA charges of the OPC unit in **VI** (O: −1.11 e, P: +0.96 e, C: −0.82 e) are very similar to those of the isolated anion OPC[−] (see above). The positive and negative charges on P and O atoms, respectively, are a consequence of the electronegativity difference, and the negative charge on the C atom is in agreement with the polarization in a NHC=C bond.^[16] The molecular electrostatic potential (MEP) on the electron density isosurface for **VI** is shown in the inset of Scheme 4 and also indicates the negative charge accumulation (attractive MEP towards a positive point charge) on the C and O atoms. The P1–O1 and P2–O1 bonds are similar and somewhat weaker than single bonds (WBIs: 0.64 and 0.66 for the bonds between the O and the σ²-P1 and the σ³-P2, respectively). The C=C bond in the heteroallene moiety is weaker than a genuine double bond (WBI: 1.46), while the C=P bond corresponds to a double



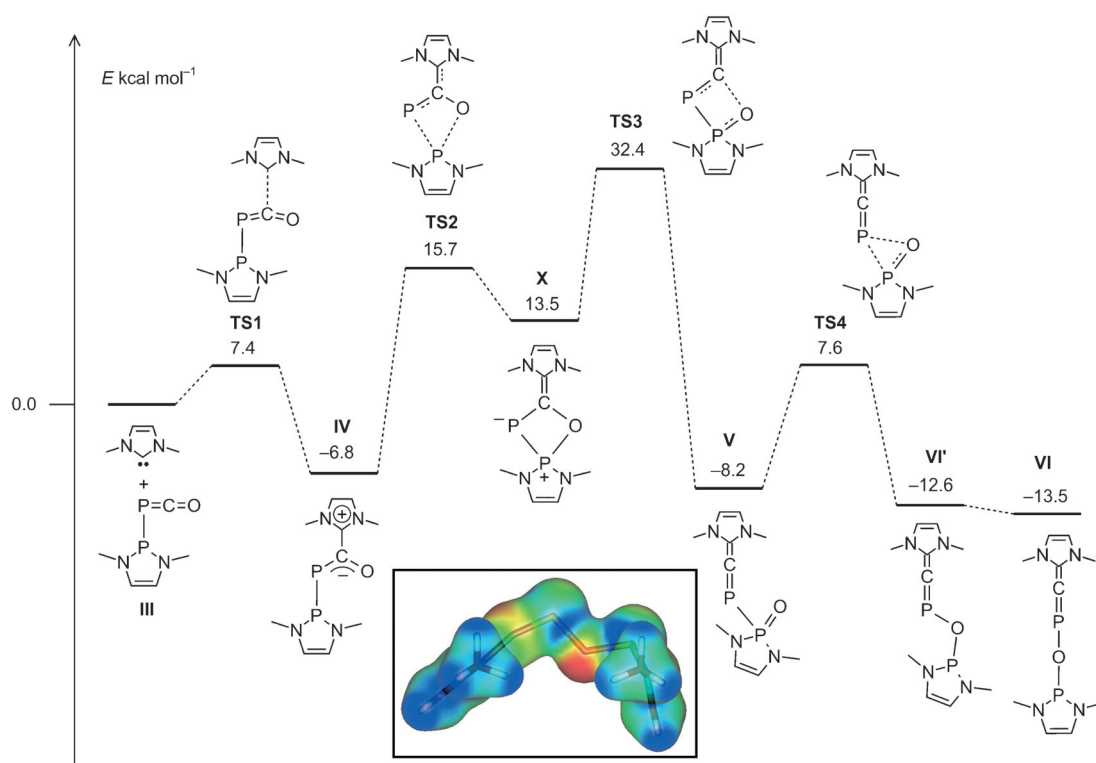
Scheme 3. Reactions of **3b**, **3c** with unsaturated NHCs (**IPr**, **IMes**) and saturated NHC, **IPr^H**.

bond (WBI: 1.93). Consequently, compound **6** may be best viewed as a zwitterionic phosphaheteroallene with a partially negatively charged phosphafulminate, $\text{NHP-O-P=C}^{\delta-}$ and a positively charged $\text{NHC}^{\delta+}$ moiety.

The experimental results suggest that adducts **4** and the phosphaheteroallenes **5** are intermediates on the reaction path from **3a–c** with a PCO group to **6ba–6cc** with an OPC

unit. In order to gain further insight into the reaction mechanism, we calculated (B3LYP/6-31 + G**) a MERP using model compounds in which the Dipp or Mes groups were replaced by methyl groups. The results are shown in Scheme 4. An exothermic nucleophilic attack of the N-heterocyclic carbene on the carbon atom of the P=C=O unit in phosphaketene **III** gives adduct **IV** via the activated complex **TS1** at a rather low activation energy.

The next step is the transformation of **IV** to intermediate **X**, which involves a migration of the PN_2C_2 moiety to the oxygen center in an endothermic reaction. This reaction has the highest activation barrier at **TS2** ($E^a = 22.5 \text{ kcal mol}^{-1}$). Subsequently, the carbon oxygen bond is broken and the P=O bond to the PN_2C_2 cycle is formed to give **V** in an exothermic reaction ($\Delta E = -21.7 \text{ kcal mol}^{-1}$). In the final step, $\text{V} \rightarrow \text{VI}$, the $\text{NHC}=\text{C}=\text{P}$ unit is shifted to the oxygen center of the P=O group in a slightly exothermic reaction with an activation barrier of $15.8 \text{ kcal mol}^{-1}$ at **TS4**. Similar rearrangements $\text{R}_2\text{P-P(=O)R}_2 \rightarrow \text{R}_2\text{P-O-PR}_2$ have been reported as “phosphorotropic tautomerism”.^[17] The transformation $\text{VI}' \rightleftharpoons \text{VI}$ involves only



Scheme 4. MERP of the reaction between a model NHC and phosphaketene **III**. The inset shows the MEP on the electron density isosurface (contour value at 0.02 a.u.) of **VI** at the B3LYP/6-31 + G* level. The blue and red areas indicate repulsive and attractive MEPs towards a positive point charge, respectively.

a conformational change, which is almost thermoneutral. Compounds **4**, **5**, and **6** were isolated as counterparts to model compounds **IV**, **V**, and **VI**. Only an analogue of **X** was not observed experimentally because passing **TS3** requires a lower activation energy ($E^a = 18.9 \text{ kcal mol}^{-1}$) than passing **TS2**.

In summary, with N-heterocyclic carbenes as reagents we were able to convert phosphaketenes $\text{R}-\text{P}=\text{C}=\text{O}$ into phosphaheteroallenes $\text{R}-\text{O}-\text{P}=\text{C}=\text{NHC}$ in which the PCO group has been converted into its constitutional isomeric OPC group. This process does not only give some insight into a fundamental isomerisation process but also allows access to new conjugated π -systems. It may also lead to the development of the chemistry of fulminate derivatives, $\text{R}-\text{O}-\text{N}=\text{C}$, which is currently unexplored.

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