Metal Containing Compounds: Precursors for new Reactions and Materials

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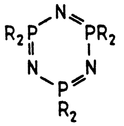
Summary

The syntheses of six-membered metallacyclophosphazenes and metal containing siloxanes are described. Phosphazene and siloxane groups are isoelectronic a concept aiding in the synthesis of the target molecules. The metal containing silicones function as model compounds for metal oxides on silica surfaces. A first example of a metal containing borazine is given. Some of the compounds function as precursors for chemical vapor deposition.

1 Introduction

The six-membered $[NP(R_2)]_3$ (**1**) and $[OSi(R_2)]_3$ (**2**) ring systems are isoelectronic. Both have an extensive chemistry forming differently substituted molecules as well as polymeric materials.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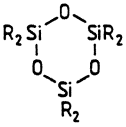
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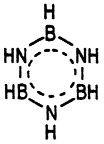
Innumerable derivatives of both the phosphazenes and the siloxanes have been prepared during the last 150 years [1]. In contrast, metal containing phosphazene and siloxane ring systems are rare. A number of metal containing four- to twelve-membered ring systems will be described.

Another well known ring system, the inorganic analog of benzene, $(HBNH)_3$ (**3**), a compound commonly called borazine, was prepared by Stock et al. [2] 76 years ago.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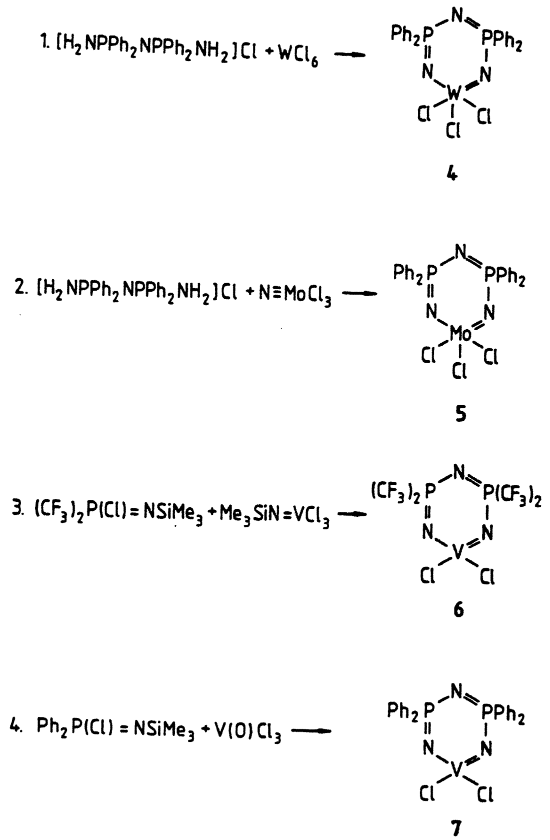
While a few metal containing benzene derivatives are known, metal containing borazines have been prepared only recently.

Particular emphasis will be given to organometallic oxides as model compounds for metal oxides on silica surfaces.

D. Enders et al. (eds.), *Organic Synthesis via Organometallics (OSM 4)*

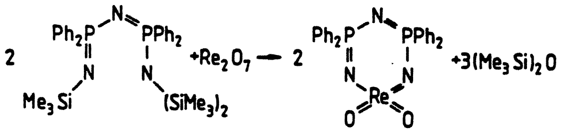
2 Metal Containing Cyclophosphazenes

In 1986 we reported on the preparation and structural investigation of the first six-membered metallacyclophosphazenes [3]. We have developed the following routes [1] for the preparation of molecules **4** - **7**.



All these ring systems **4** - **7** 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 straightforeward reaction was developed to the following equation.

