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Reactive Intermediates

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OPN and SPN: Small Molecules with Great Potential

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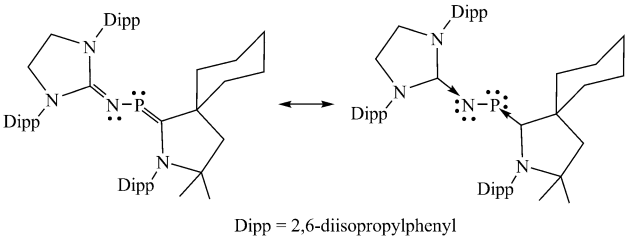
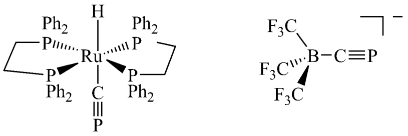
Matrix isolation is now a well-established method for the characterization of highly reactive species and reaction intermediates.[1] Most importantly, it paves the way for later work on a preparative scale. Willner and co-workers very recently reported on the preparation of the molecule OPN[2] in an inert-gas matrix by photolysis of the precursor compound $OP(N_3)_3$.[3] OPN could be photoisomerized reversibly to ONP [Eq. (1)].

$$\mathrm{OPN}\underset{193\,\mathrm{nm}}{\overset{>320\,\mathrm{nm}}{\rightleftarrows}}\mathrm{ONP} \tag{1}$$

To appreciate the scientific merit of this work, one should first consider the special importance of PO and PN bonds in chemistry. The P=O bond with a tetracoordinated phosphorus atom, which is best formulated not as a double bond but as a single bond with charges on the phosphorus and oxygen atoms, is of key importance in biomolecules such as ATP and DNA. Its stability can be used in a large variety of applications, such as the Wittig reaction. The two-atom molecule PO was isolated in matrix experiments by photolysis of P_4/O_2 mixtures.[4] The P=N bond with a tetracoordinated phosphorus atom, again best formulated as a polar single bond, is also of significant interest, and could be found for example, in cyclophosphazenes and polyposphazenes. The molecule PN, detected already very early in the gas phase,[5] was later isolated in inert-gas matrices.[6] In the solid state phosphorus mononitride PN is an oligomer of unknown structure.[7] Recently, a carbene-stabilized phosphorus mononitride was synthesized which proved to be stable at room temperature (see Scheme 1).[8] However, the P–N bond length of 170.85 pm argues for a single bond. It is part of a series of remarkable N-heterocyclic carbene(NHC)-stabilized potentially multiply bonded species like $P_2(NHC)_2$.[9] Moreover, the isoelectronic anion CP^- was isolated both as ligand in a transition-metal complex and also bound to the Lewis acid $B(CF_3)_3$ (see Scheme 2).[10] The neutral RCP compounds, first prepared by Becker and et al. (with R = *t*Bu), were shown to exhibit a rich chemistry.[11] OPN is isoelectronic to SiO_2,[12] and indeed a solid material of the composition OPN could be synthesized in both a β-cristobalite and an amorphous form (which was slightly less stable thermodynamically) by the reaction of urea or melamine with a phosphorus precursor.[13] Hence one expects that OPN will display interesting reactivity.



Scheme 1. NHC-stabilized PN.



Scheme 2. Examples of complexes of CP^-.

The story of the isolation of this molecule started with a matrix and quantum chemical study by Schnöckel, Ahlrichs, and Schunk in 1988.[14] In the introduction of their article the authors stated "*We now wanted to clarify whether P^V can also occur in compounds with coordination number two*". The molecule was formed by matrix photolysis of a PN/O_3 mixture. Surprisingly, the IR data clearly indicated formation of PNO rather than its isomer OPN. Hence, as the authors stated, "*the structure of PNO contradicts 'chemical intuition', according to which the most electropositive atom should assume the central position in a triatomic molecule.*"[14] Later PNO was further characterized in gas-phase experiments,[15] and the bond lengths were derived from microwave spectroscopic studies.[16] Attracted by the unusual structure of the molecule, theoreticians carried out a series of quantum chemical calculations, applying different levels of theory.[17] Most calculations predicted the PNO isomer to be more stable than the OPN isomer (the energy difference ranges from a few up to about 75 kJ mol^{-1}). Only one recent ab initio quantum chemical study came to the conclusion that the OPN isomer is slightly more stable.[18] Hence the PNO story shows how difficult it can be to calculate such seemingly simple triatomic molecules, and also provides a textbook example for the fruitful interaction between experimental and theoretical studies.

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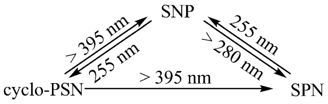
Willner and co-workers entitled their contribution "*Elusive O=P≡N, a rare example of phosphorus $\sigma^2\lambda^5$ coordination*." However, the authors themselves addressed the question about the correct description of the bonding. In principal, three Lewis structures can be discussed [Eq. (2)]. Of these, the description as O=P≡N certainly is not really relevant. The other two formulas, although having the disadvantage of formal charges, are better descriptions of the bonding situation.

$$\overset{-}{\mathrm{O}}\!-\!\overset{+}{\mathrm{P}}\!\equiv\!\mathrm{N} \longleftrightarrow \mathrm{O}\!=\!\mathrm{P}\!\equiv\!\mathrm{N} \longleftrightarrow \mathrm{O}\!=\!\overset{+}{\mathrm{P}}\!=\!\overset{-}{\mathrm{N}} \qquad (2)$$

In similar studies, the same group also prepared SPN from the photodecomposition of the azide precursor $SP(N_3)_3$.[19] In this case, three isomers were found, namely NPS, SNP, and a 16-electron tricycle (see Scheme 3). The tricycle was rightly claimed to be the first stable 16-electron tricyclic compound. It should be mentioned that Curtius first suggested a tricyclic structure for the isoelectronic HN_3 molecule. This structure is depicted on a portrait of Curtius on the staircase of the Heidelberg chemistry building. Very recently, the valence-isoelectronic compound SiS_2 was characterized in its cyclic form by microwave spectroscopy in alliance with quantum chemical calculations.[20] Although the cyclic form is of higher energy than the linear global energy minimum structure, it defines a local minimum on the potential energy surface. The lack of hybridization between the orbitals of the central Si atom (leading to a reduced tendency for π-bond formation) and especially the relatively high S–S single bond energy were made responsible for the relative stability of the cyclic form, in contrast to the situation found for CO_2.



Scheme 3. Photoisomerization of SNP.

Molecules such as OPN, SPN, and SiS_2 were shown to have special electronic properties. They certainly exhibit a rich and diverse chemistry. Matrix-isolation studies together with quantum chemical studies now form a solid basis for future preparative work.

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