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Bulky Aryloxy Catalyst Precursors for CO2 Reduction

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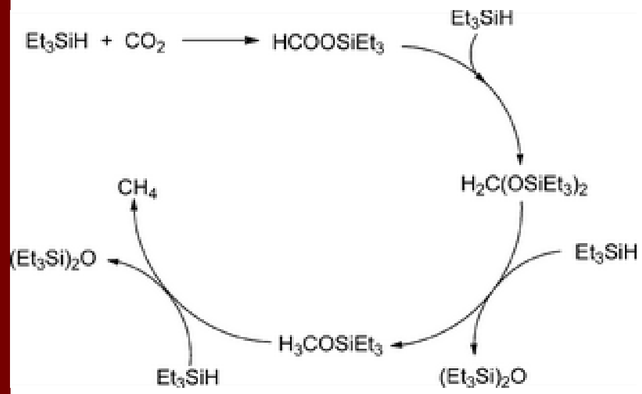
Background:

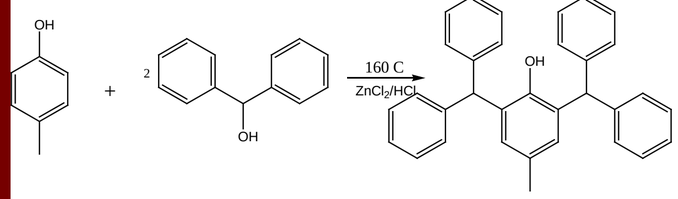
The search for a good catalyst for CO_2 reduction using triethylsilane has been a recent research topic in our lab. Since CO_2 is a greenhouse gas, its conversion into something useful on an industry level scale while removing it from the environment would be extraordinary. It has been previously hypothesized that the high strength and polarity of the Al-O bond in low coordinate cationic aluminum alkoxides and phenoxides $[(RO)_2Al]^+$ would make more reactive and robust catalysts[1]. A study has been performed for a proposed mechanism[2].



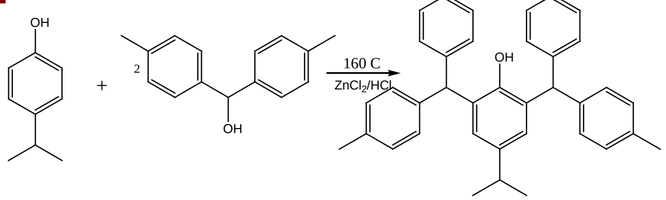
The disubstituted metal phenolates are the desired product to give the metal center less susceptibility to be attacked and form aggregates. Here we report the syntheses of 2 new phenols and 8 new mono-substituted metal phenolate compounds

Organic Syntheses

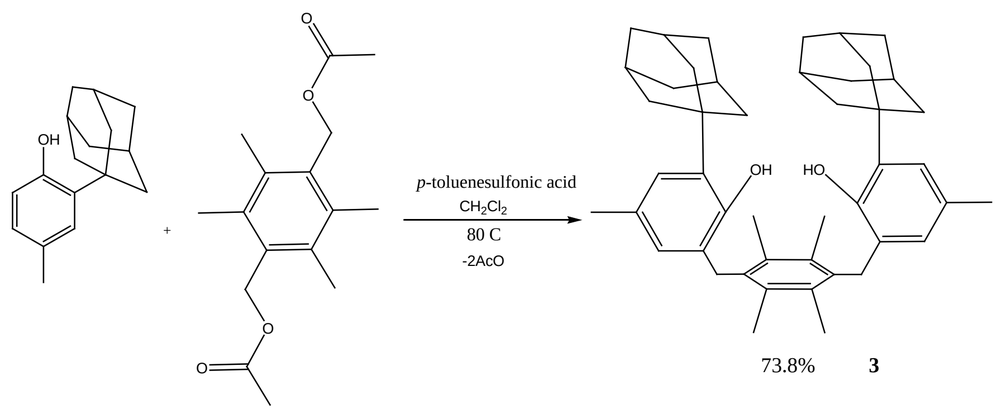
2,6-Bis(diphenylmethyl)-4-methylphenol (**1**) was prepared according to the literature procedure[3]. 2,6-Bis(ditolylmethyl)-4-isopropylphenol (**2**) was prepared in analogy to **1** using 4-isopropylphenol and ditolylmethanol. 1,4-Bis(3-adamantly-5-methyl-2-phenolmethyl)-2,3,5,6-tetramethylbenzene (**3**) was synthesized in analogy to the literature procedure[4] using 1,4-bis(acetoxymethyl)-2,3,5,6-tetramethylbenzene and 2-adamantly-*p*-cresol