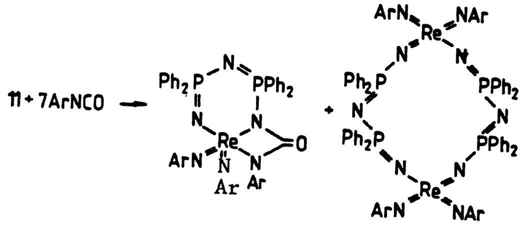


8 11

Compound **8** was prepared from $[H_2NPPh_2NPPh_2NH_2]Cl$ and KH or NEt_3 to yield $H[N(PPh_2NH)_2]$ the dehydrohalogenated intermediate. Treatment of the intermediate with Me_2NSiMe_3 resulted in the formation of $H_2NPPh_2NPPh_2NSiMe_3$ **9** or $HN(PPh_2NSiMe_3)_2$ **10**. This is only dependant on the ratio of the starting materials. $HN(PPh_2NSiMe_3)_2$ is converted to the corresponding lithium salt by means of nBuLi or $LiNH_2$ and finally treated with Me_3SiCl to yield $Me_3SiNPPh_2NPPh_2N(SiMe_3)_2$ **8** [4].

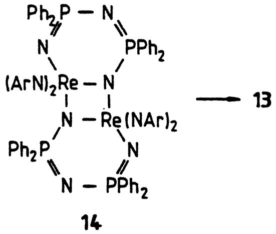
Compound **11** is the first cyclophosphazene metal oxide [5]. It appears possible that **11** is dimeric in the solid state, since the only known cyclotriazaphosphazine metal oxide $[NPPh_2NC(4\text{-}CF_3C_6H_4)NReO_2]_2$ is also dimeric, which has been established by a single crystal structure investigation. The reaction of **11** with excess ArNCO (Ar = 2.6 diisopropylphenyl) leads to a mixture of products containing the cyclophosphazene metal imides **12** and **13**.

Compound **12** is generated by a [2+2] cycloaddition reaction. This addition at the ReN double bond of **11** leads to a distorted square-pyramidal arrangement of the ligands at the rhenium in **12**. An otherwise possible planarity of the six-membered ring is therefore removed. The average deviation from the plane is 20 pm.



12 13

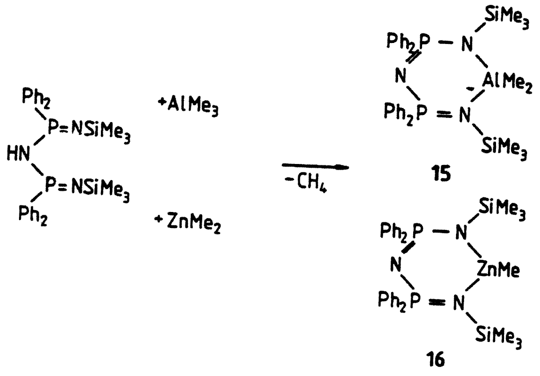
In the dimetallatetraimidophosphazene **13** which is only isolated in small quantities, the Re centers show an almost tetrahedral coordination and the twelve-membered ring is puckered. We assume that **13** is formed from the dimer **14** by opening two of the ReN bonds generating the twelve-membered ring **13**.



14

In the presence of Lewis acids the polymerization of $P_3N_3Cl_6$ leads to the corresponding polymer. Therefore, the formation of a phosphonium ion is assumed, which, as the rhenium atom in **14** initiates the cycloaddition. It is aparent that if the [2+2]-selfaddition is continued to result in larger molecules it could represent a novel polymerisation mechanism by cyclophosphazenes.

Compound $HN(PPh_2NSiMe_3)_2$ **10** has been used for the reaction with the metal alkyles $AlMe_3$, $GaMe_3$, $InMe_3$ or $ZnMe_2$ to yield for example **15** and **16** respectively under elimination of CH_4.

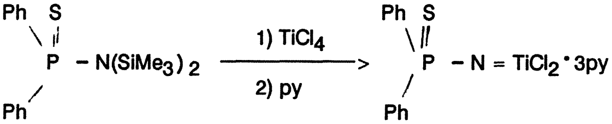


15 and **16** are crystalline white solids which have been characterized by single crystal X-ray structural analysis. In all cases we observed only the reaction of one methyl group at the metal center.

3 Compounds Containing Ti=N and Zr=N Double Bonds

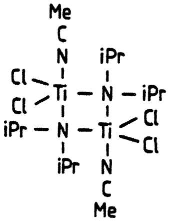
Inter- and intramolecular cyclisation reactions are widely used in organic chemistry for synthesizing carbocycles. The tendency of a molecule with carbon-carbon multiple bonds to undergo a cycloaddition reaction with another unsaturated molecule depends on two factors, whether the other molecule contains isolated or conjugated double bonds, and whether the system is activated by heat or by light.

