P,N Compounds

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The Reaction of White Phosphorus with $NO^+/NO_2^+[Al(OR^F)_4]^-$: The $[P_4NO]^+$ Cluster Formed by an Unexpected Nitrosonium Insertion**

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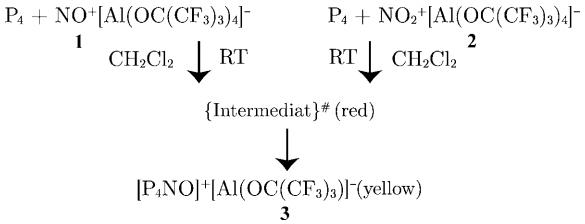
Despite decades of intense research into polyphosphorus chemistry,[1] our knowledge of homoleptic polyphosphorus cations is still limited to the results of mass spectrometry[2] and quantum chemical calculations.[3] In general, the diamagnetic cage cations with an odd number of phosphorus atoms are more stable, with P_9^+, composed of two C_{2v} symmetric P_5 cages joined by a common phosphonium atom having special stability.[4] This cage was found in one of the few types of simple inorganic phosphorus cluster cations that are known, that is, $[P_5R_2]^+$ (R = Cl, Br, I, Ph, DippN(Cl)NDipp (Dipp = 2,6-diisopropylphenyl)).[5–8] Those P_5 cages are formed by the formal insertion of carbene-analogous PR_2^+ fragments into the P–P bond of P_4 (see Ref. [9,10] for Reviews on P_4 activation).

Stable carbenes also interact with P_4, leading to compounds including P_1 up to P_{12} moieties, depending on the electronic nature of the carbene.[11] Larger cationic P_7 cages were recently prepared,[5] but all preparative approaches to true P_n^+ ions remained futile. However, we expected that an appropriate one-electron oxidant should be able to oxidize P_4 (ionization energy (IE) 9.34 eV)[12] and lead to phosphorus cluster cations P_n^+. Herein we give an account of the reaction of P_4 with the salts $[NO]^+[Al(OC(CF_3)_3)_4]^-$[13] (**1**; IE NO = 9.26 eV[14]) and $[NO_2]^+[Al(OC(CF_3)_3)_4]^-$ (**2**; IE NO_2 = 9.59 eV.[15] At least **2** was expected to be a strong enough oxidant to yield P_n^+ cations. The novel salt **2** was synthesized in 94% yield from $NO_2[BF_4]$ and $Li[Al(OC(CF_3)_3)_4]$ in SO_2 solution with precipitation of insoluble $Li[BF_4]$; it was fully characterized by X-ray diffraction and vibrational and NMR spectroscopy (for details, see the Supporting Information).

Unexpectedly, the reactions of **1** and **2** with P_4 in CH_2Cl_2 show an analogous process, regardless of the ratios of phosphorus to oxidant employed (between 3 P:1 NO_x^+ and 9 P:1 NO_x^+). They form a red intermediate and yield the same yellow final product ($[P_4NO]^+[Al(OC(CF_3)_3)_4]^-$ (**3**; Scheme 1). Compound **3** may be viewed as the insertion



Scheme 1. Reactions of **1** and **2** with P_4 in CH_2Cl_2.

product of carbene-analogous NO^+ into the P–P bond of P_4. The insertion of NO^+ into a main-group E–E bond to give the E–N(O)–E fragment is unprecedented.[16] The nature of $[P_4NO]^+$ was established by solution and solid-state NMR, IR, and Raman spectroscopy and mass spectrometry and is consistent with quantum-chemical calculations, as is also the weight balance of the reaction.

Preliminary experiments were conducted at 203 K, but due to the poor solubility of white phosphorus, the reaction mixture was warmed to 298 K. The initially colorless mixture turns dark red until one of the starting materials is consumed; thereafter the color turns pale yellow. If the entire reaction is carried out at room temperature, the red color disappears within 10 s. The ^{31}P NMR spectrum of the yellow product in CD_2Cl_2 (Figure 1 a) shows two triplets at −232 and +360 ppm (integration 1:1) with a $^1J_{PP}$ coupling constant of −160 Hz that is reminiscent of $P_5X_2^+$.[8] No further coupling was observed.

