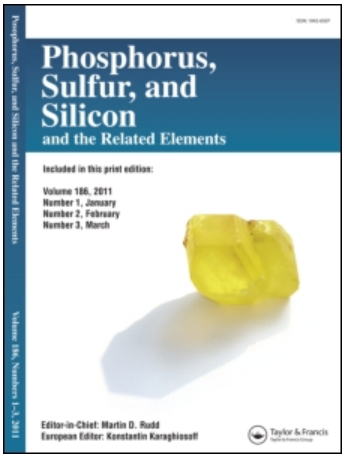

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New Cyclic and Spirocyclic Metal-Containing Phosphazenes

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NEW CYCLIC AND SPIROCYCLIC METAL-CONTAINING PHOSPHAZENES

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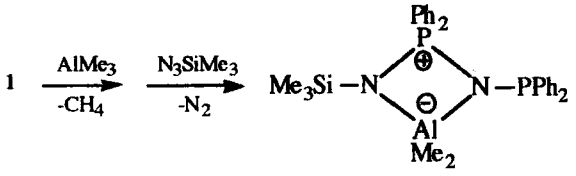
INTRODUCTION

The ligand system $[R\text{-}NPR'_2NPR'_2N\text{-}R'']^-$ has been used to build up new heterocycles. When the substituents R and R" are leaving groups such as hydrogen or trimethylsilyl ($SiMe_3$), quasi aromatic metallacycles could be obtained upon reaction with metal halides or metal oxides.[1] Group 13 metal alkyls have been shown to give cyclic chelates with R=R"=$SiMe_3$ and R'=Ph or NMe_2. Group 2 and 12 $N(SiMe_3)_2$-substituted metals form spirocycles or cubes depending on the size of the metal and the ligand.[2]

RESULTS

We have recently explored new synthetic approaches towards unsymmetrical phosphazene ligands, starting from bis(diphenylphosphino)amine **1**.[3]



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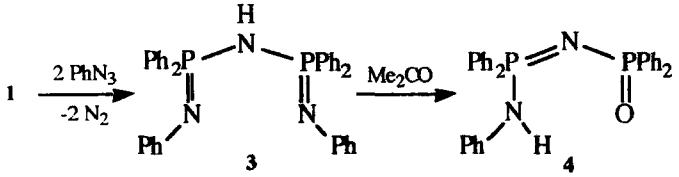
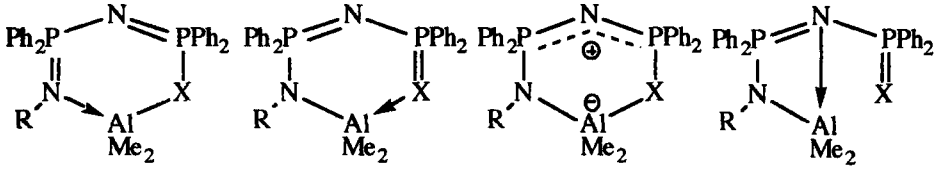


3 **4**

In our present work, we focus on the preparation of alumocycles, which is easily accomplished by adding oxidizing agents such as PhN_3, S and Se to **2** or $AlMe_3$ to **3** and **4**. In the case of PhN_3 the reaction mixture has to be heated to induce nitrogen liberation from the intermediate phosphazide. The structure of the complexes are best represented by the structure formulae **A**, **B**, **C** and **D**. The latter one may be favored for the sulfur and selenium containing compounds.



A B C D

The ^{31}P-NMR data are summarized in Table I. All compounds have been characterized by ^{1}H-NMR spectroscopy, too. Rapid decomposition of complexes occurs when they are exposed to air or moisture except for **8**. The remarkable stability of **8** (only small amounts decomposed to **4** after several weeks in air) is likely to be due to the hydrophobic pocket around the $AlMe_2$-moiety that is povided by the bulky phenylgroups.

TABLE I ^{31}P-NMR data of ligands and alumocycles.

	R	X	δ P_A[a]	δ P_B[a]	$^{2}J_{PP}$[b]
2	-	-	40.6	34.0	100
3	-	-	7.0	-	-
4	-	-	15.2	10.4	0.9
5	Me_3Si	N-Ph	25.8	22.6	8.5
6	Me_3Si	S	48.5	36.7	3.7
7	Me_3Si	Se	41.7	37.8	1.3[c]
8	Ph	N-Ph	24.6	-	-
9	Ph	O	27.9	26.0	6.9

a) in ppm; b) in Hz; c) $^{1}J_{PSe}$ = 751Hz; in $CDCl_3$ or C_6D_6.

In addition we report the spirocyclic compound $[N(PPh_2NPh)_2]_2Co$, which is obtained by lithiation of **3** and subsequent reaction with $CoCl_2$. The deep blue, paramagnetic complex has been characterized by mass spectroscopy and elemental analyses. It remains solid and unchanged upon heating to 335 °C. The geometry around the cobalt atoms is likely to be tetrahedral according to the bulkiness of the ligands and earlier investigations.[4]

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