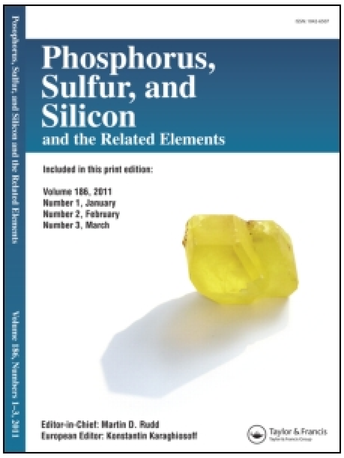

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthetic Approaches to Inorganic Ring Systems

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To cite this Article Shakir, Mohammad and Roesky, Herbert W.(1994) 'Synthetic Approaches to Inorganic Ring Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 13 — 38

To link to this Article: DOI: 10.1080/10426509408021796

URL: http://dx.doi.org/10.1080/10426509408021796

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 13-38
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SYNTHETIC APPROACHES TO INORGANIC RING SYSTEMS

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This report describes the general synthetic methods for the preparation of inorganic heterocyclic systems containing Si-O, Si-O-M, P-N, P-N-M, B-N and B-N-M units in the ring framework. Some of the compounds might function as precursors for generating new industrially important materials. The compounds with metal containing Si-O skeleton act as models for silica supported metal catalysts.

Key words: Heterocycles, Silicon, Phosphorus, Nitrogen, Boron, Metals

INTRODUCTION

The theoretical, synthetic, mechanistic and structural aspects of inorganic heterocycles have been comprehensively discussed in different monographs, reviews, and representatives for nearly every non-metal (except for noble gases) and many metals are known though these were studied mostly in relation to the chemistry of the specific elements.

The chemistry of inorganic heterocycles began in 1833, when Graham[1] obtained a compound from the thermal decomposition of NaH_2PO_4 which was later identified as trisodiumtrimetaphosphate $Na_3P_3O_9$. This compound was immediately succeeded by the discovery of trimeric dichlorophosphazene $(PNCl_2)_3$ independently by Rose[2] and Liebig and Wöhler [3] in 1834 and tetrasulfur tetranitride S_4N_4 by Gregory in 1835.[4]

The phosphazene unit, $-N{=}P(R_2)-$, is isoelectronic with the siloxane group, $-O-Si(R_2)-$, which results in the parallel properties of cyclic and acyclic as well as polymeric compounds. The importance of boron nitrogen heterocycles has been reflected from their use as potential precursors for heat-resistant polymers and ceramics.

The reasons for the significant interest in the chemistry of inorganic heterocycles and their corresponding metallaheterocycles are (i) that the synthesis of these compounds extend an area of genuine synthetic challenge (ii) that the metallaheterocycles provide an opportunity to learn about the symbiosis between main group elements and transition metals narrowing the gap extended in the periodic table and (iii) that these compounds may function as precursors to inorganic polymers and as model compounds for catalytic systems or combine the properties of transition metal oxides and silicones.

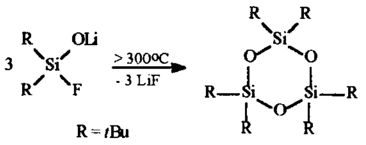
In view of the fast development of this field it becomes inevitable to discuss either a general or, alternatively, a selective topic on any aspect of inorganic heterocycles. Therefore, this article entitled "Synthetic Approaches To Inorganic Ring Systems" deals with the broader aspect of general synthetic methods to build up heterocyclic systems and their corresponding metallaheterocycles, particularly involving phosphorus-nitrogen, silicon-oxygen and boron-nitrogen moieties. "Classical" syntheses and selected more recent procedures are treated side by side.

HETEROCYCLIC Si-O RING SYSTEMS

The most general method for the synthesis of cyclic and acyclic siloxanes is the hydrolysis of dihalosilanes. The degree of oligomerisation can be directed by kinetic and thermodynamic factors and steric requirements of the substituents.[5,6] Alkali metal silanols are interesting precursors for the synthesis of cyclosiloxanes. An increase in the chain length leads to better control of the ring composition and freedom of choice of organic and functional groups.

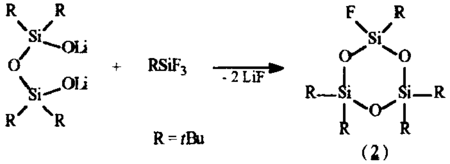
Six-membered Si-O Ring systems (Cyclotrisiloxanes)

(i) A facile and effective way for the synthesis of six-membered ring systems (1) is the thermal decomposition of lithium di-tert. butylfluorosilanolate



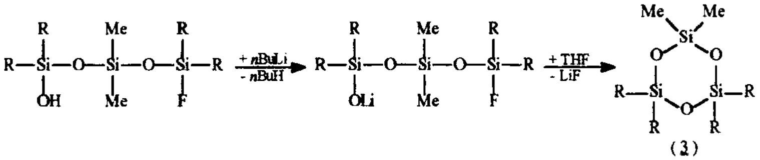
(1)

(ii) The reaction of a dilithium disiloxanediolate with a trifunctional silane leads to the formation of a functional six-membered ring (2).[8]



(2)

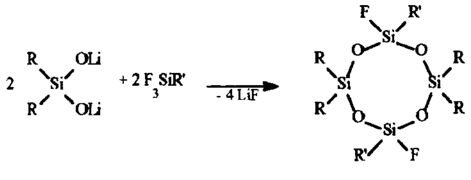
(iii) A third way of synthesising six-membered Si-O rings is the intramolecular salt elimination from metallated halofunctional trisiloxanols[9] using a donor solvent (THF) in order to weaken the Li-O bond resulting in the elimination of LiF.