The coupling pattern and also the chemical shifts suggest a C_{2v}-symmetric phosphorus cage related to $[P_5X_2]^+$ but replacing the phosphonium PX_2 unit by a heteroatom (N). The signal at −232 ppm is then assigned to the distal P–P edge (P_A) and the broader signal at 360 ppm ($\Delta\nu_{1/2}$ = 65 Hz) to the phosphorus atoms bound to nitrogen (P_X), leading to a significant deshielding of the phosphorus nuclei. The broadening of the high-frequency triplet is due to the unresolved coupling to the quadrupolar ^{14}N nucleus. The solution

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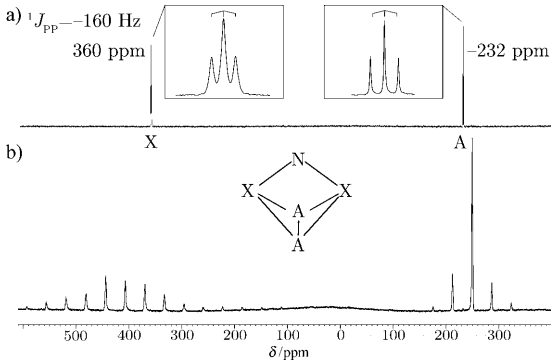


Figure 1. a) ^{31}P NMR spectrum (161.99 MHz) of **3** (spin system A_2X_2) in CD_2Cl_2 at 285 K. b) ^{31}P–MAS NMR spectrum of **3** at 6 kHz rotation and 298 K.

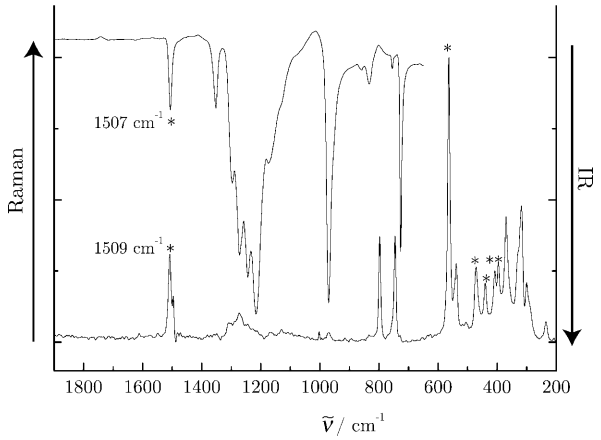


Figure 2. FT-ATR-IR (ZnSe, resolution 2 cm^{-1}, 32 scans) and FT-Raman spectrum (2048 scans, 4 cm^{-1} resolution, 32 mW laser power, 1064 nm) of **3**. ⋆ $[P_4NO]^+$ bands. All other bands can be attributed to $[Al(OC(CF_3)_3)_4]^-$.

^{14}N NMR spectrum shows a singlet at 173 ppm ($\Delta\nu_{1/2}$ = 270 Hz), which is thus assigned to the bridging nitrogen atom.

All measured chemical shifts and coupling constants are in good agreement with the calculated values (see Table 1 and Supporting Information). Many attempts to obtain crystals for single-crystal X-ray diffraction failed; we always obtained remnants that were cube-shaped in appearance. These remnants showed no extinction in polarized light and repeated X-ray measurements between 100 and 298 K showed neither reflections nor powder rings. However, solid-state NMR and vibrational spectroscopy of these remnants showed that they are not white phosphorus. Compound **3** could be repeatedly synthesized in scales of up to one gram.

Table 1: Measured and calculated NMR parameters of $[P_4NO]^+$.

Nucleus	Solution[a] δ	Solid state[d] δ_{iso}	Calculated
^{14}N	175	–	220[b]
^{31}P (A)	−232	−248	−232[b]
^{31}P (X)	360	407	348[b]
$^1J_{PP}$/Hz	−160	−160	−152[c]

[a] CD_2Cl_2. [b] CCSD(T)/aug-cc-pVDZ with reference to P_4 (δ = −521); NO^+ (CH_3NO_2) δ = 20.2 ppm. [c] B3LYP/aug-cc-pVTZ. [d] Rotational speed (6 kHz). Isotropic shift was calculated using TOPSPIN 2.1.[17]

Table 2: Calculated and measured vibrational modes of $[P_4NO]^+$.