There is a considerable interest in the extent to which M=NR functional groups undergo such reactions. During our study of the chemistry of titanium-nitrogen compounds we observed that coordination of electron pair donors at the titanium atom leads to the stabilization of imidotitanium complexes [6,7]. Thus, reaction of the thiophospinic acid amide **17**



17 **18**

with $TiCl_4$ and subsequent treatment of the initial product with pyridine (py) yields the orange red, crystalline compound **18**. In constrast, reaction of the oxygen analogue of **17** leads to an eight-membered ring compound [8]. The exchange of phenyl groups in **17** for isopropyl substituents gives the starting material **19**. The reaction of **19** with $TiCl_4$ leads in the presence of pyridine to the corresponding titanium imido complex [7], $(iPr)_2P(S)N=TiCl_2$ 3py **20**. However, the reaction of **19** with $TiCl_4$ in the presence of acetonitrile forms the [2+2] cycloaddition product **21** which can be converted to **20** in the presence of pyridine. The cycloaddition product **21** consists of a planar



21

four-membered Ti_2N_2 ring with pairwise nonequal Ti-N bond lengths of 186.3(2) and 206.0(2) pm, respectively. Thus, the monomer-dimer formation can be directed by changing the basicity of the solvents. The imido ligand in **18** and **20** is bonded almost linearly to the metal [**18** Ti-N-P 171.4(2)°, **20** Ti-N-P 172.5(2)°].

A Cp* (Cp* = C_5Me_5) substituted titanium compound **22** containing a TiN double bond was obtained according to the following reaction sequence [9].

$$Cp^*TiCl_3 + Me_3SnNHtBu \longrightarrow Cp^*TiCl_2NHtBu + Me_3SnCl$$

$$Cp^*TiCl_2NHtBu + LiN(SiMe_3)_2{\cdot}Et_2O + py \longrightarrow$$
$$Cp^*Ti(Cl)=NtBu{\cdot}py + LiCl + HN(SiMe_3)_2 + Et_2O$$

22

py = pyridine

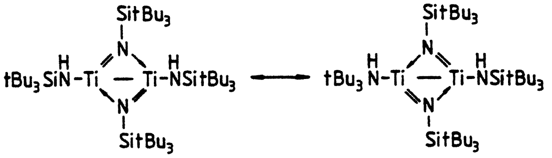
Similar to **22** $Me_3SiC_5H_4Ti(Cl)=NtBu\cdot py$ **23** was prepared. Up to date a few other monomeric titanium imido complexes have been crystallographically characterized. All compounds knwon are summarized in Table 1.

Table 1. Monomeric titanium imido complexes

Compound		TiN bond length [pm]	Literature
$Ph_2P(S)N=TiCl_2\cdot 3py$	**18**	172.0(2)	[6]
$(iPr)_2P(S)N=TiCl_2\cdot 3py$	**20**	172.3(2)	[7]
$PhN=Ti(2.6\text{-}iPr_2C_6H_3O)_2\cdot 2py'$		171.9(3)	[10]
$tBuN=Ti(Cl)C_5Me_5\ py$	**22**	169.8(4)	[9]
$(Et_4C_4NC_6H_4\text{-}NC_6H_4\text{-}NC_6H_4)Ti(OAr)_2$		170.8(5)	[11]
$tBuN=TiCl_2(OPPh_3)_2$		167.2(7)	[12]

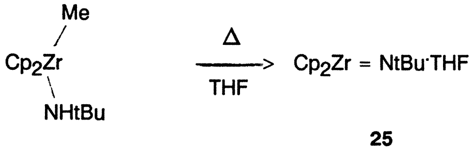
py = pyridine, py' = 4-pyrrolidinopyridine

Wolczanski reported on the exposure of the alkyl complexes $(tBu_3Si)(THF)RTi=NSitBu_3$ (R = Me, tBu) to hydrogen in benzene for 3 h at 65°C leading to the formation of $[(tBu_3SiNH)Ti]_2(\mu\text{-}NSitBu_3)_2$ **24** and concomitant methane and isobutane, respectively. A single crystal X-ray structural determination confirmed a short Ti-Ti bond distance (Ti-Ti 244.2(1) pm). The μ-$NSitBu_3$ groups form asymmetric bridges and the bonding properties are best described by the following resonance forms.



