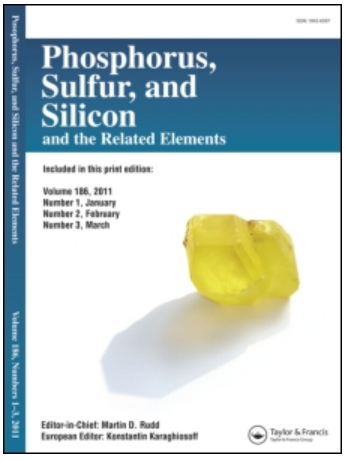

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SYNTHESIS OF CYCLIC METAL CONTAINING PHOSPHORUS-NITROGEN COMPOUNDS - A COMPARISON WITH METAL CONTAINING SILOXANES

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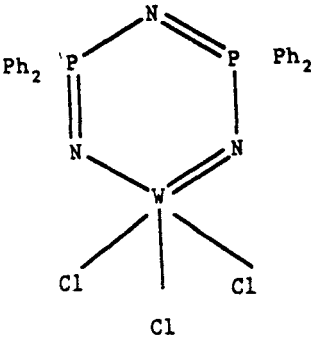
Abstract The preparation and properties of six- and higher-membered metallacyclophosphazenes is described. A new mechanism for the polymerisation of cyclophosphazenes is discussed. The PN unit is isoelectronic to the SiO unit and therefore metal containing siloxanes have been prepared. They function as model compounds for metal oxides on silica surfaces.

The phosphazene unit, $-N=P(R_2)-$, is isoelectronic with the siloxane group, $-O-Si(R_2)-$. Both have an extensive chemistry forming cyclic and acyclic molecules as well as polymeric materials. Innumerable derivatives of both the phosphazenes and the siloxanes have been prepared during the last 150 years. In contrast, metal containing phosphazene and siloxane ring systems are rare.[1,2]

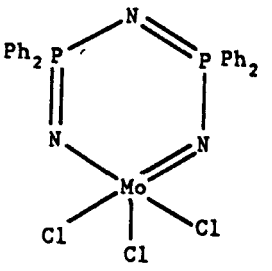
In 1986 we reported on the preparation and structural investigation of the first six-membered metallacyclophosphazenes.[3] In the meantime we have developed the following routes for the preparation of these molecules.[4]

1. $[H_2NPPh_2NPPh_2NH_2]Cl + WCl_6 \rightarrow$



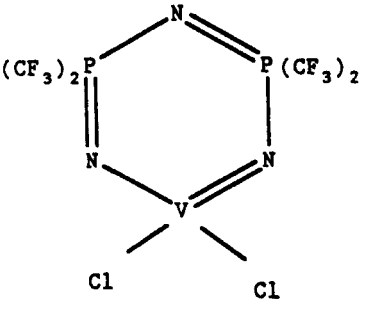
1

2. $[H_2NPPh_2NPPh_2NH_2]Cl + N \equiv MoCl_3 \rightarrow$



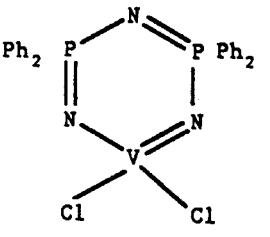
2

3. $(CF_3)_2P(Cl)=NSiMe_3 + Me_3SiN=VCl_3 \rightarrow$



3

4. $Ph_2P(Cl)=NSiMe_3 + V(O)Cl_3 \rightarrow$

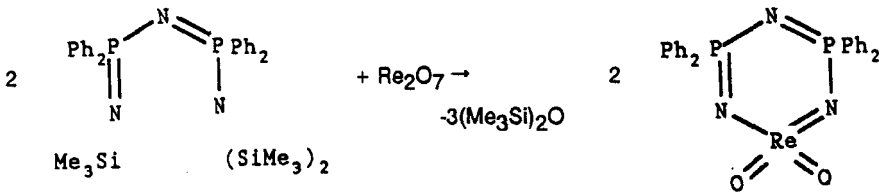


4

All these ring systems **1** - **4** might be considered to be fused from phosphazenes and metal halides in high oxidation states. The common features of these systems

are the metal halide bonds. Furthermore it turned out that nucleophilic substitution reactions often resulted in unpredicted products.

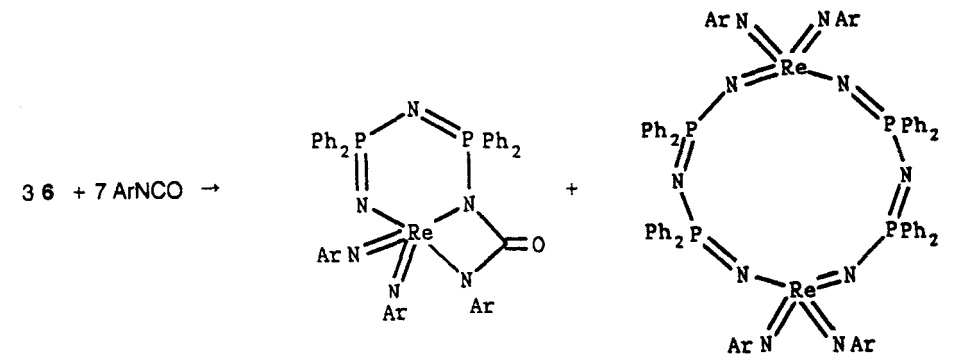
The six-membered rings can be opened to generate polymers. However, the polymers contain hydrolytically unstable metal halide bonds. Therefore we were interested in synthesizing systems containing phosphazene and metal oxides. A straightforward reaction was developed according to the following equation.[5]



5 **6**

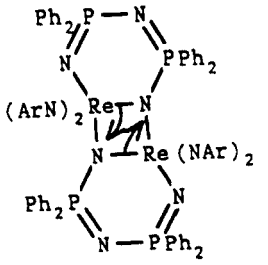
Compound **6** is the first cyclophosphazen metal oxide. Compound **5** turned out to be a versatile reagent for the preparation of metal containing ring systems.

