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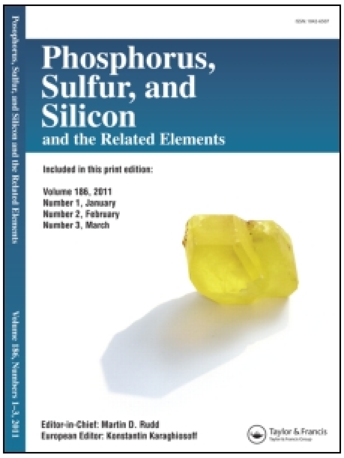

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Metal Containing New Inorganic Ring Systems Based on Siloxane and Phosphazane Frameworks

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High-field ^{31}P NMR spectroscopy and single crystal X-ray diffraction studies have been used to study the ring opening and nucleophilic substitution reactions of the λ^3-cyclotriphosphazane $[EtNPCl]_3$. The synthesis of the ring opened silicophosphonate $[RSi(OH)\{OP(O)(H)(OH)\}]_2O$ ($R = (2,6\text{-}iPr_2C_6H_3)NSiMe_3$) (1) represents the first ever molecular silicophosphonate to be isolated bearing free reactive hydroxyl groups. The structure and conformation of the bulky aryloxide substituted λ^3-cyclotriphosphazane derivative $[EtNP(OAr)]_3$ ($Ar = 2,6\text{-}iPr_2C_6H_3$) (2) has also been investigated. Interaction of 2 with transition metal precursor complexes leads to the isolation of phosphazane metal complexes with different mode of co-ordination of 2. Further, the reaction of $Cp^*Ti(OAr)Cl_2$ ($Ar = 2,6\text{-}(CH_3)_2C_6H_3OH$) with $O\{SiPh_2(OH)\}_2$ gave the eight-membered trititanosiloxane $[Cp^*Ti(Cl)\ \{O(SiPh_2O)_2SiPh_2O)$ (3). Siloxane chain expansion effects, presumed to be a consequence of ring strain, have been observed in the product. The presence of reactive Ti-Cl bond in 3 offers opportunities for its reaction chemistry to be explored.

Keywords: cyclophosphazanes; silanetriols; siloxanes; titanosilicates

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INTRODUCTION

The metal containing siloxanes and phosphates are logical precursors to assemble tailored materials. Some of the cage siloxanes have been found useful as catalysts in several organic transformations.[1] The formation of cage structures seems to depend on the number of hydroxyl groups on the silicon / phosphorus atoms.[2] In order to explore the possibility of increasing the number of hydroxyl groups, a direct reaction between a λ^3 –cyclotriphosphazane and a silanetriol has been investigated in the present study. Further we are also interested in studying and vnraveling the conformational preferences of λ^3–cyclotriphosphazanes, which seem to depend on the bulkiness of the substituents on the ring atoms. In particular, the effect of a bulkier substitution on the phosphorus atoms of the ring system is investigated.

Organosilicon compounds containing Si-O-M (M= transition metal or main group element) linkages have been synthesized around the turn of the last century. However only in the last few decades (a) metallosiloxanes derived from silanediols $R_2Si(OH)_2$ and (b) metallasilsesquioxanes which contain a metal to silicon ratio of 1:7 (derived from trisilanol with three Si-OH groups situated at the open corner of an incompletely condensed silsesquioxane) have been reported and their chemistry has evoked a lot of interest among chemists, material scientists and physicists. The presence of metal in siloxane frameworks often results in high thermal stability and catalytic and conducting properties. Moreover, silicon polymers containing metal centers in the polymer backbone have metallosiloxanes as their precursors. Metallosiloxanes are structurally similar to the modified silica surfaces. They have been found to mimic the role of catalytically active surfaces and hence are useful in unraveling the reaction mechanisms for catalytic conversions. In view of the proven properties of titanosilicates, there has been an upsurge in the synthesis of molecular titanosiloxanes with cage structures, which would model the complex catalytically active heterogeneous Ti-doped zeolite systems. Earlier work has shown that, it is possible to vary the titanium to silicon ratio by a proper choice of the starting materials.[3] The above mentioned reasons prompted us to investigate the reactions of pentamethylcyclopentadienylsubstituted titanium chlorides with silanols. Preliminary results obtained in these studies are presented herein.

