

## The Reactivity of Molecules and Solids

Examples from the Chemistry of Phosphorus

When Henning Brand, a German alchemist, discovered the element phosphorus (Greek for *bearing light*) in 1669, he opened up one of the most fascinating areas in chemistry: the realm of phosphorus compounds. Phosphorus engages in a lot of binding modes, forming a multitude of different compounds. This versatility makes phosphorus one of the *jack of all trades*: in inorganic, organic as well as biological chemistry. There are literally thousands of industrial applications of phosphorus compounds, ranging from highly specialized bio-resorbable polymers for surgical applications to bulk chemicals like detergents or even fertilizers, which are produced on a scale of millions of tons per year. Other applications include flame proofing agents, food additives, materials for non-linear optics and ferroelectrics.

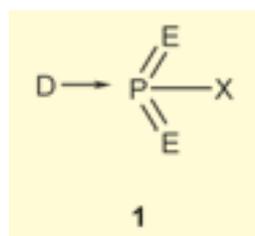
The work of our group mainly focuses on the chemistry of low coordinated compounds of pentavalent phosphorus, more specifically, donor stabilized derivatives of monometaphosphoric acid. Their basic structure is depicted in Fig. 1. We are interested in the interrelationship between the strength of the donor-acceptor bond P-N<sub>py</sub> on the one hand and the reactivity of the compound on the other hand. By tailoring their properties appropriately, these compounds could find interest as mild and selective phosphorylating agents and as starting materials for new phosphorus compounds.

Moreover, we are exploring the synthesis and structures of transition metal phosphates and phosphonates. Solid state reactions of these compounds lead to new phases with interesting applications in heterogeneous catalysis, e.g. selective oxidation and ammoxidation of hydrocarbons.

In the following sections, we will go into details of a few of the above mentioned points.

### Structure and Reactivity of Donor-Stabilized Derivatives of Monometaphosphoric Acid

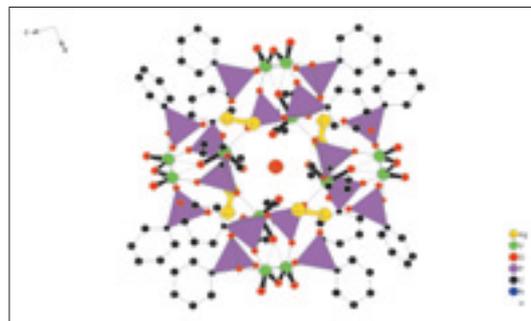
One of the paradigms of chemistry during the first decades of the 20th century was the so-called double bond rule, stating that elements of the second and higher periods of the periodic system are not capable of forming stable (p-p)- $\pi$ -bonds. Pioneering in the overthrow of this rule was the spectroscopic characterization of H-C $\equiv$ P, the phosphorus analog of hydrocyanic acid, in the gas phase during the 1960's [1]. In the aftermath of this discovery, more violations of this rule were found (many of them in phosphorus and silicon compounds), so that



**Fig. 1**  
General structure of donor-stabilized derivatives of monometaphosphoric acid. Donors *D* = heteroaromatic and aliphatic amines, phosphanes; *E* = O, S; *X* = hal, pseudohal, NR<sub>2</sub>, OR. The compounds most often used are 1a (*D*=pyridine, *E*=S, *X*=Cl) and 1b (*D*=pyridine, *E*=O, *X*=Cl).

**Table 1**  
Atomic distances in selected pyridine stabilized dithiomonometa phosphoric acid derivatives

Compound	d <sub>P,N<sub>py</sub></sub> [pm]	d <sub>P=S</sub> [pm]	d <sub>P-Y</sub> [pm]
Py → PS <sub>2</sub> (NEt <sub>2</sub> )	189.8(5)	195.0(2)	164.0(4)
Py → PS <sub>2</sub> (N <sub>3</sub> )	185.6(2)	193.5(3)	171.9(2)
Py → PS <sub>2</sub> Cl	184.9(3)	192.9(2)	206.4(2)
Py → PS <sub>2</sub> F	183.3(2)	192.4(1)	158.8(3)

