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New Cyclic and Spirocyclic Metal-Containing Phosphazenes

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NEW CYCLIC AND SPIROCYCLIC METAL-CONTAINING PHOSPHAZENES

REINHARD HASSELBRING AND PIERRE BRAUNSTEIN

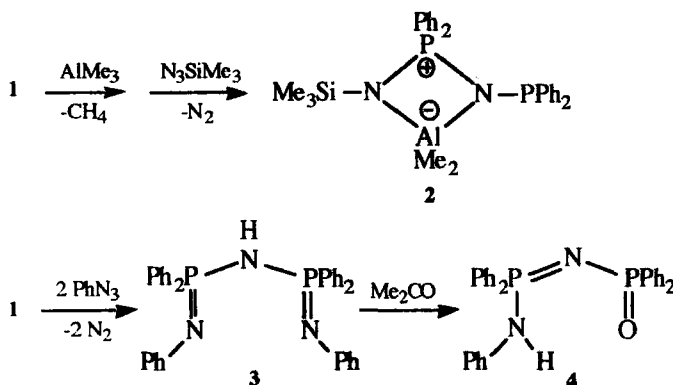
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INTRODUCTION

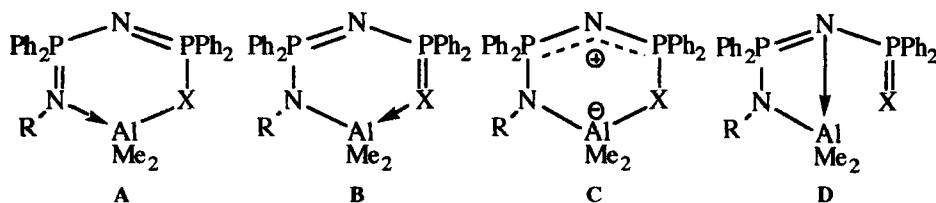
The ligand system $[R-NPR'_2NPR'_2N-R]^-$ has been used to build up new heterocycles. When the substituents R and R' are leaving groups such as hydrogen or trimethylsilyl ($SiMe_3$), quasi aromatic metallacycles could be obtained upon reaction with metal halides or metal oxides.¹ Group 13 metal alkyls 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



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.



The ^{31}P -NMR data are summarized in Table I. All compounds have been characterized by ^1H -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 provided by the bulky phenyl groups.

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

	R	X	$\delta \text{P}_\text{A}^\text{a}$	$\delta \text{P}_\text{B}^\text{a}$	$2J_\text{PP}^\text{b}$
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) $^1J_\text{PSe} = 751\text{Hz}$; in CDCl_3 or C_6D_6 .

In addition we report the spirocyclic compound $[\text{N}(\text{PPh}_2\text{NPh})_2]_2\text{Co}$, 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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