Synthesis and Characterization of Cl_3Zr-O-Si-$(O)_3$-(bulk silica gel) and (binol)-Zr-O-Si-$(O)_3$-(bulk silica gel)

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Abstract

Synthesis of $ZrCl_3$ bound to silica gel through an oxygen-zirconium bond has been attempted via the following reaction.

$ZrCl_4$ + H-O-Si-$(O)_3$-(bulk silica gel) → Cl_3Zr-O-Si-$(O)_3$-(bulk silica gel) (**I**) + HCl(*g*)

Dried silica gel was reacted with $ZrCl_4$, evolving HCl and producing a surface bound metal compound. Mass balance, a weight gain of 14.7%, indicates that some zirconium containing complex is bound. A method to determine zirconium content in the synthesized compound was developed via inductively coupled plasma (ICP)-MS and HCl evolved during the reaction was measured by KOH titration. Recent data, however, is providing inconsistent results. Regardless, an average weight gain of 14.7% and evolution of HCl during the formation of **I** suggests that $ZrCl_3$ is bound to the silica gel surface through a zirconium-oxygen bond. The supported zirconium complex reacts with 1,1'-bi-2-naphthol (BINOL) with evolution of HCl, which suggests that the following substitution occurs.

I + binol → (binol)-ClZr-O-Si-$(O)_3$-(bulk silica gel) (**II**) + 2 HCl(*g*)

In the future, **II** will be characterized by zirconium analysis via ICP-MS, IR, solid state NMR and elemental analysis and stoichiometry of the reaction will be confirmed by titrating evolved HCl with KOH.

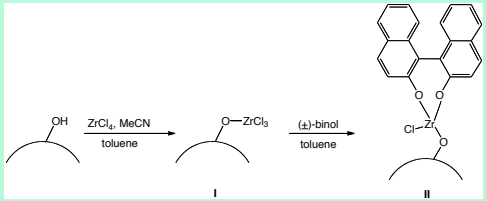
Introduction

Synthetic routes to single-enantiomer production have been widely studied and can be achieved by various means. Asymmetric synthesis, specifically the use of enantiospecific catalysts, can prevent formation of the unwanted enantiomers. Chiral Lewis acid catalysts can be used to catalyze enantiospecific formation of carbon-carbon bonds. Moreover, use of heterogeneous catalysts have a number of advantages over homogeneous catalysts including ease of separation from products and greater reusability.

Synthesis of a Lewis acid surface bound heterogeneous catalyst containing zirconium trichloride bound to silica gel through an oxygen-zirconium bond and of (binol)-ClZr-O-Si-$(O)_3$-(bulk silica gel) (**II**) has been attempted. We have a number of ways to characterize synthesized compounds, including IR, solid state NMR and elemental analysis. Yet, none of these methods can quantify zirconium content. As inductively coupled plasma (ICP) MS has low detection limits and can be used rapidly to determine elements present, a method to determine zirconium content in synthesized products was developed.

Previous work using a slightly different method for ICP-MS sample preparation has shown Cl_3Zr-O-Si-$(O)_3$-(bulk silica gel) (**I**) to contain approximately 7% zirconium by weight, corresponding to about 0.76 mmol Zr bound per gram of synthesized compound. To confirm the stoichiometry of the reaction, the moles of HCl evolved in reactions in which HCl generated was trapped in water were titrated with KOH.

Experimental



Scheme 1. Synthesis of Cl_3Zr-O-Si-$(O)_3$-(bulk silica gel) (**I**) and of (binol)-ClZr-O-Si-$(O)_3$-(bulk silica gel) (**II**)

Zirconium Analysis
- Digest sample for 20 or 72 hr in conc. HNO_3
- Vacuum filter digest and rinse filter with conc. HNO_3
- Use filtrate to determine zirconium content

Determination of Zirconium content via ICP-MS
- Make 4 standards containing 50.0ppb, 25.0ppb. 12.5ppb, and 6.25ppb Zr in 2% HNO_3 or 0.632M HNO_3 by volume via 1:1 serial dilutions
- Dilute filtrate in 2% HNO_3 or 0.632M HNO_3
- Measure mean intensity of standards and samples via ICP-MS
- Use the outputted standard curve equation (from linear regression) to calculate the concentration of Zr in the diluted sample
- Calculate the %Zr by wt from the original sample

Table 1. Weight gain, zirconium content and the amount of HCl generated for different synthetic runs.