(3)

Eight-membered Si-O Ring Systems (Cyclotetrasiloxanes)

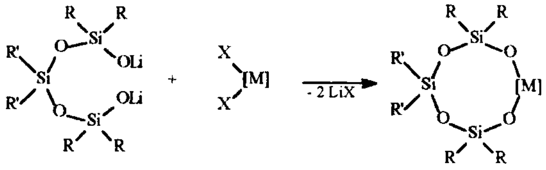
(i) The reaction of dilithium silanediolates with di-, tri-, or tetrahalosilanes is a facile route for the synthesis of eight-membered Si-O rings.[10]



R = tBu; R' = F, Me

(4)

(ii) Reactions of a dilithium trisiloxanediolate with several dihalides yield a variety of eight-membered ring systems including heteroatomic species.[11]



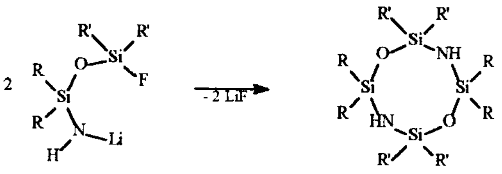
(5)

[M] = $SiMe_2$, SiF_2, BF, AlCl, $GeCl_2$, AsF, TiF_2, PF

R = *t*Bu; R' = Me; X = halogen

Eight-membered Si-O-N Ring Systems (Cyclotetrasiloxazanes)

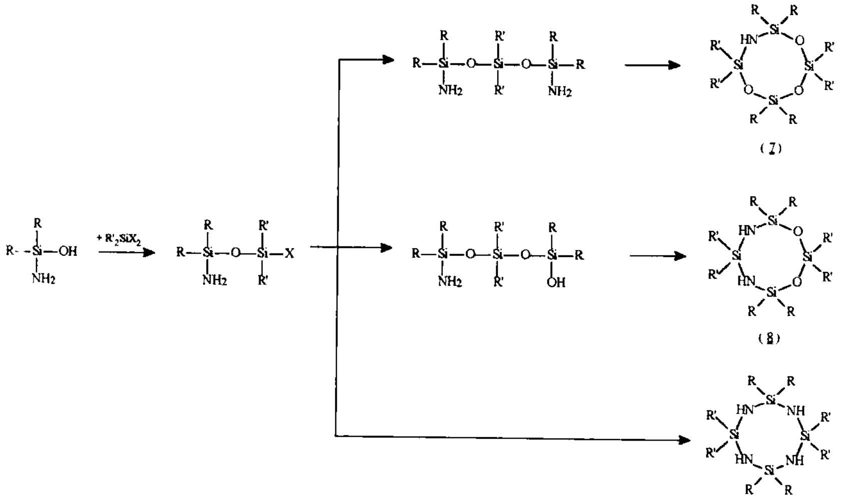
(i) A symmetric compound of this class (6) can be synthesised via condensation of a lithiated aminofluorodisiloxane.[12]



R = Me; R' = *t*Bu

(6)

ii) Asymmetric cyclosiloxazanes (7) and (8) together with a cyclotetrasilazane (9) are available according to the following scheme.[13]



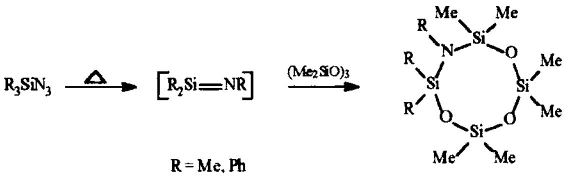
(7)

(8)

(9)

R = *t*Bu, R' = Me, X = halogen

(iii) N-substituted cyclotetrasilatrioxazanes (10) have been synthesised by insertion of silaimine intermediates, generated by thermal decomposition of silylazides at 610 °C, in cyclotrisiloxane (1).[14]



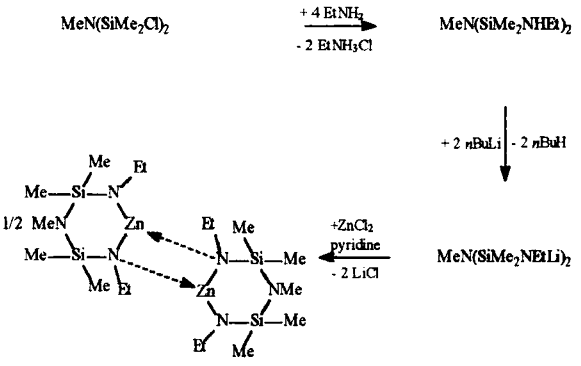
(10)

(iv) Silyloxi-substituted cyclodisilazanes undergo rearrangement to yield symmetric cyclotetrasiladioxadiazanes (6), R = R' = Me.[15]

METALLACYCLOSILAZANES, -SILOXAZANES AND -SILOXANES

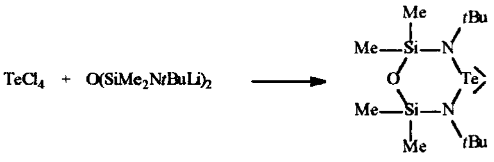
Six-membered Ring Systems

(i) A dimeric six-membered metallacyclosilazane (11) is available according to the following reaction sequence.[16]

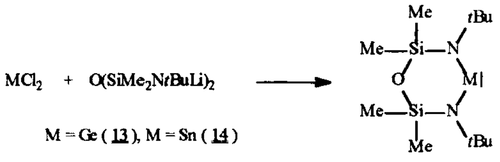


(11)

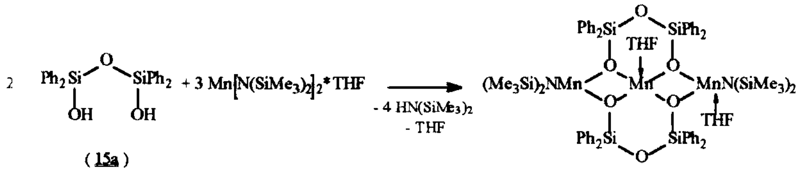
Similarly, six-membered heterocycles of the type $O(SiMe_2NtBu)_2M$ [M = Te(II) (12), Ge(II), (13) Sn(II), (14)] have been synthesised[17] by reacting $O(SiMe_2NtBuLi)_2$ with the corresponding metal halides as shown below.