24 **24**

The first structural characterized zirconium imido complex of composition $Cp_2Zr = NtBu\cdot THF$ **25** was prepared in 1988 by Bergman et al. [14]. The starting material can be generated by heating Cp_2ZrMe_2 with one equivalent of $tBuNH_2$. This results in loss of one equivalent of methane and generation of the zirconocene methyl amide. Alternatively, the methyl amide can be prepared by treatment ofCpZrMe(Cl) with the lithium salt of $tBuNH_2$.



$$Cp_2Zr(Me)(NHtBu) \xrightarrow[THF]{\Delta} Cp_2Zr = NtBu\cdot THF$$

25

When the zirconozene methyl amide is subjected to thermolysis in THF compound **25** can be isolated.

The X-ray structural analysis of **25** showed a Zr-N bond length of 182.6(4) pm.

Rothwell et al. [15] reported on the structural characterization of [Zr(NC_6H_3iPr-2.6)($NHC_6H_3iPr_2$-2.6)$_2$·2py' **26** (py' = 4-pyrrolidinopyridine) and [Zr($OC_6H_3tBu_2$-2.6)(NPh)·2py' **27** with Zr-N bond lengths of 186.8(3) and 184.4(9) pm, respectively.

(η^5-C_5Me_5)Zr($NHC_6H_3iPr_2$-2.6)$_3$ **28** reacts at 85°C in the presence of pyridine under elimination of $H_2NC_6H_3iPr_2$-2.6 to yield ($\eta^5$$C_5Me_5$)Zr($NHC_6H_3iPr_2$-2.6)$NC_6H_3iPr_2$-2.6)·py **29** [16].

(η^5-C_5Me_5)Zr(NHR)$_3$ + py ——> (η^5-C_5Me_5Zr(NHR)(NR)·py + H_2NR

28 **29**

R = 2.6-$iPr_2C_6H_3$

The formation of **29** is based on ^{1}H-NMR and MS spectra. The monomeric structure of **29** was determined by a single crystal structure investigation. Compound **29** has a distorted piano-stool structure and contains three different Zr-N bonds. The bond length of the coordinating pyridine [234.5(6) pm], the amido Zr-N bond length [210.6(5) pm] and the imido bond distance [187.6(4) pm). The Zr=N-C bond angle is almost linear [171.4(4)°].

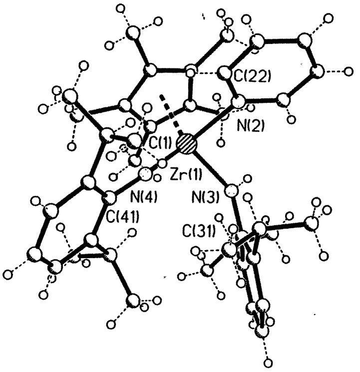
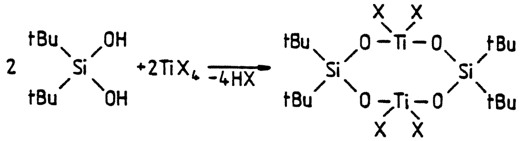


Figure 1 Molecular structure of **29**

4. Metallacyclosiloxanes

The phosphazene unit, -N=P(R_2)-, is isoelectronic with the siloxane group -O-Si(R_2)$_2$-. Consequently after preparing cyclometallaphosphazenes we were interested in synthesizing metallacyclosiloxanes. Our studies began with the reactions of $(tBu)_2Si(OH)_2$ **30** with $TiCl_4$, $TiBr_4$ and TiI_4 leading to the eight-membered ring compounds **31** [17].