RING OPENING AND NUCLEOPHILIC SUBSTITUTION REACTIONS OF λ^3-CYCLOTRIPHOSPHAZANE $[EtNPCl]_3$

Unusual hydrocarbon soluble molecular silicophosphonate $[RSi(OH)\{OP(O)(H)(OH)\}]_2O$ (R = $Ar(SiMe_3)N$-) (**1**), which contains Si-O-P linkages along with abundant –OH groups is obtained in considerable yields from a direct reaction between a kinetially stabilized silanetriol $RSi(OH)_3$[4] and λ^3–cyclotriphosphazane $[EtNPCl]_3$.[5] Analytically pure sample of **1** was characterized by elemental analysis, EI-MS, IR, and NMR spectroscopic techniques. The IR spectrum of the sample shows the characteristic P-H stretching vibration.[6] The resonance due to the P-H proton in ^{1}H NMR appears at δ 5.73 ppm with a large $^1J_{PH}$ value of 670 Hz. The proton coupled ^{31}P NMR spectrum shows a doublet at δ -9.4 ppm, while the ^{29}Si NMR spectrum shows a doublet centered at –82.9 ppm. The molecular structure has been determined by single crystal X-ray diffraction studies. The molecule is built around a HO-P-O-Si(OH)-O-Si(OH)-O-P-OH inorganic backbone. Each of the phosphorus atoms has a (SiO)P(O)(H)(OH) local geometry. The only organic residue in the molecule is in the form of an R group on each silicon atom. Solubility of the compound in a variety of organic solvents is due to the complete enclosement of the inorganic core by the bulky organic moiety (R).

Although the chemistry of unsaturated phosphorus-nitrogen ring compounds are known for a very long time, trivalent saturated λ^3–cyclotriphosphazanes are relatively new and are less studied.[7],[8] Krishnamurthy and co-workers have studied alkoxide and aryloxide substitution reactions of λ^3–cyclotriphosphazane $[EtNPCl]_3$.[5],[9] We have now isolated a new bulky aryloxy group substituted compound and studied the effect of substituents on the six-membered ring conformation. Treatment of the *cis-trans* isomeric mixture of $[EtNPCl]_3$ with sodium salt of 2,6-diisopropylphenol followed by crystallization of the product yields *cis*-$[EtNP(OC_{12}H_{17})]_3$ (**2**) in 80%. Pure compound, recrystallized from petroleum ether (60-80°C), has been characterized by elemental analysis, IR, NMR and mass spectroscopy. All the phosphorus atoms are in a similar environment and give a singlet at δ 99.9 ppm in ^{31}P NMR spectrum. The molecular structure of this molecule has been determined by single X-ray diffraction studies. The steric hindrance of the aryl substitution causes all the nitrogen and phosphorus to the on single plane. The conformation of the ring is almost planar and the phosphorus atoms have distorted tetrahedral geometry around them.

CHARACTERISATION OF A TITANISILOXANE RING

Apart from the interest in the chemistry of titanosilicates, the last few years have also witnessed a sudden upsurge in the chemistry of titanium aryloxides due to their use as Diels-Alder and cross coupling / oligomerization catalysts. There have been reports also on the use of [CpTi(ArO)Cl_2] for the preparation of cationic alkyl derivatives of titanium. These compounds have been found to be useful as homogeneous catalysts. It has been possible to make heterogeneous catalysts by anchoring these cyclopentadienyl aryloxy titaniumdichloides on silicon surfaces. In order to explore the feasibility of such an approach, we have investigated the reactions of [(C_5Me_5)Ti(ArO)Cl_2] with silanols. A 1:1 reaction of Cp*Ti(OAr)Cl_2 with O{$SiPh_2$(OH)}$_2$ at room temperature has been carried out with the aim to synthesize model compounds representing cyclopentadienyl titanium (aryloxy) chloride anchored on silica surface. The work up of the reaction mixture resulted in the deposition of golden yellow crystals of the trititanosiloxane [Cp*Ti(Cl){O($SiPh_2O$)$_2$$SiPh_2O$)] (3) along with a dark brown amorphous material (which has been characterized as the starting precursor Cp*Ti(OAr)Cl_2). The titanosiloxane 3 has been fully characterized with the aid of elemental analysis, and IR and NMR spectroscopic studies. The compound shows a fairly good thermal stability. The microanalysis of the product suggested a possible ring expansion[10],[11] reaction with three SiR_2O units instead of two of them in the starting material. The IR spectrum of the compound contains bands due to the ν(Ti-O) at *ca.* 910 cm^{-1} and ν(Si-O-Si) at *ca.* 1156 cm^{-1}. There is also a strong peak around 980 cm^{-1}, which we attribute to Ti-O-Si stretching vibration, based on the earlier assignment by Roesky and co-workers through ^{18}O labeling studies.[12] The ^1H-NMR spectra shows a singlet for the protons of the methyl groups of C_5Me_5 ring (δ 1.94). It also shows a very complex multiplet pattern for the protons of the phenyl rings present on the three different silicon atoms. In order to clearly establish the structure of **3** in the solid-state, its molecular structure has been determined by single crystal X-ray diffraction studies. The Ti atom in the compound has a distorted tetrahedral geometry. Further the structure reveals that the eight membered siloxane ring exits in an open-book conformation, in contrast to the commonly observed crown structure for several metallasiloxanes.

We have also recently found that it is possible to generate several interesting ring and cage group 13 metallosiloxanes starting from group 13 "-ate" complexes and silanols such as $Ph_2Si(OH)_2$ and $O(Ph_2SiOH)_2$.

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