Compound **6** can be converted by ArNCO to generate a [2+2] cycloaddition product **7** and the first metal containing twelve-membered puckered ring **8.**



7 **8**

We assume that compound **6** is already a dimer and that the formation of compound **8** ist the first step in forming generally P-N polymers by [2+2]self-adduct formation **9**.

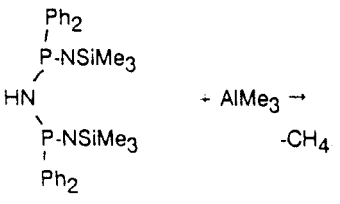


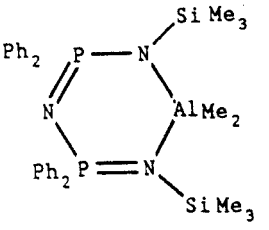
→ **8**

9

The polymerisation of $P_3N_3Cl_3$ proceeds in the presence of a Lewis acid. An intermediate of type **9** might be the initial step for generating a twelve-membered ring which then is converted stepwise to the linear polymer according to the mechanism mentioned above. A product of type **9** was isolated and then characterized as the first cyclotriazophosphorine metal oxide of composition $[\overline{N=PPh_2N=C(4\text{-}CF_3C_6H_4)\text{-}N=ReO_2}]_2$.

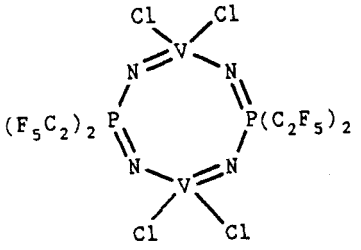
Compound **5** and its protonated derivative $HN(PPh_2NSiMe_3)_2$ have been used for the reaction with metal alkyles. An example is given in the following equation.[6]



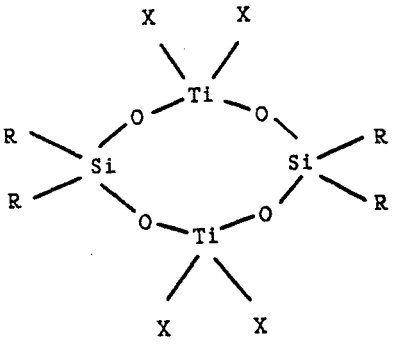


10

Eight-membered rings **11** are prepared from $(C_2F_5)_2P(Cl)=NSiMe_3$. Eight- and twelve-membered metal containing siloxanes **12** are using $(tBu)_2Si(OH)_2$ and metal halides as educts for the preparation.[7]



11



12

Especially the titanium compounds of type **12** have very interesting properties. The hydrolysis of $Cp^*TiCl_2OSitBu_2OH$ ($Cp^* = C_5Me_5$) leads to the first dinuclear hydroxide **13** of Ti(IV). Compound **13** represents a frozen situation of a product in a process of eliminating a water molecule.[9]

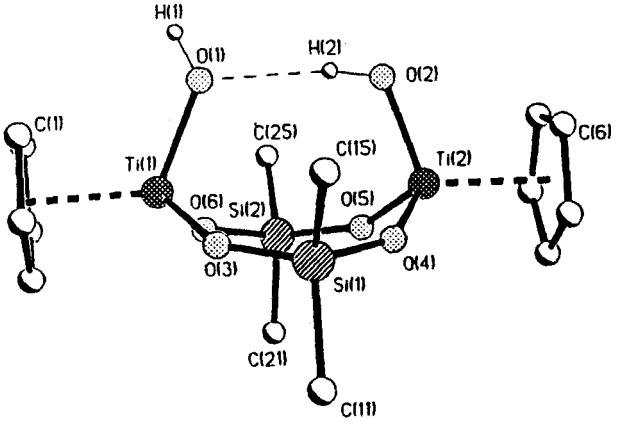


FIGURE 1 Molecular structure of **13** in the crystal (side view). The methyl groups are omitted for clarity.

Using $tBuSi(OH)_3$ and Re_2O_7 as starting materials leads to the siloxane metal oxide,[10] $[tBuSiOReO_4]_4$ **14**. The molecular structure of **14** in the solid state is shown in Figure 2. The metal containing siloxanes might be considered as model compounds for metal oxides on silica surfaces.

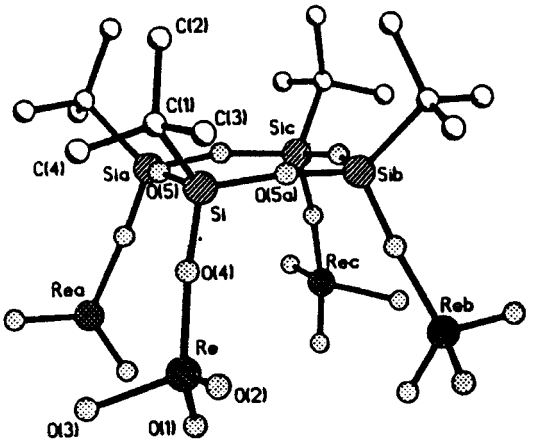


FIGURE 2 Molecular structure of $[tBuSiOReO_4]_4$ **14**

All the compounds mentioned above have been characterized by single crystal X-ray structural analysis.

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