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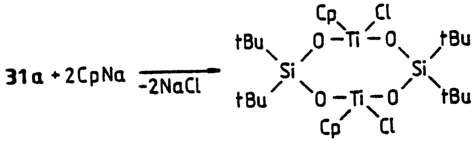
31

31a: X = Cl
31b: X = Br
31c: X = I

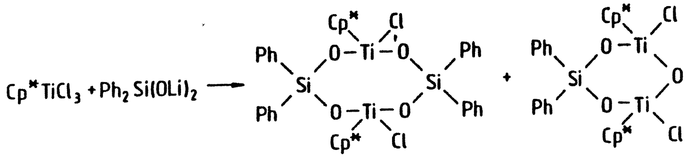
Compounds **31a** and **31b** were both investigated by X-ray diffraction. In both there is distorted tetrahedral geometry at the titanium atoms. The halides in **31a** may be replaced by different methods. When **31a** was reacted with CpNa(Cp = C_5H_5) the Cp substituted Ti compound **32** was isolated.



32

Compound **32** is also obtained by the reaction of $CpTiCl_3$ with $(tBu)_2Si(OLi)_2$. Substitution at Ti in **31a** was found to be difficult, possibly as a result of the steric demands of the tBu_2Si groups. However, the reaction of $(Me_3Si)_2NLi$ leads to $[(Me_3Si)_2NClTiOSitBu_2O]_2$ **33**.

Attempts to react $Cp^*M(Cp^* = C_5Me_5$, M = Li, Na) with **31a** were unsuccessful. However, when $Cp{*}TiCl_3$ was treated with $Ph_2Si(OLi)_2$ the eight-membered ring **34** as well as the six-membered ring **35** were formed [18].



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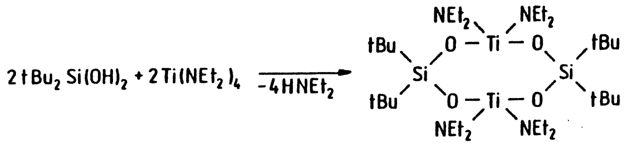
The halide-free eight-membered ring **36** is obtained by the reaction of **30** with $Ti(NEt_2)_4$.

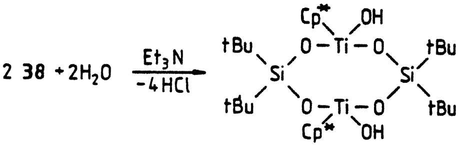


30 36

Of particular interest is compound **37**. It is formed according to the following equations.

$$Cp^{*}TiCl_3 + tBu_2Si(OH)_2 \longrightarrow Cp^{*}TiCl_2\text{-}OSitBu_2OH$$

30 38



37

The structure of **37** was determined by X-ray diffraction. Compound **37** contains one O-H···O bond and one non-bridging OH group. The Ti-O bond length with the additonal hydrogen bond is longer [Ti-O 187.2(2) pm] in comparison to the other exocyclic Ti-O bond length [Ti-O 183.7(2) pm]. Thus, compound **37** demonstrates a frozen position of eliminating a water molecule. A side view of the molecular structure in the crystal is shown.

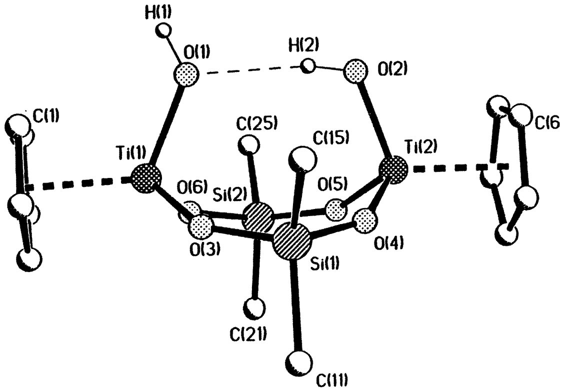
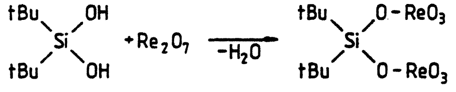


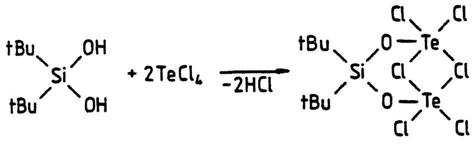
Figure 2 Side view of the molecular structure of **37**. The methyl groups are omitted for clarity

two molecules of THF as additional ligands, while the boron has a distorted trigonal planar coordination sphere [17,20].