(12)



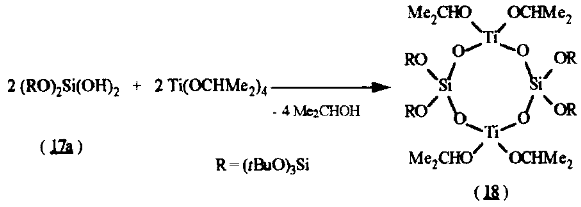
The reaction of manganese bis(bis(trimethylsilyl)amide) with disiloxanediol (15a) in a 3 2 molar ratio yields tetracyclic (16)[18].



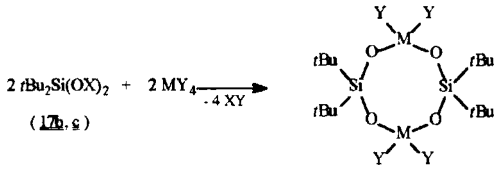
(16)

Eight-membered Tetraoxadisiladimetallocines

The first eight-membered metal containing cyclotetrasiloxane (18) was prepared by transesterification of tetraisopropylorthotitanate with silanediol (17a) but was not structurally characterised.[19]

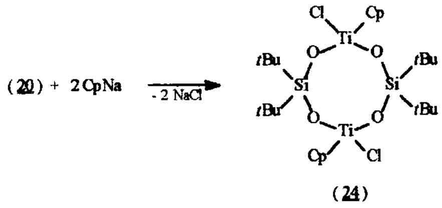


Likewise, Ge-^{20}, Ti- and Zr-dihalide^{21} containing eight-membered rings (19 - 23), are available as products of condensation reactions of the tetrahalides and silanediol (17b), in the case of Zr the dilithium salt (17c) is required to promote reaction.

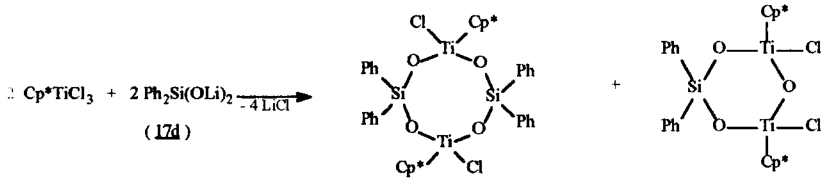


X	Y	M	
H	Cl	Ge	(19)
H	Cl	Ti	(20)
H	Br	Ti	(21)
H	I	Ti	(22)
Li	Cl	Zr	(23)

One chlorine atom on each titanium in compound (21) can be replaced by C_5H_5 (Cp).^{22}

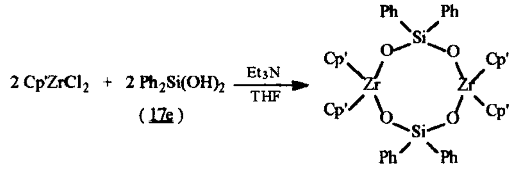


Compound (24) may also be synthesised by reacting $CpTiCl_3$ with $tBu_2Si(OLi)_2$ (17c) in a 1 : 1 molar ratio. However, if Cp^*TiCl_3 ($Cp^* = C_5Me_5$) is treated with $Ph_2Si(OLi)_2$ (17d), both the eight-membered (25) as well as the six-membered (26) rings are formed.^{22}



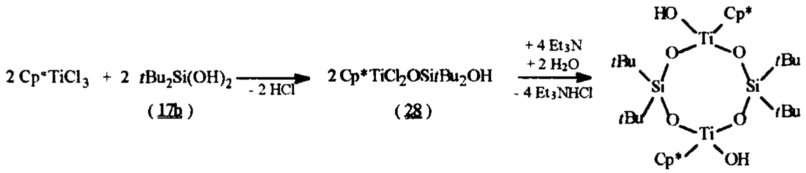
(25) (26)

The reaction of $Ph_2Si(OH)_2$ (17e) with Cp'_2ZrCl_2 ($Cp' = C_5H_4Me$) in the presence of Et_3N yields fully carbon substituted (27).[23]



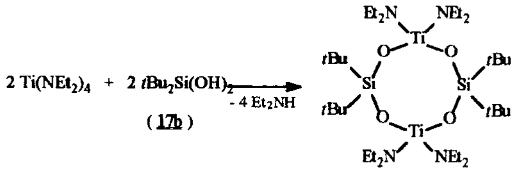
(27)

A hydroxi-substituted titanasiloxane heterocycle (29) is available via base-induced condensation of isolable intermediate titanyloxisiloxanol (28).[28]



(29)

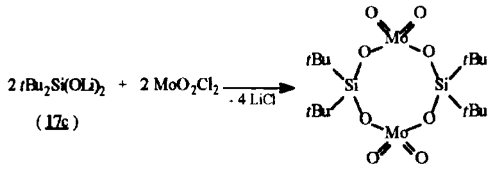
A cyclic titanasiloxane bearing bis(trimethylsilyl)amino groups, $[(Me_3Si)_2NClTiOSitBu_2O]_2$ (30) is available from (20) and $LiN(SiMe_3)_2$. Fully amino substituted heterocycle (31) has been synthesised via elimination of diethylamine from titanium tetrakis(diethyl)amide and silanediol (17b).[22]



(31)

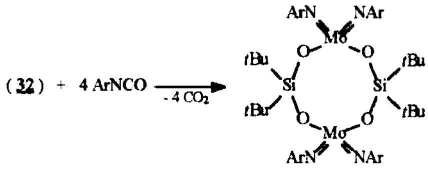
Group VI tetraoxadisiladimetallocines with oxidation state +VI and co-ordination number 4 have been synthesised according to the following equations.