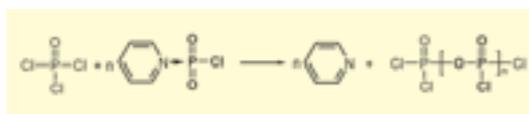


**Fig. 2**  
Structure of the complex anion in [Ph<sub>3</sub>PMe]<sub>2</sub> [(V<sub>2</sub>O<sub>3</sub>)(VO<sub>2</sub>)<sub>4</sub>(PhPO<sub>3</sub>)<sub>14</sub>(PhPO<sub>3</sub>H)<sub>2</sub>]<sub>4</sub>(Ag<sub>2</sub>)<sub>2+</sub>, H<sub>2</sub>O]·8 MeCN viewed along *b*. Thick lines mark V-O bonds, dotted lines stand for donor-acceptor bonds V=O...V.

it finally had to be abandoned. Later on, kinetically stabilized phosphalkynes and -alkenes were synthesized, that are stable even at room temperature and in condensed phase. Nowadays, these compounds are not mere lab curiosities anymore but their synthetic potential is put to use in chemistry [2].

We entered the field of low coordinated phosphorus compounds, namely those of the  $\sigma^3-\lambda^5$  type when dealing with the synthesis of condensed thio- and oxothio-phosphoryl chlorides. It was found, that the reorganization reaction between P<sub>4</sub>O<sub>10</sub>/P<sub>4</sub>S<sub>10</sub> and POCl<sub>3</sub>/PSCl<sub>3</sub> becomes markedly faster and gives higher yields under less harsh conditions, when a small amount of pyridine was added to the mixture of reactants. As the process appeared to be catalytic in nature, the reactive intermediate was sought for. Soon, it turned out to be of the structure given in Fig. 1a and b, respectively.

Thus, the catalyzed reaction proceeds as follows: As shown in Fig. 3, the formation of condensed polyphosphoric acid chlorides can be interpreted as an insertion of PE<sub>2</sub>Cl units into P-Cl bonds. Being liberated again in this process, it becomes clear, that pyridine functions as a real catalyst here.



**Fig. 3**  
Mechanism of the reaction forming condensed polyphosphoric acid chlorides using pyridine as a catalyst.

During the last few years, we succeeded in synthesizing and characterizing many derivatives of 1. Looking for regularities, we found in the group of py $\rightarrow$ PS<sub>2</sub>X compounds a clear dependence of P-N<sub>py</sub> distances from electronic properties of the nature of the substituent X, as shown in Table 1.

It becomes clear that (within certain limits) the length of the P-N<sub>py</sub> bond and the reactivity of derivatives of 1 can be adjusted by variation of substituents. Distances between P and N<sub>py</sub> of about 185 pm vs. some 170 pm in compounds with usual P-N single bonds support the description of these compounds in terms of donor-

acceptor complexes rather than as betaines. This adduct-type approach seems even more justified, when one takes into account their thermal behaviour: we found it possible to study the products of thermal dissociation (450°C, 10 Pa) of certain derivatives of 1, leading to  $\text{PO}_2\text{Cl}$ ,  $\text{PS}_2\text{Cl}$ ,  $\text{PS}_2\text{F}$  and pyridine, respectively, by means of photoelectron spectroscopy [3].

