

Polyiminoalanes

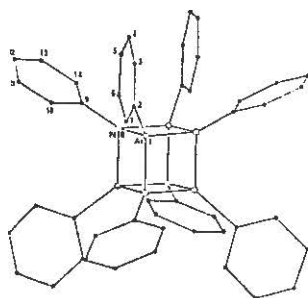
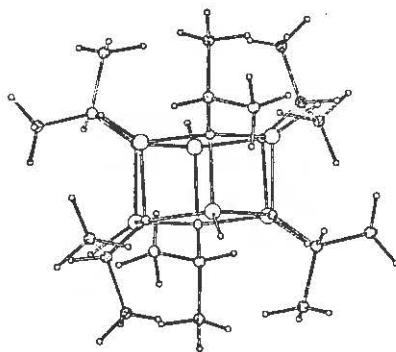
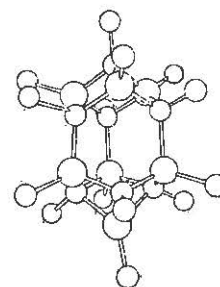
Curtis Schwartz

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Compounds having the composition $(\text{RAlNR}')_n$ (R=alkyl, halogen, H; R'=alkyl) are known as polyiminoalanes (PIA). Early information concerning the structures of PIA's were indefinite since the PIA's isolated were either insoluble polymers or slightly soluble crystalline polymers which were studied by infra-red spectroscopy, cryoscopy, mass spectrometry, elemental analysis, and x-ray powder diffraction [1-3]. The first structural characterization of a PIA was reported in 1962 on crystalline $(\text{C}_6\text{H}_5\text{AlNC}_6\text{H}_5)_4$ made by reaction of aniline and hexaphenyldialuminum in refluxing benzene [4]. Its structure was shown by single crystal x-ray diffraction to consist of a cubic cage of alternating aluminum and nitrogen atoms with phenyl substituents filling the fourth coordination position around each aluminum and nitrogen atom. Since this discovery, new soluble PIA's have been prepared in crystalline form for $n=4-8$, and their structures elucidated by single crystal x-ray diffraction [5-9].

All of the basic cage structures adopted by PIA's from $n=4-8$ are made up of 4 and/or 6 membered rings of alternating aluminum and nitrogen atoms in different ring conformations. For the compound $(\text{HALN-iso-C}_3\text{H}_7)_6$, the cage is found to be that of a hexagonal prism made up of a nearly planar 4 and 6 membered rings, whereas for $(\text{CH}_3\text{AlNCH}_3)_7$, the cage is made up of a total of 5 six membered rings, three of which are in the boat and two in the chair conformations. The molecule $[(\text{HALN-iso-C}_3\text{H}_7)_2(\text{H}_2\text{AlNH-iso-C}_3\text{H}_7)_3]$ contains a 6 membered ring in the skew boat conformation.

 $(\text{C}_6\text{H}_5\text{AlNC}_6\text{H}_5)_4$  $(\text{HALN-iso-C}_3\text{H}_7)_6$  $(\text{CH}_3\text{AlNCH}_3)_7$

Several approaches have been utilized for the synthesis of PIA's [10,11], which may be isolated as moisture sensitive crystals from ether or hydrocarbon solvents from the following chemical reactions:

- $\text{RNH}_2 + \text{AlR}'_3 \longrightarrow \frac{1}{n}(\text{R}'\text{AlNR})_n + 2\text{R}'\text{H}$
- $\text{RNH}_2 + \text{MAlH}_4 \longrightarrow \frac{1}{n}(\text{HALNR})_n + \text{MH} + 2\text{H}_2 \quad \text{M=Li, Na}$
- $\text{Al} + \text{RNH}_2 \xrightarrow{\text{H}_2} \frac{1}{n}(\text{HALNR})_n + \frac{1}{2}\text{H}_2$

The degree of polymerization and product distribution are strongly dependent on the conditions under which the synthesis is carried out as well as the type of amine. Isopropyl, *n*-propyl, and *t*-butyl amine have yielded PIA's of principally a single degree of polymerization. With *t*-butyl amine, PIA's of *n*=4 are preferred, whereas with isopropyl, cyclohexyl, and *sec*-butyl amine, the hexameric *n*=6 PIA's are preferred. PIA's made from ethyl or *n*-butyl amine give mixtures of oligomers which are difficult to separate.

Since the cage structures of PIA's can be shown to be derived from 4 and 6 membered heterocyclic rings of aluminum and nitrogen atoms, hypotheses may be formulated concerning the mechanism of cage formation. Reaction intermediates in the synthesis of PIA's from equation 3 have been characterized spectroscopically and a reaction sequence suggested [11]. A reaction intermediate in the synthesis of $(\text{CH}_3\text{AlNCH}_3)_7$ has been isolated and characterized by x-ray diffraction. However, it is not clear how the reaction intermediate collapses to the PIA product in this particular case [12].

PIA's are reactive molecules. The hydrogen atoms bound to aluminum may be substituted with alkyl substituents [13,14] or chlorine [15] without cage decomposition by several routes. The aluminum hydride fragment may also be completely replaced by a Ca or Mg atom coordinated to 3 and 1 THF solvent molecules, respectively [16,17]. Other derivatives of PIA's are also known [18-21].

It has been found that PIA's exhibit very high activity as hydrogenation cocatalysts with organotransition metal complexes [22]. PIA's have also been used effectively as cocatalysts with TiCl_4 in the polymerization of *cis*-polyisoprene [23].

References

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