SAND2019-14100C

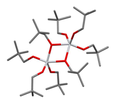
Trapped Intermediate of a Meerwein-Pondorf-Verley Reduction of Hydroxy Benzaldehyde to a Dialkoxide by Titanium Alkoxides

Fernando Guerrero, Timothy J. Boyle**,** Todd M. Alam, Kaylee A. Dunnigan, Jeremiah M. Sears, David R. Wheeler
Sandia National Laboratories, Advanced Materials Laboratory

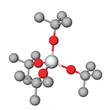
Introduction

The pervasive use of electronic ceramics coupled with the demand by customers for smaller and more advanced devices has led to the need for increased control over the final materials' properties via chemistry.

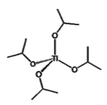
One of the most widely used precursors to these electronic ceramic materials are metal alkoxides ([M(OR)z]) however, the low charge to large cation size often leads to oligomerization and unexpected structural arrangements. For this effort, bidentate ligands with an active second binding site [versus the standard Lewis basic moieties (i.e., methoxide or amino)] were of interest to allow further chemical manipulations after binding.



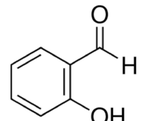
$Ti_2(ONep)_8$



$Ti(OBu^t)_4$

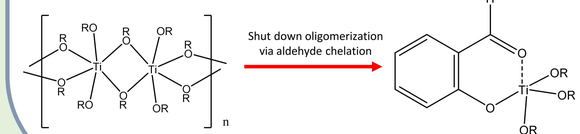


$Ti(OPr^i)_4$

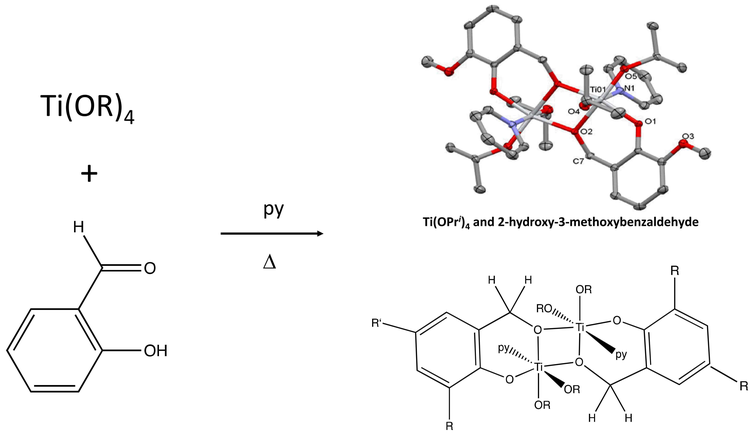


2-hydroxybenzaldehyde

In particular, phenolic benzaldehydes (HO-BzA-Lx) were explored, as the hydroxide and the carbonyl oxygen of the aldehyde could coordinate to the metal, leaving the reactive hydrogen for additional chemical manipulation.



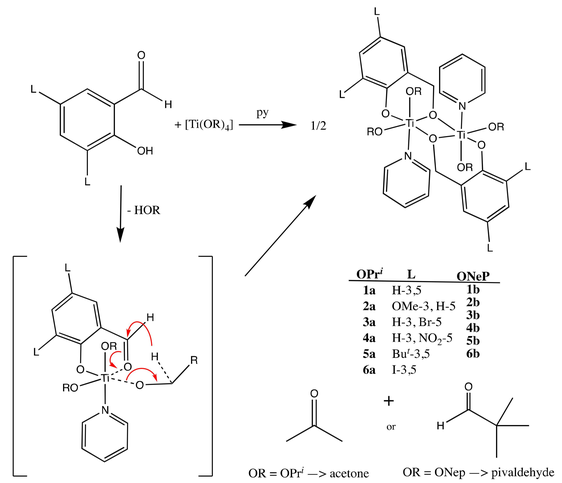
Unexpected Aldehyde Reduction



$Ti(OPr^i)_4$ and 2-hydroxy-3-methoxybenzaldehyde

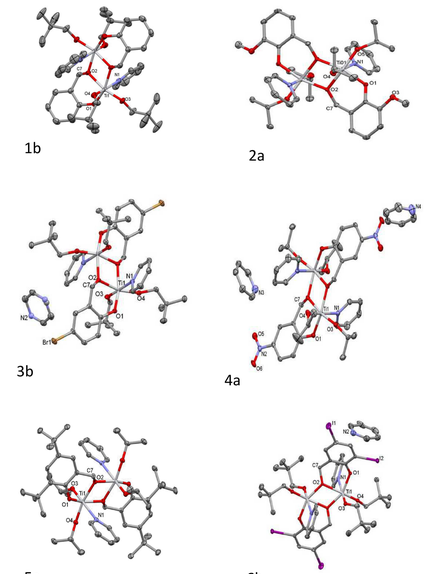
The titanium alkoxides were reacted with the aldehydes in pyridine and with heat. The solutions were then allowed to cool and crystals were grown via slow evaporation. All 12 resulting crystals showed an identical reduction of the aldehyde in a dimer configuration with bridging oxygens. This result was unexpected and prompted an investigation on the mechanism for the reaction.