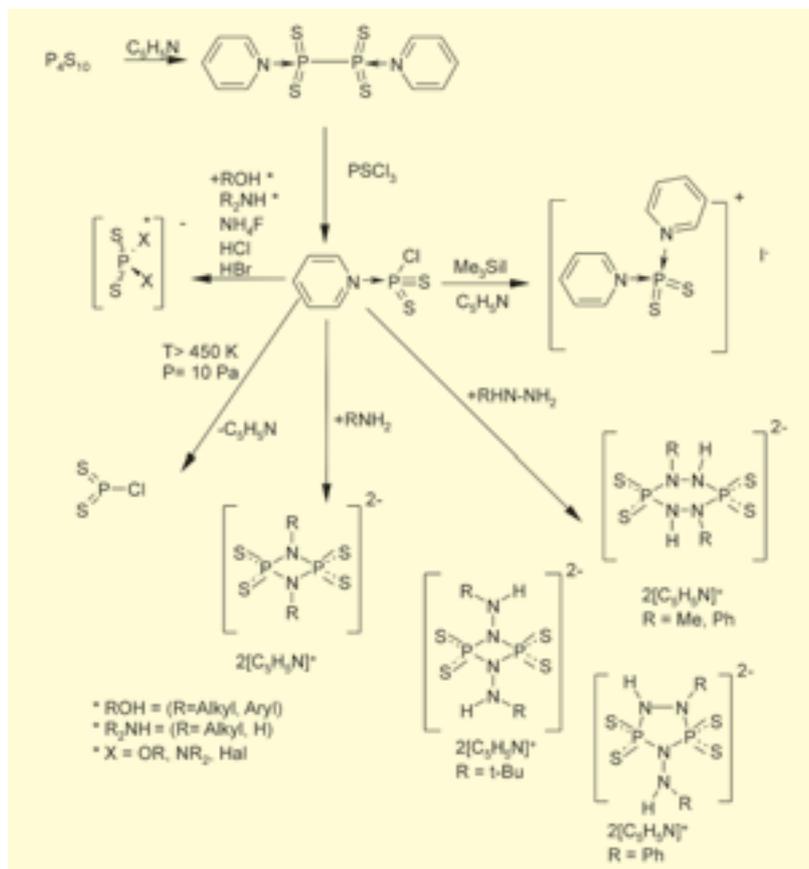
The chemical behaviour of compounds of type 1 has been studied most thoroughly for the case of  $\text{py} \rightarrow \text{PS}_2\text{Cl}$ . This is due to both its convenient synthetic accessibility and handling and the reactivity of its functionalities  $\text{P}-\text{N}_{\text{py}}$  and  $\text{P}-\text{Cl}$  towards a vast array of reagents. All reactions studied so far can consistently be explained by assuming an either free (*i.e.*, uncoordinated) or solvent associated  $\text{PS}_2\text{Cl}$  moiety as an intermediate. It engages in both nucleophilic substitution and cycloaddition reactions. The first group of reactions, employing typical reagents like halides, pseudohalides, alcohols, excesses of primary and secondary amines and hydrazines or mixtures thereof, gives the corresponding dialkyl-, diaryl-, diamino or alkoxy-amino dithio phosphates. The products are obtained in good to excellent yields even in cases, where the usual synthetic approaches to the same products fail or give only poor to moderate yields. The versatility of these reactions can be seen from the scheme shown in Fig. 4, summarizing the outcomes of many experiments.

Recently, we started to explore the reactivity of  $\text{py} \rightarrow \text{PS}_2\text{Cl}$  towards organometallic reagents and related compounds. Only two reactions may serve as an example here. Adding a solution of tertiary butyl lithium or a solution of sodium bis(trimethylsilyl)amide, respectively, to a solution of  $\text{py} \rightarrow \text{PS}_2\text{Cl}$  leads to the formation of four-membered heterocycles, as shown in Fig. 5.

Featuring a double bond, the  $\text{PS}_2\text{Cl}$  moiety is also capable of attacking multiple bond systems, *e.g.* the

### Phosphorchemie

Es wird über Arbeiten zur Reaktivität von niederkoordinierten Verbindungen des Phosphors am Beispiel der donorstabilisierten Monometaphosphorsäurederivate sowie über Zusammenhänge zwischen Bindungseigenschaften und Reaktionsverhalten unter dem Aspekt des Einsatzes dieser Verbindungen als Synthesebausteine berichtet. Der zweite Teil des Beitrags gibt einen Einblick in die faszinierende strukturelle Vielfalt von Organophosphonaten der Übergangsmetalle und zeigt potentielle Anwendungsfelder für diese Verbindungen.



triple bond in tolane (diphenylethine). Here, five-membered heterocyclic compounds (2, 3) are formed as a result of several consecutive steps. (see Fig. 6)

Attempts to remove sulfur from the disulfide linkage in 1 unexpectedly lead to the formation of heterobicyclic compounds like 4. The molecular structure of 2 as determined by single crystal X-ray diffraction is shown in Fig. 7.