IR [cm^{-1}]	Raman (%) [cm^{-1}]	Calcd[c]	Calcd[d]	Assignment
1507[a] (1496)[b]	1509 (31)	1545	1558/ *1517*	A_1 ν_s(NO)
	563 (100)	555	538/*540*	A_1 δ_s(P_4N)
		558	547/*531*	B_1 δ_{as}(P_2NO)
	470 (26)	466	435/*426*	A_1 δ_s(P_4N)
	441 (21)	436	420/*415*	B_2 ν_{as}(PP)
	408 (25)	405	387/*384*	B_1 ρ(PP)
	397 (28)	392	379/*374*	A_1 δ(PNP)

[a] ZnSe ATR IR. [b] CH_2Cl_2 solution in situ (REACT-IR on silicon). [c] CCSD(T)/aug-cc-pVTZ. [d] BP86/aug-cc-pVTZ. The values given in italics are obtained by anharmonic correction.

From solid-state NMR spectroscopy, we conclude that the anion remained intact (^{19}F, ^{27}Al). The MAS–^{31}P NMR spectrum bears a remarkable resemblance to that of the solution; that is, two signals at δ_{iso} = −248 and + 407 ppm (Figure 1 b). The high-frequency signal has a significant anisotropy (δ_{11} = 500, δ_{22} = 463, δ_{33} = 258 Hz), which suggests further neighboring heteroatoms. At rotation frequencies of 15 kHz, the low-frequency signal resolves to a triplet with $^1J_{PP}$ = −160 Hz. Thus, the cationic structure in solution and the solid state remains the same.

The vibrational spectra of **3** (Figure 2 and Table 2) show, aside the intact anion signals, N = O stretching vibrations at 1507 (IR)/1509 cm^{-1} (Raman), an intense phosphorus cage mode at 563 cm^{-1} (Raman: A_1, partial overlap with anion band) and further cage modes at 471, 440, 408, and 393 cm^{-1}. These assignments are supported by comparison with known[18] spectra of the anion and the calculation of the (harmonic) vibrational spectra of the cation structure of **3** up to the CCSD(T)/aug-cc-pVTZ level. Anharmonic corrections of the DFT level calculations led to a further improvement for the NO stretching frequency, and the calculated values show excellent agreement with the experimental values (Table 2).

Free gaseous $[NO]^{\bullet}$ has a vibrational frequency of 1903 cm^{-1}, and $[NO]^+$, as reported for several solid-state structures, about 2300 cm^{-1}.[19,20] The NO modes of metal complexes[21] with terminal nitrosyl ligands are in the range of 1664–1789 cm^{-1}, and η^2-bridging NO absorbs in the region 1445–1603 cm^{-1}. Matrix-isolation experiments of PNO, the only other known compound containing an P–NO moiety, gave an absorption at 1755 cm^{-1}.[22] The bond lengths of NO compounds vary from 106 pm $[NO]^+$, 115 pm $[NO]^{\bullet}$, up to 123 pm in NO complexes. Thus, with the average NO stretch in **3** at 1508 cm^{-1}, we expect a NO bond length of between 115 and 123 pm that arises from a slightly negatively charged NO group. The P_4 cage then has to bear the positive charge of the cation. This assignment is in agreement with the results of our calculations (Figure 4 and Table 3).

The recorded ESI mass spectrum also supports formulation as monomeric $[P_4NO]^+$ (see Supporting Information). The expected peak at m/z 153.8 for $[P_4,N_1,O_1]^+$ was observed, and this fragment yields upon CID (40 eV, laboratory frame, Xe as collision gas) two main fragments at m/z 123.8 $[P_4^+]$ and 92.8 $[P_3^+]$ from the expected loss of NO and PNO, respectively.

The formation of $[P_4NO]^+$ from NO^+ and P_4 is an exergonic process (Figure 3). A comparison of the thermochemistry ($\Delta_R U$) for the formation of $[P_4NO]^+$ at the

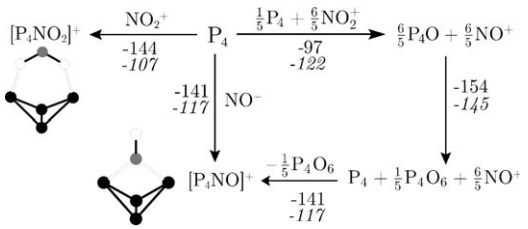


Figure 3. Energetics of the reaction of the NO^+ and NO_2^+ cations with P_4 to form $[P_4NO]^+$ and $[P_4NO_2]^+$. Gibbs reaction energies ($\Delta_R G$) are given at 298 K, and solvated values are given in italics (COSMO model: CH_2Cl_2, $\varepsilon_r = 8.93$[23]) at the B3LYP/aug-cc-pVTZ level.