Re_2O_7 and **30** yield the acyclic $tBu_2Si(OReO_3)_3$ **38** under elimination of water, while $TeCl_4$ gives the chloro-bridged $tBu_2Si(OTeCl_3)_2$ **34** with pentacoordinated tellurium atoms [21].

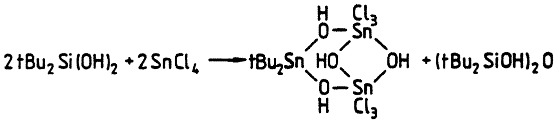


30 **38**



30 **39**

In the case of $SnCl_4$ the formation of an eight-membered ring was not observed. The reaction proceeds according to the following scheme under formation of the adduct **40**.



30 **40** **41**

$$2\,\mathbf{30} \longrightarrow (tBu_2SiOH)_2O + H_2O$$

41

$$\mathbf{30} + 2\,[SnCl_3OH] \longrightarrow \mathbf{40}$$

42

This reaction can be interpreted in such a way that the silandiole **30** is converted to the disiloxandiole **41** under formation of water. Obviosly this water hydrolizes partially $SnCl_4$ forming $[SnCl_3OH]$ **42** [20].

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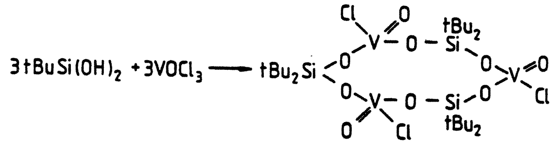
The compounds $[tBu_2Si(O_2)MoO_2]_2$ **43** and $[tBu_2Si(O_2)V(O)Cl_2]_3$ **44** have been prepared using **30** and $VOCl_3$ or MoO_2Br_2, respectively [22]. While **43** forms an eight-membered ring **44** was isolated as a twelve-membered ring compound. In **44** the ring is puckered and the Si-O-V angels are varying between 141.7(2) and 173.8(3)°. These great differences are frequently observed in Si-O-metal systems.



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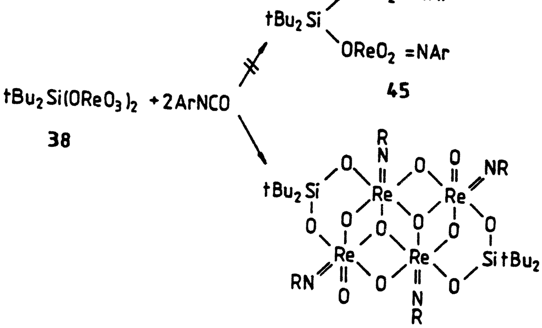
5. Model compounds for metal oxides on silica surfaces

Heterogeneous silica supported transition metal oxides play an important role as catalysts in industry [23,24]. These catalysts have increased the interest in the chemical processes which occur on the surface of heterogeneous catalysts. But to a large extent the processes taking place on the catalyst surface are not understood. Their study is hindered by the complicated structure of these silicate surfaces making the synthesis of model substances essential. Compounds **38** and **43** are models for silica supported metal catalysts which structurally resemble transition metal containing surface sites.

The substitution of two oxygen atoms in **38** occurs under elimination of CO_2 when this compound is treated with excess of 2.6-diisopropylphenylisocyanate (ArNCO). However, the compound expected is not the monomeric derivate **45** but rather the cluster **46**.



45

38

46

In contrast to the starting material **38** where a distorted tetrahedral surrounding of the rhenium atoms is observed, in **46** a distorted octahedral geometry is found. The replacement of oxygen by the isolobal NR group changes the coordination number at rhenium from four to six. Under this observation we are assuming that the energy differences between tetrahedral and octahedral geometries are small and might be responsible for the catalytic properties of rhenium(VII) [25].