Proposed MPV pathway for HO-BzA-Lx reduction



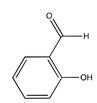
OPr^i	L	ONeP
1a	H-3,5	**1b**
2a	OMe-3, H-5	**2b**
3a	H-3, Br-5	**3b**
4a	H-3, NO_2-5	**4b**
5a	Bu^t-3,5	**5b**
6a	I-3,5	**6b**

Crystallographic structures

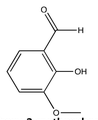


Crystal structures of the series demonstrate identical dimer configurations with each respective combination of precursors

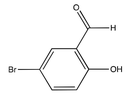
Reactivity of a 2-hydroxybenzaldehyde family



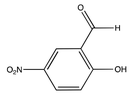
(1) Salicylaldehyde



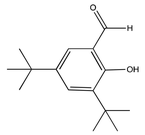
(2) 2-hydroxy-3-methoxybenzaldhyde



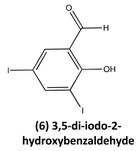
(3) 5-bromosalicylaldehyde



(4) 2-hydroxy-5-nitrobenzaldehyde

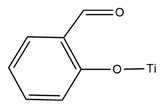


(5) 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde

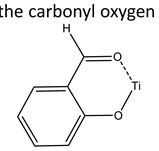


(6) 3,5-di-iodo-2-hydroxybenzaldehyde

A family of 2-hdroxybenzaldehyde precursors were used to determine the behavior of the competitive reactive sites on the molecule. Initially there were two possibilities discussed for the binding of the aldehyde to the metal. First there was the monodentate binding mode which sees a single bond on the deprotonated OH. Second was a bidentate mode which shows an interaction between the carbonyl oxygen as well as the binding to the OH.

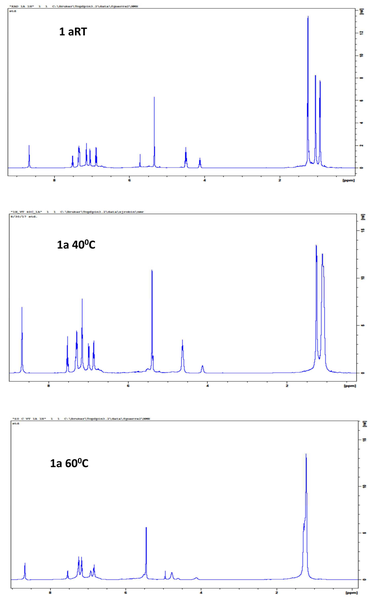


Monodentate binding



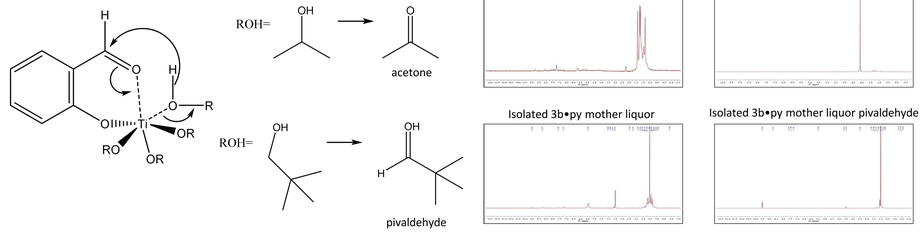
Bidentate binding

Variable Temperature ^{1}H NMR



Variable temperature NMR led us to believe that a monomer-dimer exchange was present in solution with the monomer being favored at higher temperatures

Finding MPV By-products



DOSY Solution Behavior

Diffusion Ordered Spectroscopy is an NMR method that reports diffusion coefficients by utilizing magnetic field gradients. DOSY can be helpful when analyzing mixtures of small and oligomeric states. DOSY measurements of these molecules suggest a monomer-dimer behavior but only in sterically hindered neopentoxide derivatives

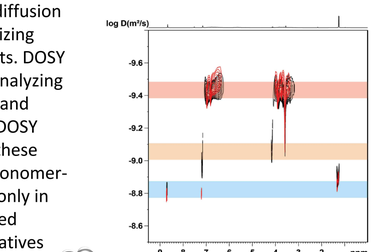
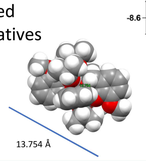
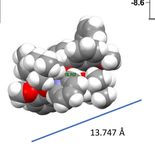


Figure 3. DOSY representation of the PFG NMR diffusion experiments for **2a** at 298K (blue) and 333K (red).





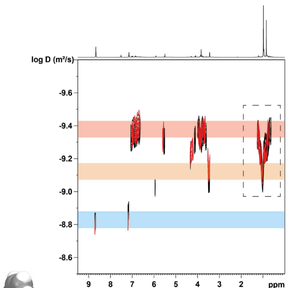


Figure 4: DOSY representation of the PFG NMR diffusion experiments for **2b** at 298K (blue) and 333K (red).

Summary

- Synthesis of reduced aldehyde titanium derivatives
- Stopped Oligomerization of titanium complexes
- Characterization of compounds via ^{1}H NMR, ^{13}C NMR, and FT-IR
- Completed Variable Temperature Studies
- Completed DOSY measurements
- Confirmation of MPV mechanism
- Publication in process

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.