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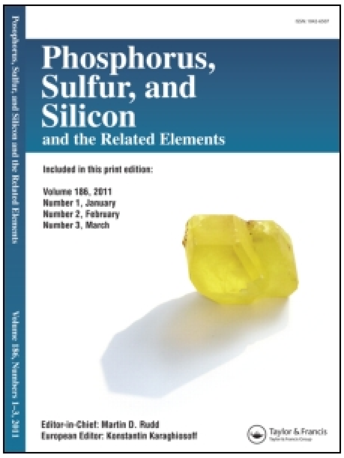

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The Range of Five-Coordinate Group 13-Salen Compounds

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The present publication will provide an overview of the formation of selected five-coordinate aluminum, gallium, and indium compounds.

Keywords: Aluminum; Gallium; Indium; Chelate

INTRODUCTION

The synthetic and catalytic use of aluminum reagents has generally relied upon the fourth Lewis acidic site on the metal center. However, there is growing evidence that aluminum (and by extension gallium and indium) forms five- and six-coordinate complexes during the reaction of interest. This is undoubtedly true when bidentate substrates are involved. As a research target, however, higher-coordinate aluminum was not actively pursued until the mid 1980's when Robinson began an aggressive campaign to explore the structures of these compounds.[1] His systematic work, as well as publications from other early pioneers in group 13 chemistry has established the means by which five-coordinate group 13 compounds may be formed. Now a great deal of structural information is available on five-coordinate group 13 compounds.

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Over the past five years we have, in turn, developed an extensive series of five-coordinate group 13 complexes based upon use of the Salen ligand system.[2] We have prepared five-coordinate aluminum, gallium[3] and indium[4,5] alkyls and halides and aluminum amides,[6] alkoxides,[2,3,] siloxides,[7] hydroxides,[6] azides,[8] and cations[9] (including many related six-coordinate derivatives).[10] It should be noted that our work had as its foundation the work of Goedken on five-coordinate alkyls[11] and that of Barron on five-coordinate alkoxides.[12] Sporadic contributions have been made by others as well.[13, 14]

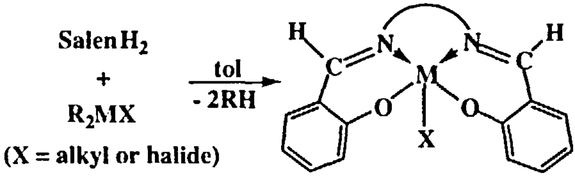
Early-on we discovered that these compounds, and the related six-coordinate cationic aluminum, were useful as catalysts for the polymerization of oxiranes. These applications, too, had precedence in the efforts of Spassky[15] and in the substantial work of Inoue.[16] More recently, applications involving the five-coordinate alkoxides have have been developed much more extensively. There are two reports of catalytic lactide polymerization,[17] as well as the use of Salen-AlR as an initiator methylmethacrylate polymerization.[18]

It is clear that many more applications will be found for five-coordinate aluminum. It would be useful, though, to understand both the range of compounds that may be accessed as well as the nature of the bonding at the fifth (non-Salen) coordination site. The present publication will provide an overview of the formation of these five-coordinate aluminum, gallium, and indium compounds.

RESULTS AND DISCUSSION

A. SalenAlR and SalenAlX (where R = alkyl and X = halide)

Salen group 13 alkyl complexes are conveniently prepared by combining the ligand with a trialkyl group 13 reagent in non-oxygenated solvents at ambient temperatures (Scheme 1). The choice of solvent depends on which Salen ligand is being used, and the ligand's solubility characteristics but toluene generally works well. Salen group 13 halide compounds, SalenMX, are prepared similarly, but with R_2AlCl as the group 13 reagent. In the syntheses there was no evidence for the formation of cation-anion pairs of the sort, [Salen(^{t}Bu)In^+] [Salen(^{t}Bu)InX_2^-].[19]

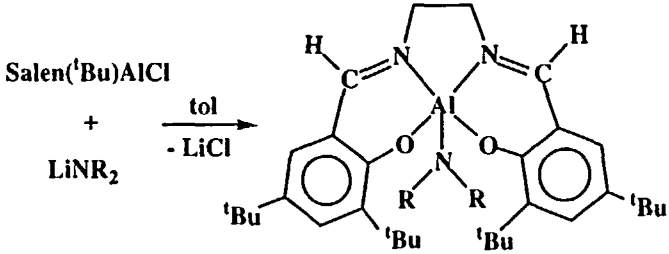


Scheme 1. General syntheses of the five-coordinate alkyl and halide derivatives. The connection between the two nitrogens can be $(CH_2)_2$ (for Salen(^{t}Bu)), $(CH_2)_3$ (for Salpen(^{t}Bu)), C_6H_4 (for Salophen(^{t}Bu) and 4,5-$(Me_2)C_6H_2$ (for Salomphen(^{t}Bu)).