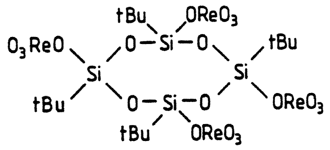
An interesting starting material for generating model compounds for metal oxides on silica surfaces is $tBuSi(OH)_3$ **47**. This compound was prepared by hydrolysis from $tBuSiCl_3$ and water in the presence of aniline in 94% yield.

$$tBuSiCl_3 + 3H_2O \xrightarrow[-3HCl]{} tBuSi(OH)_3$$

47

The X-ray crystal structure revealed that molecules of **47** are linked by hydrogen bridges to form corrugated layers. Bonding interactions between the layers are prevented by the hydrophobic tBu groups [26].

The reaction of **47** with Re_2O_7 in a 2:1 molar ratio affords $[tBuSiO(ReO_4]_n$ (n = 3,4) after elimination of water and exchange of H for ReO_3. Recrystallization of the initial precipitate from boiling acetonitrile gave transparent crystals of $[tBuSiO(ReO_4)]_4$ **48**.



48

Compound **48** is the first example of a molecule containing four ReO_4 groups. In the crystal structure of **48** we observed that in the solid state all ReO_4 groups are on one side of the molecule.

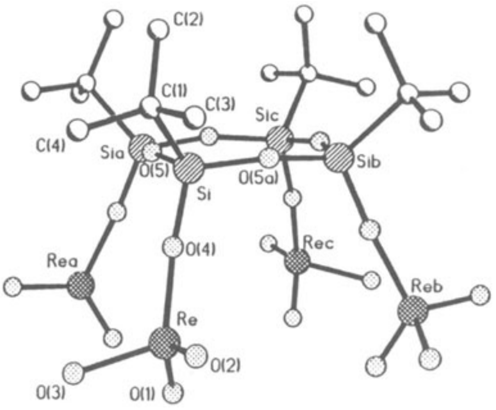


Figure 3 **Molecular structure of 48 in the crystalline state**

An introduction of two ReO_4 groups at antimony is possible when triphenylstibinoxide is treated with Re_2O_7 [27].

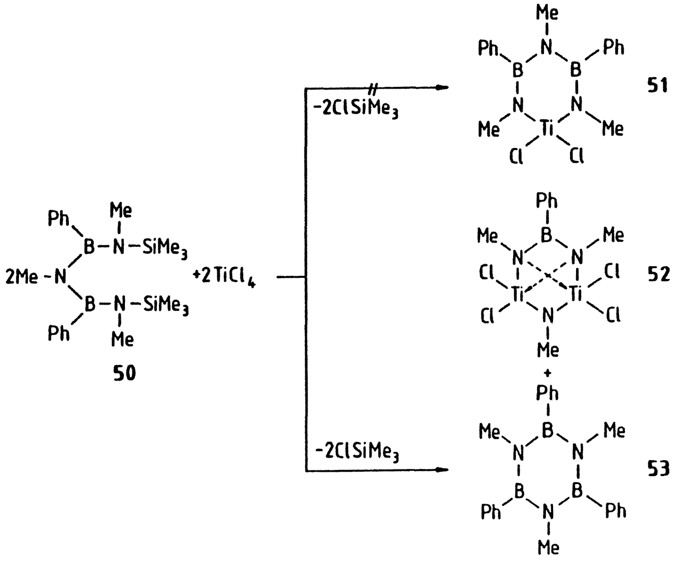
$$(Ph_3SbO)_2 + 2Re_2O_7 \xrightarrow{\hspace{3em}} \underset{\mathbf{49}}{2Ph_3Sb(OReO_3)_2}$$

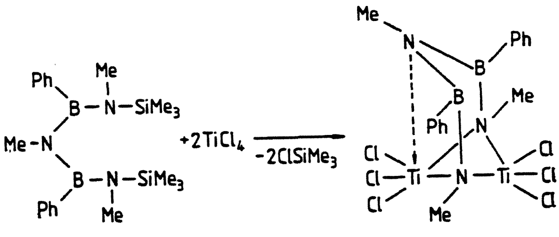
In compound **49** antimony has a trigonal bipyramidal geometry where the phenyl groups are in equatorial and the ReO_4 groups in axial positions.