Dilithium salt (17c) reacts with MoO_2Cl_2 to form heterocycle (32).[25]



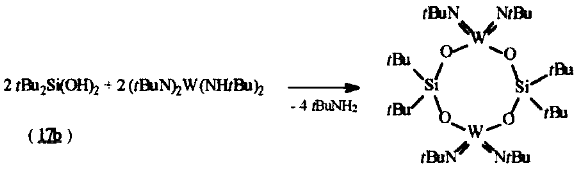
(32)

The exocyclic oxygen atoms can be exchanged by arylisocyanates to yield imides(33).[18]



Ar = 2,6-iPr$_2$C$_6$H$_3$; 3-CF$_3$C$_6$H$_4$ (33)

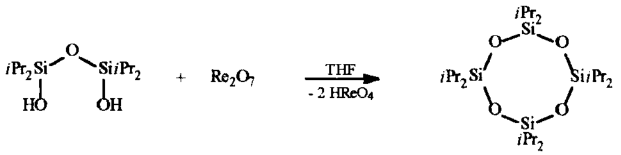
A straight forward synthesis has been found for tungsten homologue (34).[18]



(34)

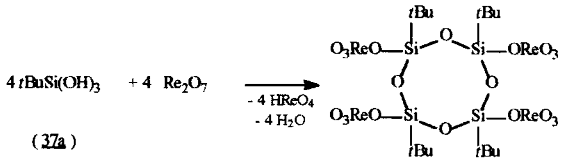
Silylesters of perrhenic acid, $tBu_2Si(OReO_3)_2$ (35) and $O(tBu_2SiOReO_3)_2$ (36) have been obtained with elimination of water from $tBu_2Si(OH)_2$ (17b)[26] and $O(tBu_2SiOH)_2$ (15b),[18] respectively.

Reaction of 1,1,3,3-tetraisopropyldisiloxane-1,3-diol (15c) with Re_2O_7 in THF at room temperature gives an eight-membered cyclotetrasiloxane (4a) instead of an expected rheniaheterosiloxane.[18]



(15c) (4a)

A cyclotetrasiloxane containing exocyclic ReO_4 units (4b) is available from silanetriol (37a) and Re_2O_7.[27]

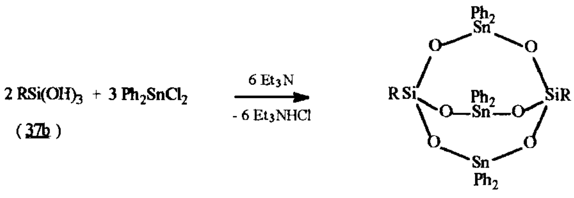


(37a)

(4b)

Rheniaheterosiloxanes (4b, 35, 36) can be considered as model compounds for metal oxide catalysts on silica surfaces.

The reaction of $RSi(OH)_3$ (37b) with Ph_2SnCl_2 in a 1 : 1 molar ratio in the presence of Et_3N in a THF/hexane mixture at room temperature resulted in a tricyclic system (38).[28]



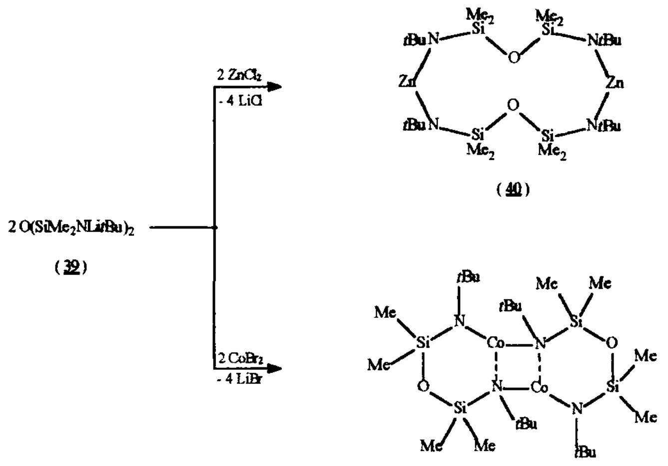
(37b)

R = 2,6 - $iPr_2C_6H_3NSiMe_3$

(38)

Twelve-membered Ring Systems containing Si, O, M (and N)

Reaction of $O[SiMe_2N(tBu)Li]_2$ (39) with $CoBr_2$ and $ZnCl_2$ in THF resulted in the formation of novel twelve-membered metallaazacyclosiloxanes (40) and (41)[29] where the ligand $[O(SiMe_2NtBu)_2]^{2-}$ stabilizes low coordination states.



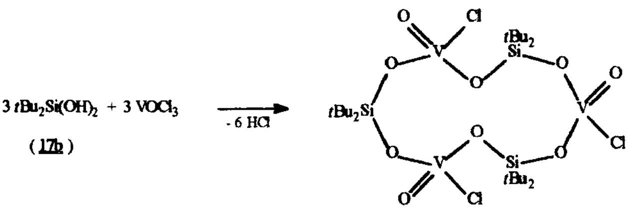
(39)

(40)

(41)

Similarly, transition metal-containing twelve-membered metallaheterocycles of the same type $[\{MO(SiMe_2NtBu)_2\}_2]$ (M = Cr (42), Mn (43), Fe (44), Ni (45)) have been synthesised analogously[17].

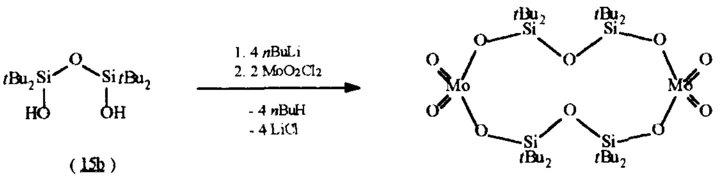
The reaction of $tBu_2Si(OH)_2$ (17b)with $VOCl_3$ results in the formation of a twelve-membered ring (46)[25].