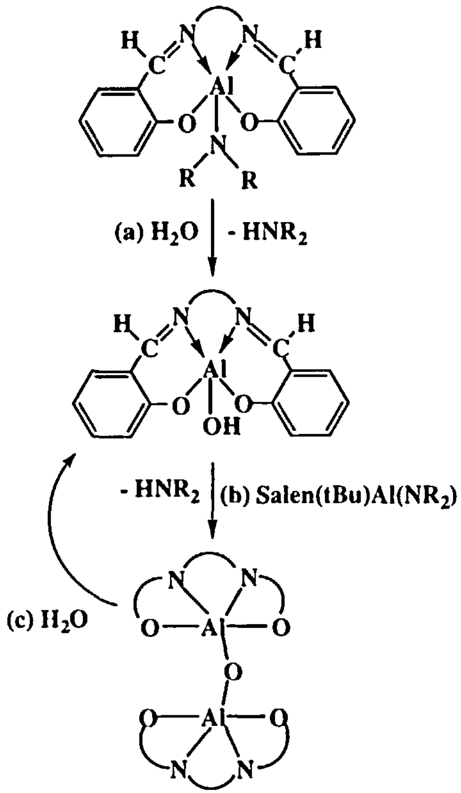
The compounds contain a five-coordinate group 13 atom (Al, Ga, In) that is either trigonal bipyramidal (tbp) or square pyramidal (sqp) depending on the nature of the connection between the two nitrogens of the ligand (the ligand "backbone"). With more flexible backbones, $(CH_2)_n$ n > 2, a tbp geometry is obtained probably due to the fact that a sqp geometry would cause the methylene hydrogens to be eclipsed. In the tbp geometry they are staggered. With an ethyl, $(CH_2)_2$, or *o*-aryl backbone the metal adopts a sqp geometry. This ligand-geometry correlation is a fundamental property of the Salen ligands and is observed in all of the other derivatives.

B. SalenAl(NR_2) and SalenAlOH

The combination of a SalenAlCl starting material with a lithium amide leads to the formation of a unique class of five-coordinate aluminum amides (Scheme 2). These are the first compounds to possess terminal amido groups on a five-coordinate aluminum atom. The yellow and orange compounds are highly moisture sensitive and hyrolyze readily (Scheme 3). The hydrolysis is slowed by the presence of bulky groups.



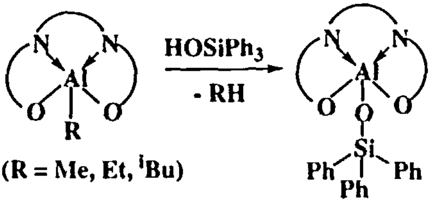
Scheme 2. The formation of terminal five-coordinate aluminum amides.



Scheme 3. Formation of aluminum hydroxides (a and c) and a bridged oxo compound (b).

C. SalenAl(OR) (R = alkyl or SiR_3)

Combination of a SalenAlR reagent with an alcohol leads to an alkane elmination and the formation of the alkoxide derivatives. The first compound to be prepared in this manner, SalenAlOMe, was thought to be monomeric but was not fully characterized.[20] Subsequently, it was shown that compound was, in fact, dimeric. The use of the non-tert-butlyated Salen ligand allows the formation of dimers in a manner similar to conventional lower-coordinate alkoxides (in general like $[R_2Al(\mu\text{-}OR)]_2$ (where R = alkyl, etc.). Accordingly, $[AcenAl(\mu\text{-}OMe)]_2$ and $[SalpenIn(\mu\text{-}OMe)]_2$ are also dimeric. The aluminum atoms in these structures adopt distorted octahedral geometries.



Scheme 4. The formation of terminal aluminum siloxides.

CONCLUSION

A variety of routes may be used to prepare five-coordinate group 13-Salen compounds. Except for the amido derivatives the compounds are air and moisture stable and have high thermal stability. It is clear that many other types of related compounds, with just about any uninegative ligand can be accessed in a like manner. The use of the compounds in effecting organic transformations and in catalysis has only just begun. This will be a growing area of applied chemistry in the next few years.

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