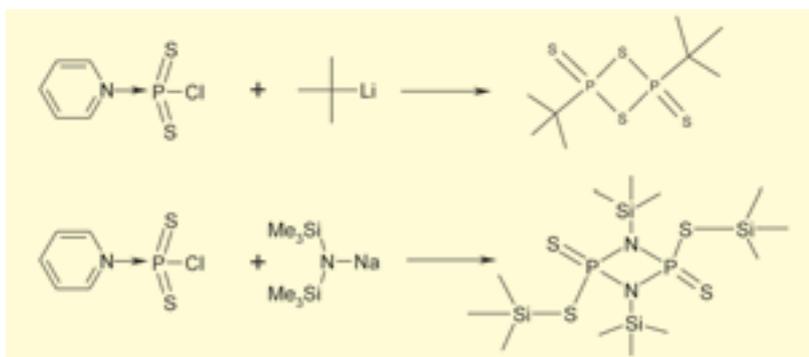
In order to account for the products isolated and identified so far, we assume the dissociation and cycloaddition of  $\text{PS}_2\text{Cl}$  to the triple bond of tolane to be the initial steps of an intricate reaction sequence involving rearrangements and redox steps (Fig. 8) [4].

### Some Aspects of Formation and Structure of Oxovanadium Organophosphonate Clusters and Coordination Polymers

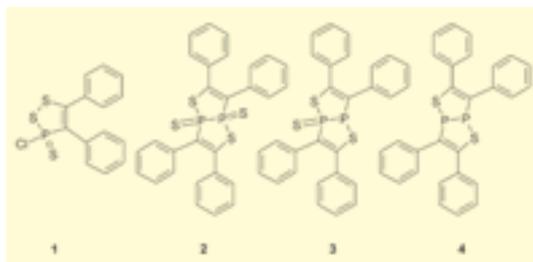
The last two decades saw an enormous development of the chemistry of polyoxoanions. This increase in interest was, at least in part, driven by the prospect of get-

Fig. 4 Summary of several reactions leading to /starting from  $\text{py} \rightarrow \text{PS}_2\text{Cl}$ .

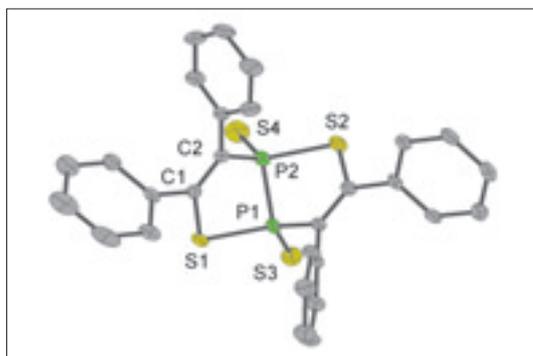
Fig. 5 Reactions between  $\text{py} \rightarrow \text{PS}_2\text{Cl}$  and metalorganic reagents leading to four-membered heterocycles.



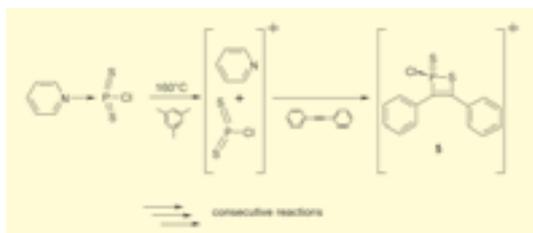
**Fig. 6**  
Heterocyclic compounds formed during the reaction of  $py \rightarrow PS_2Cl$  with tolane in mesitylene.



**Fig. 7**  
Molecular structure of compound 2 as determined by single crystal X-ray diffraction.



**Fig. 8**  
Schematic view of the first steps of the cycloaddition reactions starting from  $py \rightarrow PS_2Cl$  and tolane.



**Fig. 9**  
Structures of  $[(VO)_6(tBuPO_3)_8 \subset Cl^-]$  (left) and  $[(V_3O_5)(VO)_4(NO_3)_8]$  (right). Secondary building groups are rendered as polyhedra. Templates ( $Cl^-$  and  $NO_3^-$  at the center) and hydrogen atoms were omitted for clarity. The additional  $[OVO_4]$ -pyramid in the  $NO_3^-$ -templated structure comes without hatching.

ting new materials for fields like catalysis and sensors [5]. A second route followed was to connect metal oxygen polyhedra by means large numbers of organic ligands. Recently it was shown, that organophosphonates and -arsonates can act as versatile ligands for the formation of structurally novel clusters and coordination polymers [6, 7].