(17b)

(46)

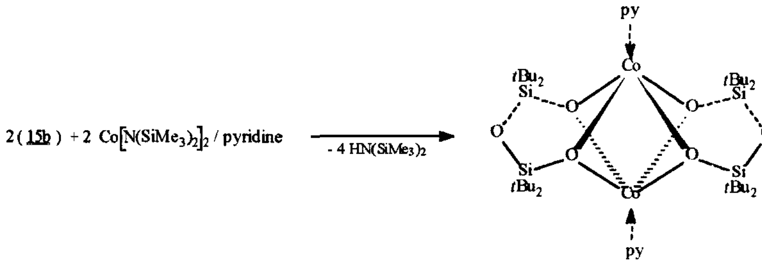
Dilithiated (15b) reacts with MoO_2Cl_2 under formation of hexaoxatetrasiladimolybdacyclododecane (47).[25]



(15b)

(47)

Moreover, the reaction of (15b) with cobaltbis(bis(trimethylsilyl)amide) in the presence of pyridine gave metallaoxacyclosiloxane (48) with the proposed structure depicted below.[18]



(48)

HETEROCYCLIC P(V)-N RING SYSTEMS

Six-membered P=N Ring Systems (Cyclophosphazenes)

Rose[2] and Liebig and Wöhler[3] in 1834 studied the reaction between PCl_5 and NH_3 and NH_4Cl, respectively, and have isolated, among others, a compound later identified as $(Cl_2PN)_3$.[30] The latter method has been improved by Schenck and Römer[31] and is still used on both laboratory and industrial scale. Besides the trimer substantial amounts of the tetramer and smaller quantities of higher cyclic ($5 \leq n \leq$ ca. 20) and linear oligomers have also been obtained.[32]

Substituted cyclophosphazenes have mainly been synthesised by the following procedures.

(i) Adopting the above mentioned method, the majority of equally substituted $(RR'PN)_n$ has been synthesised according to.[32]

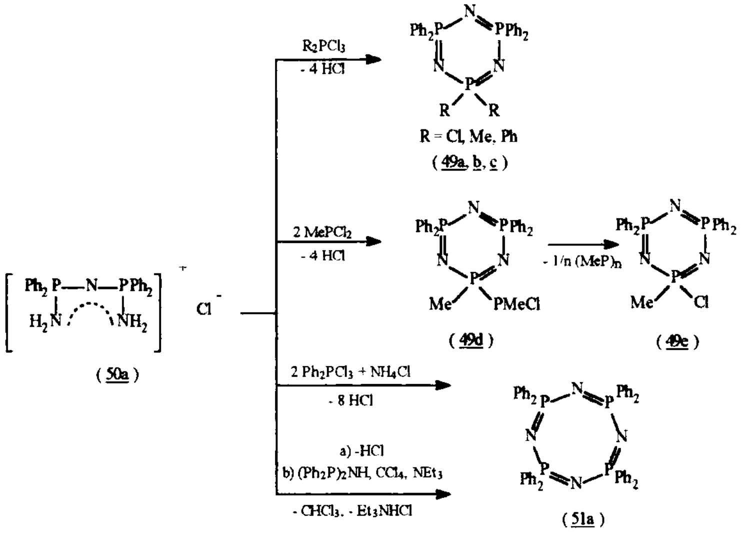
$$n\, RR'PX_3 + n\, NH_4X \longrightarrow \underset{(\underline{49})}{(RR'PN)_n} + 4n\, HX$$

R, R' = Cl, Br, Aryl, Alkyl; X = Cl, Br

(ii) Exchange of halogen atoms in (49) with amines, Grignard reagents, and inorganic alkali salts yield substituted cyclophosphazenes. On the way to fully substituted species two different pathways have been observed, a geminal and a non-geminal mechanism.[32-34]

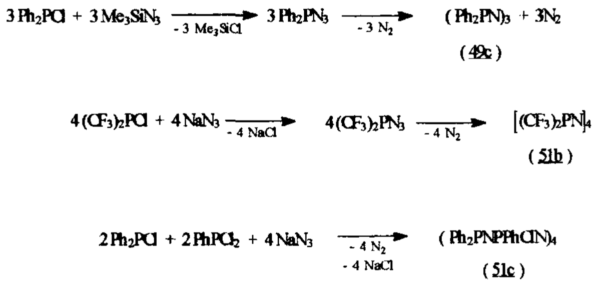
(iii) Cyclisation of acyclic phosphorus nitrogen compounds.

The following reaction scheme shows exemplarily some reactions[35-39] of phosphazene salt (50a) which has also been successfully employed in the incorporation of heteroelements (vide infra).



(iv) Thermal decomposition of azidophosphanes

This method[41-43] involves the metathetical exchange between halophosphanes and a metal azide, followed by careful decomposition of the resulting azidophosphanes.



$$3\,Ph_2PCl + 3\,Me_3SiN_3 \xrightarrow[-3\,Me_3SiCl]{} 3\,Ph_2PN_3 \xrightarrow[-3\,N_2]{} (Ph_2PN)_3 + 3N_2$$

(49c)

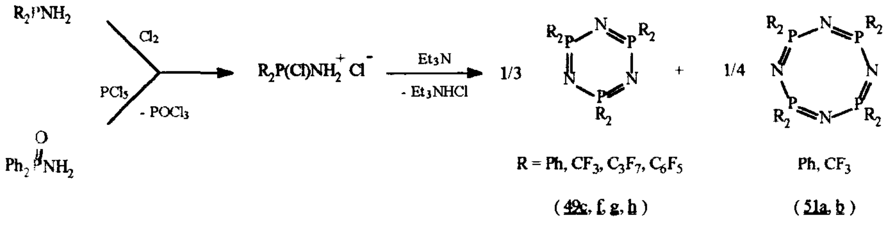
$$4(CF_3)_2PCl + 4\,NaN_3 \xrightarrow[-4\,NaCl]{} 4(CF_3)_2PN_3 \xrightarrow[-4\,N_2]{} [(CF_3)_2PN]_4$$

(51b)

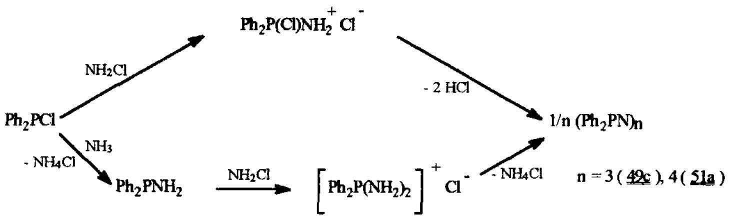
$$2\,Ph_2PCl + 2\,PhPCl_2 + 4\,NaN_3 \xrightarrow[-4\,N_2,\ -4\,NaCl]{} (Ph_2PNPPhClN)_4$$

(51c)

(v) Chlorination of aminophosphoranes or reaction of $Ph_2P(O)NH_2$ with PCl_5 yields aminochlorophosphonium chlorides which can be dehydrohalogenated to yield cyclotri- and -tetraphosphazenes depending on the nature of the organic group.[44-47]