5. Cyclometallaborazines

Borazine was first reported by Stock and Pohland [2]. It is also known as inorganic benzene and was isolated from the mixture of products obtained by reacting B_2H_6 and NH_3. Borazine has a resemblance to benzene and the physical properties of the two compounds are similar. The planarity of the borazine molecule is shown by MO calculations to be stabilized by the π bonding, however, the π electrons are only partially delocalized. The number of borazines substituted at the ring framework is legion. Only recently the first examples were reported which contain transition metal atoms as building blocks in the borazine framework.

Methyl-bis(methyl(trimethylsilyl)aminophenylboryl)amine **50** served as educt for the synthesis of the target molecule.

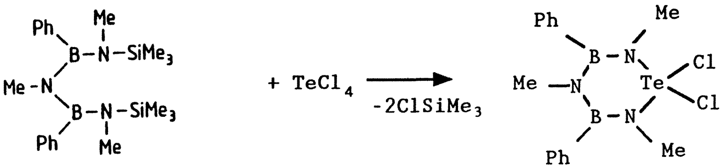




50 **54**

Compound **54** decomposes via an S_{Ni} reaction to give **52** and $PhBCl_2$. The latter compound then reacts with a further equivalent of **50** to give **53**. The structure of **52** can be described as a geometric body whose surface consists of four bent irregular squares. The reason for this nonplanar configuration are the strong intramolecular Ti···N interactions [28].

The first six-membered borazine containing a tellurium atom as a building block in the ring frame-work was obtained from **50** and $TeCl_4$. Compound **55** was investigated by an X-ray structural analysis showing the six-membered ring in a non planar configuration [29].



50 55

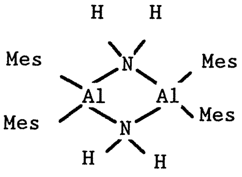
In addition it is worth mentioning that the number of metal containing aromatic systems are rare [30-33].

6. Organometallic precursors for CVD

Aluminum microstructures can be generated efficiently using thermal CVD from (trimethylamine)trihydridoaluminum **56** on laser generated spatially selective prenucleation pattern of a Pd-catalyst. The aluminum structure generated at 200°C was 50 μm wide and 7 μm high. The two step process combines the advantages of two methods. The laser induces the spatially selective pattern of the Pd-catalyst, whereas the macroscopic growth is done by conventional well-understood chemical vapor deposition [34].

AlN is generated by CVD using $[Mes_2AlNH_2]_2$ **57**(Mes = Mesityl) as a starting material [35]. Compound **57** is prepared from Mes_3Al and ammonia resulting in the formation of the adduct $Mes_3Al{\cdot}NH_3$ which eliminates at elevated temperatures MesH to yield **57**. The advantage of compound **57** for this process is prenucleation pattern of a Pd-catalyst. The aluminum structure generated at 200°C was 50 μm wide and 7 μm high. The two step process combines the advantages of two methods. The laser induces the spatially selective pattern of the Pd-catalyst, whereas the macroscopic growth is done by conventional well-understood chemical vapor deposition [34].

AlN is generated by CVD using $[Mes_2AlNH_2]_2$ **57**(Mes = Mesityl) as a starting material [35]. Compound **57** is prepared from Mes_3Al and ammonia resulting in the formation of the adduct $Mes_3Al{\cdot}NH_3$ which eliminates at elevated temperatures MesH to yield **57**. The advantage of compound **57** for this process is its remarkable stability towards traces of moisture compared to alkyl derivatives of aluminum [35].



57

The generation of pure InP using $[(Me_3SiCH_2)_2InPHtBu]_2$ **58** and a 514.5 nm Ar-ion-laser for pyrolysis was not successful. Besides InP the sample contained a high percentage of SiC [36]. Another precursor was prepared from $(Me_3SiCH_2)_3In$ and $AdPH_2$ (Ad = adamantyl) in the presence of $AgNO_3$ leading to $[(Me_3SiCH_2)_2InPHAd]_2$ **59** in 30% yield [37]. Pyrolysis experiments have so far not been accomplished.

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