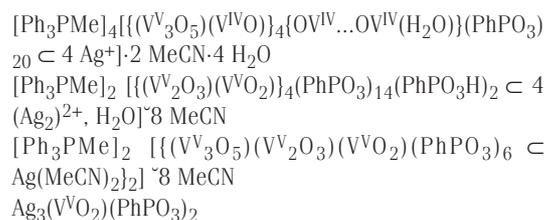
In extension of our systematic study of the formation of oxovanadium phosphates in aqueous media [8–10]

we included investigations on oxovanadium phosphonates with the aim of obtaining new phases suitable as precursors for potential oxidation catalysts. Furthermore, we wanted to know, how the conditions of formation of oxovanadium clusters influence the structure of the final products, *i.e.*, catalyst precursors.

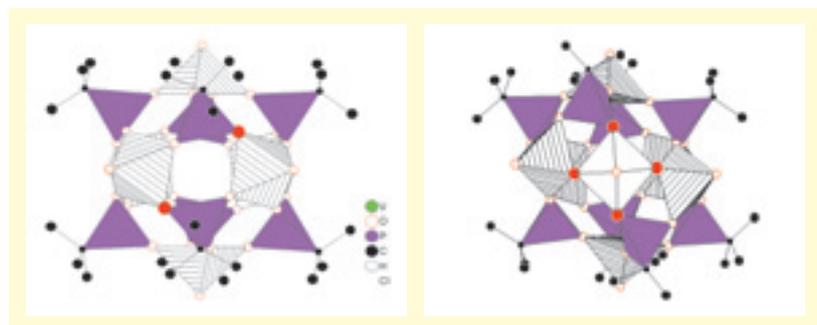
Thus, we studied the directing influence of templates and of the cation  $M^+$  in the starting dichlorovanadate,  $M[VO_2Cl_2]$ . Additionally, the influence of steric demand of the phosphonic acids used on the formed oxovanadium structures has been investigated.

One of the reactions we studied in greater detail was the solvothermal reaction of  $(Ph_4P)[VO_2Cl_2]$  with  $RPO_3H_2$  ( $R=Ph, tBu$ ) in  $CH_3CN$  or  $CH_2Cl_2$ , respectively. For different template anions ( $T$ ) large, spherical molecules of the general formula  $[(VO)_6(RPO_3)_8 \subset T]$  (Fig. 9 left) were found to be the main products of the reaction. Better than ordinary hotels, the thereby formed cavities adapt to the size of the included guests: for guests of diameters  $\leq 2.2 \text{ \AA}$  the cavities undergo a slight distortion, whereas for larger guests an additional  $[OVO_4]$  unit in the circumferential walls provides the extra room needed for a comfortable fit. Thus, the complexes formula reads no longer  $[(VO)_6(RPO_3)_8 \subset T]$  but becomes  $[(V_3O_5)(VO)_4(RPO_3)_8 \subset NO_3^-]$  instead (Fig. 9 right) [11].

In another set of experiments we studied the influence of stoichiometry on the phase formation in the system  $(Ph_3PMe)[VO_2Cl_2] / PhPO_3H_2 / AgNO_3 / MeCN$ . What makes this reaction special is the intermediary formation of  $[VO_2(NO_3)_2]^-$  and of the  $VO_2^+$  cation respectively as potential building blocks. These are capable of forming oligomeric oxovanadium groups by condensation. After complete removal of chloride by precipitation in the form of  $AgCl$  using an excess of  $Ag^+$  ions and the addition of different amounts of phosphonic acid one obtains silver containing oxovanadium phosphonates of variable composition and structure depending on the  $Ag/V$  and  $H^+/V$  ratios, *e.g.*



For ratios of  $H^+/V$  in the range 1...6, anions with condensed oxovanadium groups are formed whereas for ratios  $H^+/V$  lower than 1 only the coordination poly-



meric compound  $\text{Ag}_3(\text{VO}_2)(\text{PhPO}_3)_2$  featuring monomeric  $\text{VO}_2$  – units was obtained. Examples for the different structural motifs of silver containing oxovanadium phosphonates are given in the following Figures.