(vi) The reactions of diarylchlorophosphanes with chloramine or ammonia and chloramine result in the synthesis of cyclotri- and -tetraphosphazenes.[48,49]

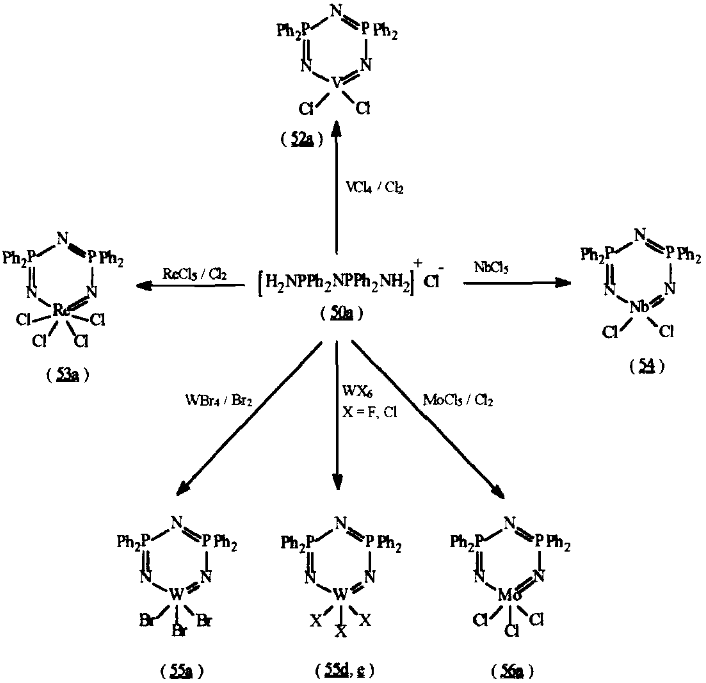


METALLACYCLOPHOSPHAZENES

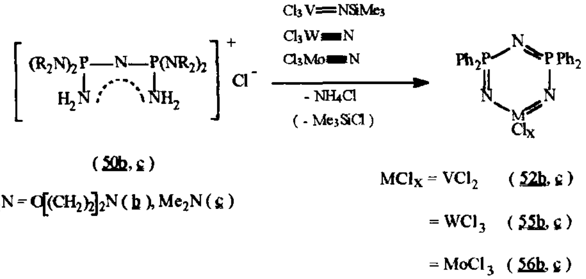
The corporation of main group and transition metal centers in cyclic sulfur-nitrogen[50] and phosphorus-nitrogen compounds has established a new dimension in heterocyclic chemistry. A series of different synthetic routes has been employed to substitute one or two PR_2 units by transition metal centers.

Six-membered P_2N_3M Ring systems

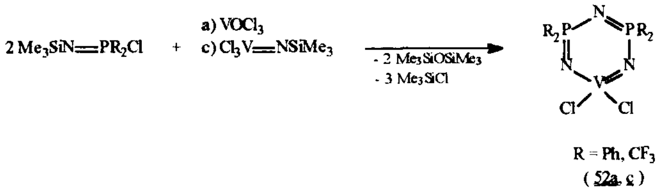
(i) The reactions of acyclic phosphazene salt (50a) with transition metal halides in their highest oxidation states or solutions of lower valent halides and the appropriate halogen yield delocalised metallacyclophosphazenes (52 - 56) according to the following scheme.[51-55]



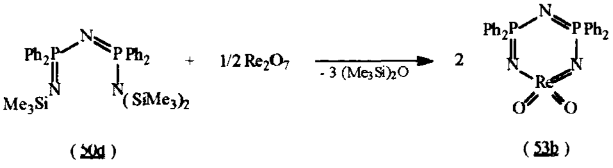
(ii) In the case of hydrolytically labile groups on phosphorus like secondary amines, metal halide nitrides have been used.[55] Mo-heterocycle (56a) can be synthesised by the same reaction.[52]



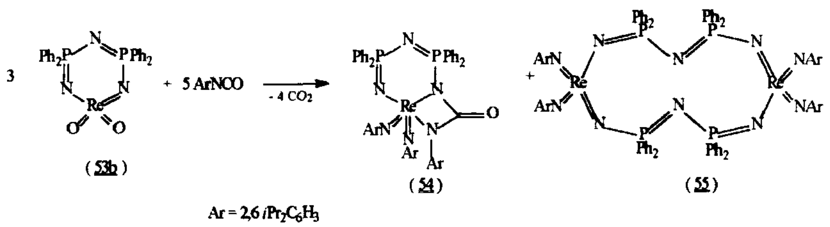
(iii) V-heterocycles (52a, c) have been obtained from silyliminochlorophosphoranes and $VOCl_3$ and $Cl_3V{=}NSiMe_3$ respectively, in a 2 : 1 molar ratio.[56,57]



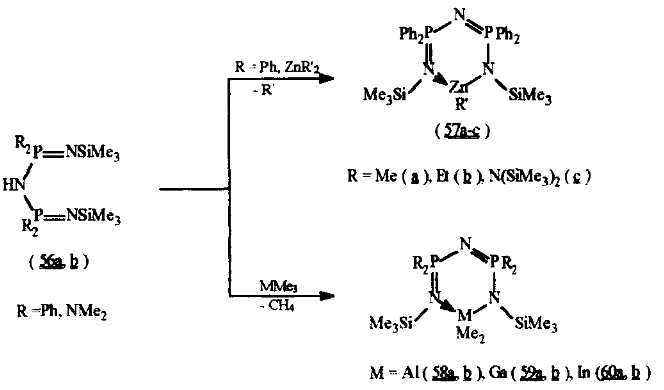
(iv) A silylated acyclic phosphazene (50d) derived from (50a) has been reacted with dirheniumheptoxide to yield oxygen substituted Re-heterocycle (53b). The same compound has been obtained with $Me_3SiOReO_3$.[59,60]



