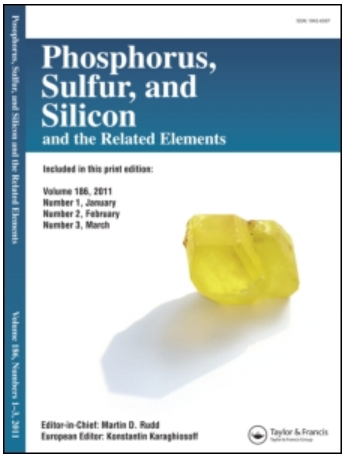

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INORGANIC HETEROCYCLES CONTAINING TWO OR THREE TRANSITION METAL ATOMS

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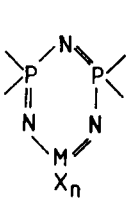
Abstract Syntheses and structures of novel inorganic heterocycles containing two or three transition metal atoms are reported. Examples include the first triazatrimetallabenzene derivative, $[Cp^*Ta(Cl)N]_3$, as well as eight-membered phosphazene rings containing two vanadium atoms.

INTRODUCTION

The chemistry of unsaturated inorganic heterocyles is of current interest. Recently we have developed general synthetic routes to cyclometallaphosphazenes[1-3]. Typical examples are the six-membered heterocycles 1 and 2, in which a phosphorus atom of the phosphazene ring is replaced by a transition metal atom:



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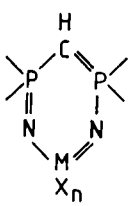

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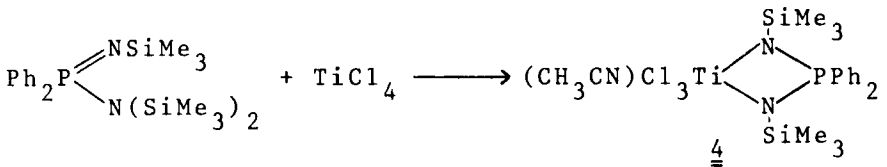
RESULTS AND DISCUSSION

Four-membered titanaheterocycles are formed in the reaction of the silylated amino-iminophosphorane 3 with $TiCl_4$[4]. Two cyclic products, orange yellow 4 and pale yellow 5 are isolated in moderate yield by fractional crystallization from acetonitrile:



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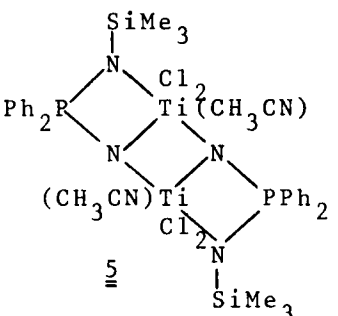


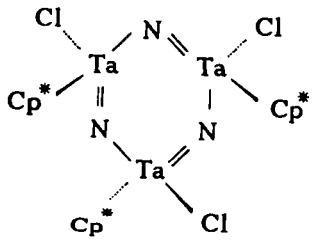
5

The molecular structures of 4 and 5 were determined by X-ray crystallography.

Nitrido complexes of the early transition metals form a variety of different structures[5]. Monomers and dimers are known as well as tri- and tetranuclear complexes and linear polymers. We describe here the preparation of the first cyclic trimer of a metal nitride. Cp^*TaCl_4 reacts with $N(SnMe_3)_3$ in toluene solution at room temperature to give the yellow metallacycle 6 in 67% yield:[6]

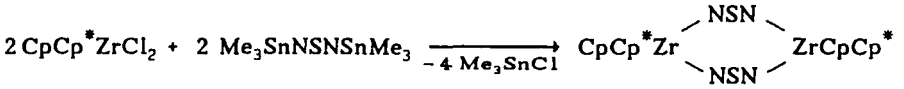
$$3\ Cp^*TaCl_4 + 3\ N(SnMe_3)_3 \xrightarrow{-9\ Me_3SnCl} \underset{6}{[Cp^*Ta(Cl)N]_3}$$