CCSD(T)/aug-cc-pVTZ ($-151\ kJ\,mol^{-1}$) versus the B3LYP/aug-cc-pVTZ ($-186\ kJ\,mol^{-1}$) level shows that hybrid DFT is sufficient to describe the thermochemistry. In the following we investigated the reaction of NO_2^+ with P_4 using the latter model chemistry. We assume that the formation of unstable phosphorus oxides such as P_4O with concomitant reduction of NO_2^+ to NO^+ is probably the first step of the reaction (Figure 3). This proposal was further supported by REACT-IR experiments that showed the intermediate formation of NO^+ in the reactions starting with NO_2^+. P_4O further disproportionates, giving, for example, less-soluble P_4O_6 (or other higher phosphorus oxides) and P_4, which is in agreement with the observation of a small amount of an insoluble material that is formed during these reactions. This energetically favored disproportionation is probably the reason for the observed formation of $[P_4NO]^+$ instead of $[P_4NO_2]^+$.

The proposed reaction pathway leading to formation of $[P_4NO]^+$ is supported by in situ IR spectroscopy (REACT-IR). At first only the solvated free NO^+ band at 2242 cm^{-1} is present, immediately followed by a weak intermediate band at 1650 cm^{-1}, and finally the product $[P_4NO]^+$ band at 1496 cm^{-1}. The progress can be explained by the lengthening of the NO bond during the reaction (Figure 4). The appearance of color is in agreement with the calculated UV/Vis spectra ((RI-)CC2/def2-TZVPP level; see Supporting Information). The main contributions are electronic excitations from P_4 orbitals into one of the π^* orbitals of the NO bond (Figure 4).

The red color visible for a few seconds at room temperature points to an intermediate; this intermediate is not observable by NMR spectroscopy, and is assigned to a C_s-symmetric $[P_4{\rightarrow}NO]^+$ adduct, which is about 27 $kJ\,mol^{-1}$ higher in energy than the product cation $[P_4NO]^+$ (Figure 4). This is probably an orbital-controlled process:

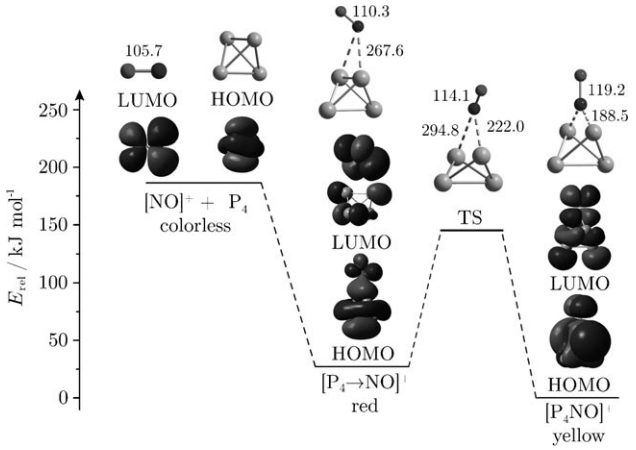


Figure 4. Reaction profile (SCF energies) of the formation of $[P_4NO]^+$ (B3LYP/aug-cc-pVTZ). Distances are given in pm.

the π^* LUMO of NO^+, which bears the largest coefficient at nitrogen, interacts with the HOMO of P_4 to form the red intermediate and form finally the $[P_4NO]^+$ cation through a C_s-symmetric transition state (Figure 4). Similar observations have been made in a computational study of the insertion of silylene SiH_2 into one of the edges of P_4.[24]

The bonding in the $[P_4NO]^+$ cation can be accounted for in the Lewis picture by the resonance structures shown in Figure 5. The resonance structures imply that the phosphorus

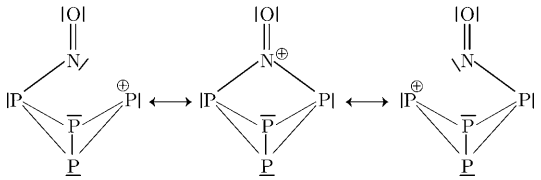
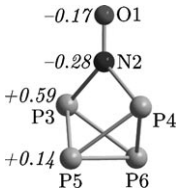


Figure 5. Lewis resonance structures of $[P_4NO]^+$. The left and the right structures bear considerable weight.

atoms P3 and P4 bear the positive charge. This result is supported by the NPA charges (Scheme 2 and Table 3) and a NBO analysis, which suggests that the main donor–acceptor interaction is negative hyperconjugation from the oxygen lone pair in the σ^* orbital of the N–P bond, thus elongating this bond. This charge distribution is, in some respect, related to the metal–(η_2-NO) complexes,[21] as supported by the (calculated) similar NO bond length and also the observed NO stretching frequency. Moreover, in the NMR spectra, the signals of the positively polarized phosphorus atoms are shifted to higher frequencies.