(v) A compound (54), where Re is surrounded by only nitrogen atoms has been found in the reaction of (53b) with an arylisocyanate. The four-membered ring arises from a formal 2+2 cycloaddition of the C=N bond to an endocyclic Re=N bond. Additionally, twelve-membered dirheniacyclophosphazene (55) is formed in low yield.[59]



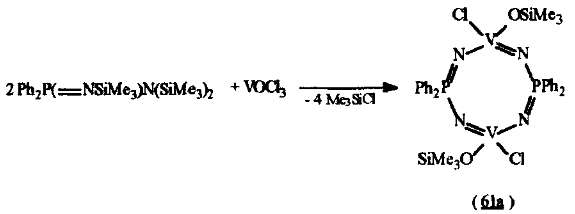
(vi) Non-conjugated metallacyclophosphazenes have been obtained by reactions of bissilylated open-chain phosphazenes (56a,b) with zinc alkyls and amides[61] and with group 13 trimethyls.[60,62]



Eight-membered Metallacyclophosphazenes

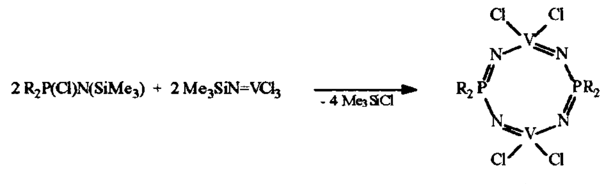
Eight-membered phosphazene heterocycles containing one or two metal atoms have been synthesised by different routes.

(i) The reaction of an iminoaminophosphorane with VOCl$_3$ affords dimetallacyclophosphazene (61a).[63]



(61a)

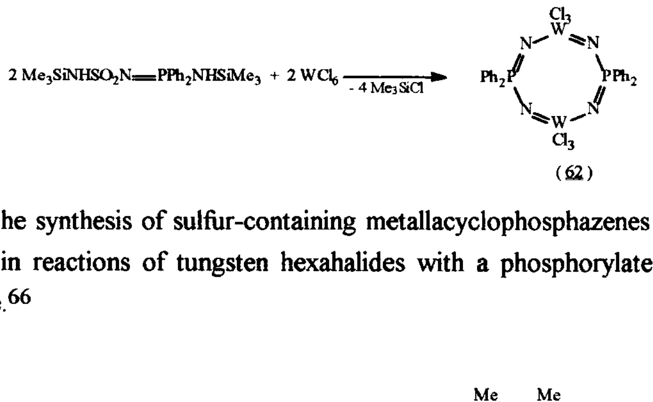
(ii) Similarly, iminochlorophosphoranes and trimethylsilyliminovanadiumtrichloride yield tetrachlorosubstituted species (61b,c).[64,56]



(61b,c)

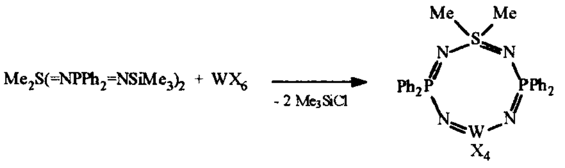
R = Ph (a), CF$_3$ (b)

(iii) Attempting to incorporate sulfur+VI in a metallacyclophosphazene restulted in the foramtion of (62). The mechanism can be rationalised by the elimination of chlorosulfonamide.[65]



(62)

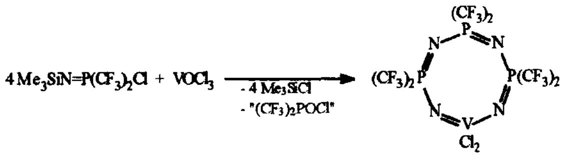
(iv) The synthesis of sulfur-containing metallacyclophosphazenes (63) has been achieved in reactions of tungsten hexahalides with a phosphorylated sulfodiimide derivative.[66]



(63a,b)

X = F, Cl

(v) The use of $VOCl_3$ instead of $Me_3SiN{=}VCl_3$ (vide supra) in the reaction with $Me_3SiN{=}P(CF_3)_2Cl$ affords the only authentic sample (64) of a heterocycle with a P_3N_4M-core, [56] evidence of a WCl_3-substituted ring has been detected in the mass spectrum of a seven-membered open chain phosphazenium hexachlorotungstate(V).[67]



(64)

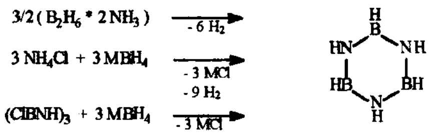
HETEROCYCLIC B-N-SYSTEMS

Six- and Eight-membered B-N Ring Systems (Triazatriborines and Tetrazatetraborocines)

The chemistry of triazatriborines and tetrazatetraborocines; or more conveniently borazines and borazocines, has been thoroughly compiled in the boron section of the Gmelin handbook,[68,69] several books on inorganic ring systems, e.g.[70,71] and a vast number of review articles.

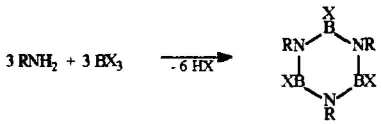
The following selected procedures are most commonly used in the syntheses of these heterocycles, the original citations may be taken from refs.[68-71]

(i) The parent compound, $(HNBH)_3$ (65) was first prepared by Stock and Pohland in 1926[72] and later by Wiberg and Bolz[73] by pyrolysis of the diborane-ammonia-adduct. Newer methods involve pyrolysis of ammoniumchloride and alkaliborohydrates or the reduction of trichlorotriazatriborine (66), R = H, with alkaliborohydrides.



(65)

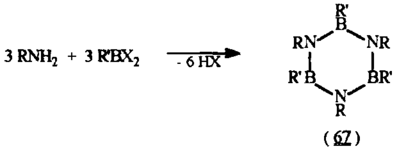
(ii) N-functional haloborazines (66) are most widely synthesised by condensation of boron trihalides with primary amines or amine hydrochlorides.



(66)

N-silylated amines can be employed similarly.