run	product	% weight gain	calibration curve	% Zr by weight	mmol Zr per g of product	mmol HCl evolved per g of product
1	**I**	-0.196*	A	6.79	0.744	-
2A**	**I**	17.1	B	7.20	0.789	-
	I**	25.3	-	9.37	1.03	1.03
2B**	**I**	17.1	C	12.45	1.37	-
3	**I**	11.7	C	12.90	1.41	0.9101±0.0048
4	**I**	21.1****	-	-	-	2.124±0.012
5	**I**	15.4	C	14.11	1.54	-
6	**II**	-6.29*	C	9.83	1.01	-

*A relatively small amount of starting materials were used.
**Runs 2A and 2B used the same product for Zr analysis.
***This row contains computed values using 2g silica gel and 0.6g $ZrCl_4$, assuming that all $ZrCl_4$ reacts and one HCl is lost, forming one Zr-O bond per $ZrCl_4$.
****The product contained visible $ZrCl_4$ (starting material). Thus, Zr analysis was not performed.

Results and Discussion

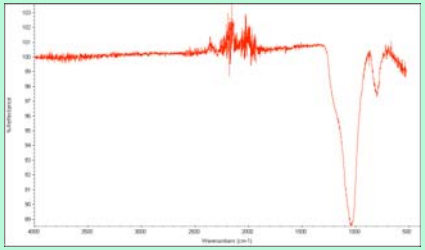


Figure 1. IR spectrum of **I**

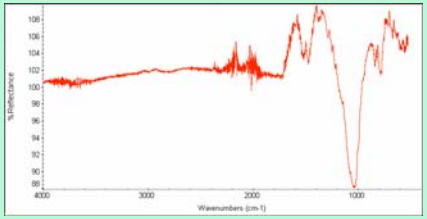


Figure 2. IR spectrum of **II**

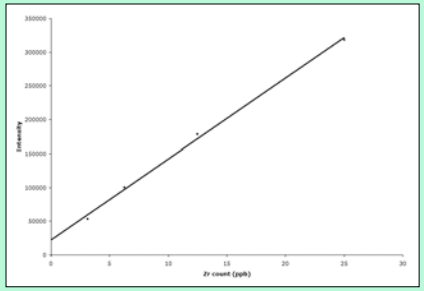


Figure 3. Calibration curve for ICP-MS

In Table 1, Zr analysis of **I** for runs 2B, 3 and 5 used a modified method for sample preparation and detected an average of 13.15% Zr by wt. This value is greater than 9.37% Zr by wt, the maximum value for the percentage of zirconium based on the amount of starting material used. However, previous Zr analysis gave consistent results for runs 1 and 2A, detecting about 7% Zr by wt corresponding to an average of 0.76mmol Zr bound per gram of **I**. Although the samples for runs 1 and 2A were digested for 20 hr whereas the samples for runs 2B, 3 and 5 were digested for 72 hr, the duration of digestion cannot account for the inflated Zr content data for runs 2B, 3, and 5. On the other hand, the weight gain for runs 2A (2B), 3 and 5 are consistent. In combination with the Zr analysis data, this suggests that a systematic instrumentation error may be causing the difference in Zr content between runs 2A, 2B, 3 and 5.

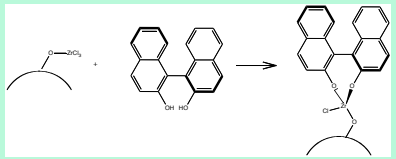
For the titration data, calculations for run 3 found 0.9100 mmol HCl evolved/g of product, which is close but less than the theoretical value of 1.03 mmol HCl evolved/g of product. It is possible that only a fraction of HCl evolved that is trapped from the reaction. We are currently investigating the causes of the fluctuating zirconium content and HCl generation values.

Nonetheless, an average weight gain of 14.7% and evolution of HCl during the formation of **I** suggests that $ZrCl_3$ is bound to the silica gel surface through a zirconium-oxygen bond.

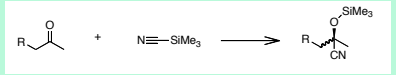
Zirconium analysis of **II** determines the product to contain 9.83% Zr by wt, which is also greater than the theoretical value for zirconium content of 8.73% Zr by wt. Comparing IR of **I** and **II**, the spectrum for **II** shows aromatic ring breathing between 1800 - 1300 cm^{-1} and lacks O-H peaks between 3400 - 3300 cm^{-1}, which suggests that binol is bound to the product.

Future Work

-Determine the cause of inflated Zr content measured and HCl evolved.
-Characterize **II** through solid state NMR and elemental analysis.
-Test **I** and **II** for catalytic activity in the silylcyanation reaction.
-Synthesize *(R)*-(binol)-ClZr-O-Si-$(O)_3$-(bulk silica gel).



Scheme 2. Synthesis of (*R*)-(binol)-ClZr-O-Si-$(O)_3$-(bulk silica gel)



Scheme 3. Silylcyanation reaction

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