This very stable compound can be sublimed at ca. 250°C under high vacuum. The mass spectrum shows the molecular ion and the ^{1}H-NMR data (singlets at δ 2.09 and 2.13 ppm) indicate that the molecule contains non-equivalent Cp* ligands. An X-ray structure determination clearly shows the presence of the first triazatritantalabenzene derivative:



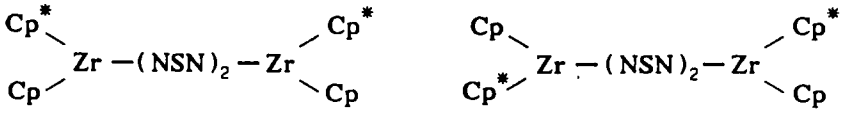
The six-membered Ta_3N_3 ring is not exactly planar but slightly distorted towards a boat conformation. The average tantalum-nitrogen bond length is 188(2) pm. This value lies right between those found for Ta=NR (174-178 pm) and Ta-NR_2 (195-203 pm). It is interesting to note that a cyclic trimer of a metal nitrido complex had already been postulated by Hoffmann et al. in 1986 [7].

Two eight-membered ring systems have recently been discovered using different synthetic routes. Treatment of $CpCp^*ZrCl_2$ with $Me_3SnNSNSnMe_3$ gives an unsaturated eight-membered metallacycle 7 with two zirconium atoms in the ring[8]:



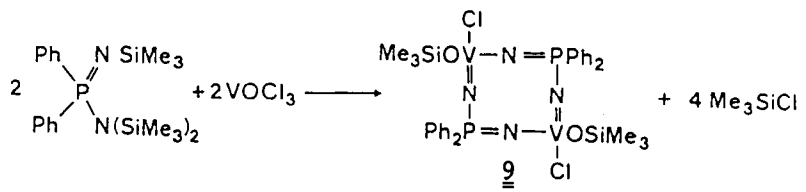
7

The yellow complex 7 is isolated in 65% yield and the by-product Me_3SnCl is easily removed by sublimation. The corresponding hafnium derivative 8 is obtained in an analogous manner. ^{1}H-NMR spectra of 7 and 8 exhibit two sets of signals for the Cp and Cp^* ligands in a ratio of approximately 1:2. This can be explained by the existence of two isomers. It can be assumed that isomer B is favored for steric reasons:



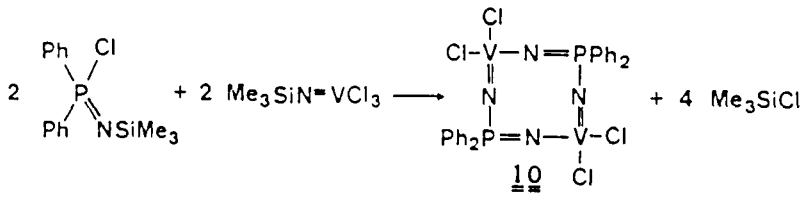
A B

Silylated iminophosphoranes were used as starting materials for the synthesis of the first eight-membered cyclometallaphosphazene ring system[9,10]. Treatment of $VOCl_3$ with $Ph_2P[N(SiMe_3)_2]NSiMe_3$ in acetonitrile solution results in the formation of dark red, crystalline 9 in 80% yield. This material is formed by elimination of four equivalents of Me_3SiCl and migration of trimethylsilyl groups to the oxygen atoms:



9

An X-ray analysis demonstrates that the ring system is exactly planar. The two vanadium atoms are tetrahedrally coordinated. The V-N distances (ave. 167.0(5)) are similar to those found in vanadium nitrene complexes. Using $Ph_2P(NSiMe_3)Cl$ and $Me_3SiNVCl_3$ as starting materials the tetrachloro derivative of the new ring system was synthesized in high yield:



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