The electron density at the (3,−1) bond critical points (BCP) of the P–P bond in $[P_4NO]^+$ (0.67 e $Å^{-3}$) is slightly higher compared to P_4 (0.61 e $Å^{-3}$; see Supporting Information). At the BCP the electron density in the N–O bond decreases from NO^+ (4.99 e $Å^{-3}$) to $[P_4NO]^+$ by about 1.4 e $Å^{-3}$. Finally, the low electron density on the P–N BCP in $[P_4NO]^+$, if compared with that of $H_2P{-}NH_2$ (1.08 e $Å^{-3}$),



Scheme 2. Calculated structure of $[P_4NO]^+$ with the NPA charges shown in italics (see also Table 3). The angles (3-2-4) and (2-3-5) are 104.1 and 81.6°, respectively.

supports the Lewis resonance structure formulation in Figure 5.

From the preceding results, it followed that $[P_4NO]^+$ might indeed serve as a source of phosphorus cations. To investigate this, we reacted $[P_4NO]^+$ with the σ-donor $P(C_6H_5)_3$. The addition of $P(C_6H_5)_3$ to a CD_2Cl_2 solution of **3** led to immediate and exclusive formation of the known[26] triphosphenium ion $[P(P(C_6H_5)_3)_2]^+$ (for spectra, see the Supporting Information). In this case, $[P_4NO]^+$ acts as a pure "P^+" donor, which points to the loss of neutral species, for example, PNO,[22,27,28] which was also observed in the mass spectrum. This result shows the promising versatility of $[P_4NO]^+$ as synthetic tool, perhaps leading to other interesting phosphorus cations.

Table 3: Calculated structural and bonding parameters of $[P_4NO]^+$ (see also Scheme 2).

Atoms	d [pm][a]	$\rho(\mathbf{r})$ (3,−1) [e Å^{-3}]	$\varepsilon(-3,1)$[b]	WBI[b,c]
(1-2)	119.3[a]	3.58[b]	0.05[b]	1.70[b]
(2-3)	183.1[a]	0.88[b]	0.20[b]	0.74[b]
(3-5)	224.4[a]	0.67[b]	0.40[b]	0.90[b]
(5-6)	219.3[a]	0.67[b]	0.02[b]	1.04[b]

[a] (FULL-)CCSD(T)/aug-cc-pVTZ. [b] BP86/aug-cc-pVTZ.[25] [c] Wiberg bond indices.

In conclusion, we note that the preparation of phosphorus cations still remains an unresolved challenge. NO^+ and NO_2^+ salts are not able to oxidize P_4 to form P_n^+ in all of the ratios tested. Although at least NO_2^+ should provide enough ionization energy to oxidize P_4, instead the intriguing cluster cation $[P_4NO]^+$ formed by the unprecedented E–N(O)–E insertion of NO^+ into a main group bond. With its tendency to delocalize the positive charge over the phosphorus atoms, $[P_4NO]^+$ is a further advance towards the elusive pure lighter Group 15 cluster cations and is the starting material for further novel phosphorus cation chemistry. Furthermore, we have presented the facile synthesis of $NO_2[Al(OC(CF_3)_3)_4]$ as a potential oxidizer for further applications.

Experimental Section

3: $NO[Al(OC(CF_3)_3)_4]$ (250 mg, 0.25 mmol) and freshly sublimed P_4 (31 mg, 0.25 mmol) were weighed into a double-bulb Schlenk vessel equipped with a G4 frit plate. At −196 °C, CH_2Cl_2 (ca. 15 mL; stored over CaH_2) was condensed onto the reagents. The reaction mixture was allowed to warm to room temperature with stirring or shaking. A red color was apparent until the reaction was completed. After the color of the reaction mixture turned slightly yellow, it was cooled again to −10 °C and CH_2Cl_2 was completely removed in vacuo (10^{-3} mbar). The product (256 mg) had a pale yellow color and was isolated in 91% yield. It is moisture-, light-, and air-sensitive, but could be stored at 2 °C for several months.

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