Fig. 2 (see above) shows the anion of  $[\text{Ph}_3\text{PMe}]_2 \{(\text{V}^{\text{V}}_2\text{O}_3)(\text{VO}_2)_4(\text{PhPO}_3)_{14}(\text{PhPO}_3\text{H})_2 \subset 4(\text{Ag}_2)^{2+}, \text{H}_2\text{O}\} \cdot 8 \text{ MeCN}$ . Key features are condensed  $\text{V}_2\text{O}_3$  units and the diatomic  $\text{Ag}_2^{2+}$  cations. The structure of  $\text{Ag}_3(\text{VO}_2)(\text{PhPO}_3)_2$ , depicted in Fig. 10 does not contain oligomeric oxovanadium units but monomeric di-oxovanadyl cations  $\text{VO}_2^{2+}$  in distorted trigonal bipyramidal coordination instead. This cation is part of a branched  $\{(\text{VO}_2)(\text{PhPO}_3)_3\}_\infty$  single stranded chain resembling the chains of tetrahedra in alkaline metavanadates or polyphosphates, respectively. The chains are connected by  $\text{Ag}_3$  and oxygen atoms not involved in the chain structure. Thus, layers are formed, which are separated from each other by hydrophobic phenyl groups. Between two of these layers a dense network of  $\text{Ag}_1$ - $\text{Ag}_2$  metal bonds with  $d(\text{Ag}-\text{Ag}) = 3.13 - 3.42 \text{ \AA}$  is formed.

Initial experiments to check the suitability of the aforementioned oxovanadium organophosphonates as precursors for heterogeneous catalysts did show that these compounds due to their structural and stoichiometric variability open up new, promising routes towards catalytically active  $\text{VP}_x\text{O}_y$  systems. Thus, the thermal decomposition of  $(\text{Ph}_4\text{P})[(\text{VO})_4(\text{PhP}(\text{O})_2\text{OP}(\text{O})_2\text{Ph})_4 \subset \text{Cl}]$  in air gives pure crystalline  $\beta\text{-VO}(\text{PO}_3)$  whereas from  $[(\text{VO})_6(\text{tBuPO}_3)_8 \subset \text{Cl}]$  a mixture of  $\beta\text{-VO}(\text{PO}_3)$  and a mixed valence vanadium oxide is formed.

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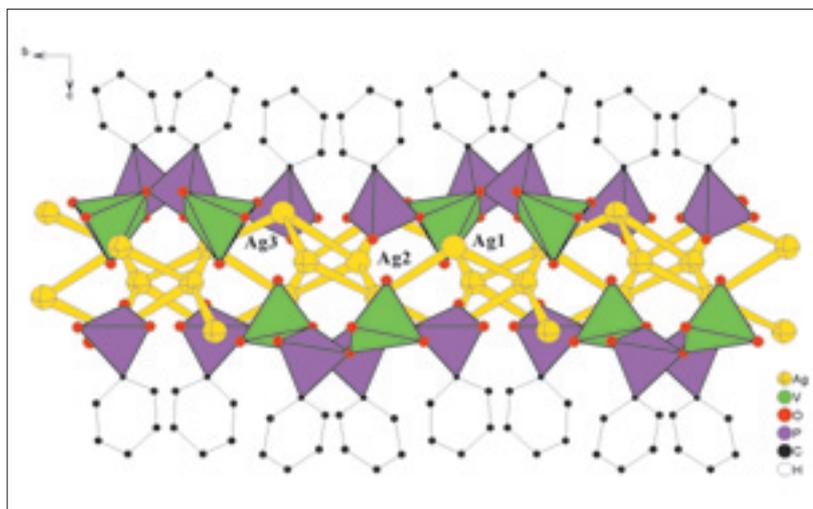


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**Fig. 10**  
Schematic structure of  $\text{Ag}_3(\text{VO}_2)(\text{PhPO}_3)_2$ . View along crystal axis a showing different sites of silver ions and the network of metal-metal-bonds.