49.1% **1**



38.5% **2**



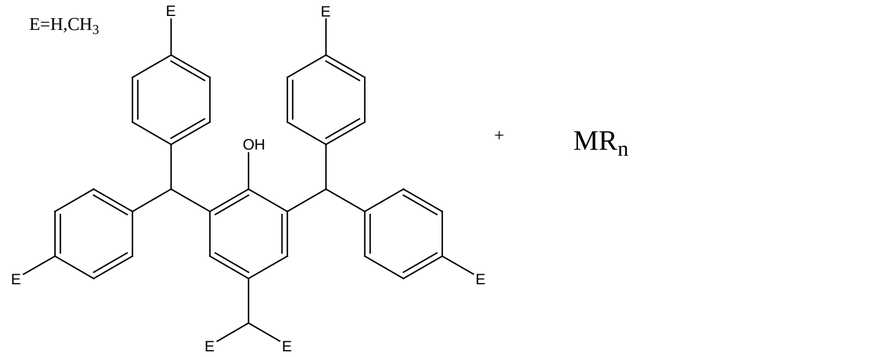
73.8% **3**

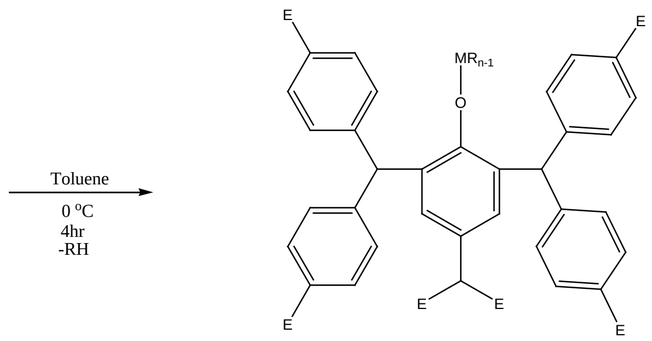
Inorganic Syntheses:

Several 2:1 reactions involving **1** and $AlEt_3$ respectively were carried out, and no product was isolated. Several 1:1 reactions involving **3** and $AlEt_3$ were carried out also no product was isolated. Since the desired 2:1 product was not forming, the 1:1 reaction of **1** and $AlEt_3$ was attempted and afforded a clean product.

General Procedure:

Using standard air-free procedures. To a solution of the bulky phenol in toluene was added MR_n (M=Al, Ga (R=Et), (n=3), Mg (R=*n*-Bu), Zn (R=Et), (n=2)) in toluene at 0 °C on a 1:1 scale. The reaction was let warm to room temperature and stir for 4 hr. The solvent was pumped off and afforded the product mixture $MR_{n-1}(ArO)$.





Results:

	H	CH_3
Al	48%	Recrystallizing
Ga	69%	Recrystallizing
Mg	Not Isolated	Not Isolated
Zn	53%	50%

Table 1: Percent Yields of 1:1 MR_n + **1,2**

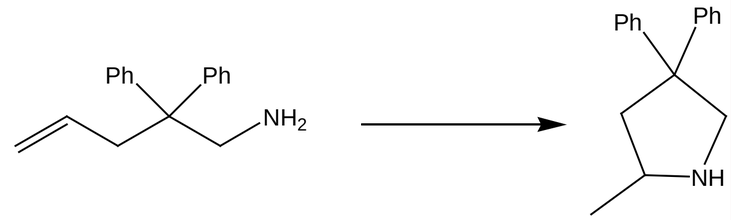
Conclusion:

All the 1:1 reactions with **1** and **2** proceeded for all the metal alkylates. The bidentate phenol **3** unfortunately did form a product. Computational studies have shown that if the bidentate product with **3** formed, that the metal-ligand bonds would be too long to form a stable product.

Future Work

Attempting the 2:1 reactions with **1** and **2** with the other metal alkylates and reacting **3** with larger metals such as zirconium. The synthesized metal phenolate compounds can be further converted into ionic species for the CO_2 catalytic studies. Hydroamination can be another way to determine the catalytic properties of the ionic species.

$$(MR_{n-1}ArO) + (CPh_3)(CHB_{11}Cl_{11}) \longrightarrow (MR_{n-2}ArO)^+(CHB_{11}Cl_{11})^-$$



Acknowledgements:

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