(iii) N,B functional borazines (67) are obtained in an analogous fashion from organodihaloboranes



(67)

(iv) Thermal decomposition of the diphenylborylazide-pyridine-adduct yields hexaphenyltriazatriborine via anionic migration of a phenyl group, probably via an instabile monomeric intermediate.[74]

$$Ph_2BN_3{*}py \xrightarrow[-N_2\,-\,py]{\Delta} \left[PhB{=}NPh\right] \longrightarrow 1/3\,(PhBNPh)_3$$

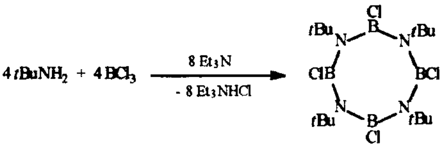
(v) Functionally substituted borazines have been obtained either by metathesis with e.g. alcohols, thiols, amines and pseudohalides or by cyclisation of appropriate precursors. They have been extensively compiled[68-71] and will not be discussed.

Eight-membered B-N Ring Systems (Tetrazateraboracines)

Few examples of eight-membered B-N heterocycles have been found due to the fact that they are far less stable than their six-membered congeners. This is reflected in the thermal behaviour of $(FBNMe)_4$ which during the attempt of sublimation decomposes to a mixture of trimer and polymers. It has been generated by reduction of methylamine-trifluoroborane or methylammoniumtetrafluoroborate with Al dust.[75]

$$n\,MeNH_3^+BF_4^- + n\,Al \longrightarrow (MeNBF)_n + n\,AlF_3 + 3n/2\,H_2$$
$$n = 3, 4$$

Steric control is required for the synthesis of B-halogeno-N-alkyltetrazatetraborines because only with tertiary amines have the desired tetramers been obtained,[76] e.g. (68).



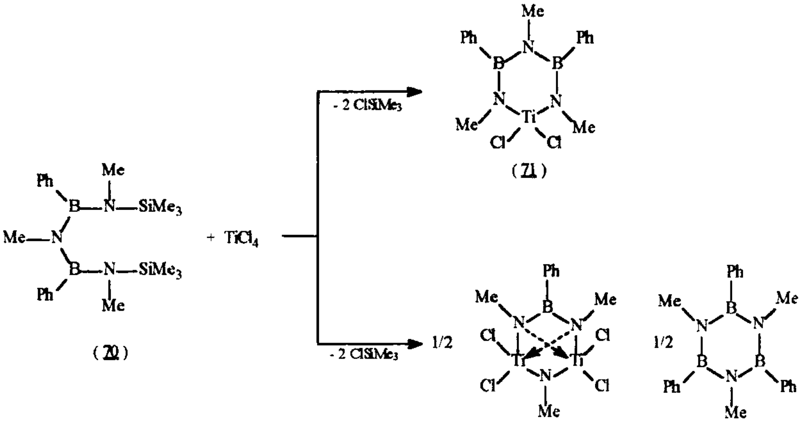
(68)

A fully organosubstituted derivative ($(t\text{BuNBPh})_4$) (69) has been obtained similarly and in addition to the trimer, to which is converted by heating it to 250 °C.[77]

METALLACYCLOBORAZINES

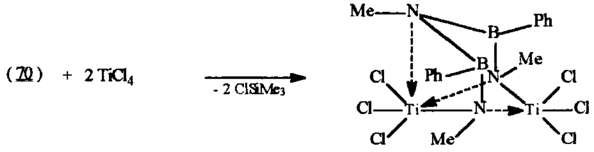
Starting from open chain precursor (70) two metal-containing six-membered boron-nitrogen heterocycles have been synthesised.

The reaction of (70) with $TiCl_4$ in a 1 : 1 molar ratio in $CHCl_3$ did not lead to the expected six-membered product (71), but instead produced a six-membered ring (72) containing two titanium atoms along with substituted borazine (67a) in quantitative yield.[87]



(70) (71) (72) (67a)

However, the reaction of (70) with $TiCl_4$ in a 1 : 2 molar ratio in hexane led to an unstable intermediate (73).



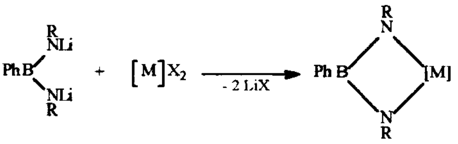
(73)

The X-ray structural analyses as well as the experimental results suggest the reaction sequence in which compound (70) reacts with $TiCl_4$ in a 1 : 2 molar ratio to give compound (73) which decomposes rapidly via an S_{Ni} reaction to give (72) and one equivalent of $PhBCl_2$. The $PhBCl_2$ then reacts with a further equivalent of (73) to give (67a), whereby two equivalents of titanium tetrachloride are liberated which themselves then react again with (70).[78]

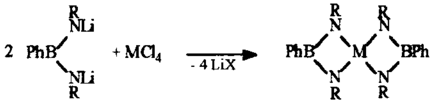
The first six-membered borazine containing a tellurium atom as a building block in the ring framework (74) was obtained when (70) was reacted with $TeCl_4$.[79]

(74)

Mono- and sprirocyclic diazaborametalletidines are known from a series of main group and transition metals.[79,80]



R = tBu [M]= SnMe2 (75), ZrCp2 (76)



	M	R
(77a):	Ge	*i*Pr
(77b):	Ge	*t*Bu
(78):	Sn	*t*Bu
(79):	Te	*t*Bu
(80a):	Ti	*t*Bu
(80b):	Ti	$SiMe_2$*t*Bu

PROSPECTS

In view of the significance of these compounds from theoretical, synthetic, mechanistic, structural and technological aspects, the chemistry of metallacycles becomes a frontier field for further explorations. Although the heterocyclic rings of nearly every non-metal and many metals have been thoroughly investigated, the chemistry of metallacycles involving the elements of the actinides and lathanides in heterocyclic frameworks is still underdeveloped and merits further investigation. The applications of the metallacycles (particularly the combination of silicones and transition metal oxides) as models for catalytic systems, inorganic polymers and precursors for new organometallic compounds need special attention to design and synthesise the reagents for the synthesis of metallaheterocycles.

ACKNOWLEDGEMENTS

We are thankful to Dr. M. Witt for reading this manuscript and for his valuable comments. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is highly acknowlegded.

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