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Homogeneous and Supported Niobium Catalysts as Lewis Acid and Radical Catalysts.

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Abstract

The synthesis of tetrachlorotetraphenylcyclopentadienyl group 5 metal complexes has been accomplished through two routes, one a salt metathesis with lithiumtetraphenylcyclopentadiene and the other, reaction with trimethyltintetraphenylcyclopentadiene. The reactants and products have been characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The niobium complex promotes the silylcyanation of butyraldehyde.

The grafting of metal complexes to silica gel surfaces has been accomplished using tetrakisdimethylamidozirconium as the metal precursor. The most homogeneous binding as determined by CP-MAS ^{13}C NMR and infrared spectroscopy was obtained with drying at 500°C at 3 mtorr vacuum. The remaining amido groups can be replaced by reaction with alcohols to generate surface bound metal alkoxides. These bound catalysts promote silylcyanation of aryl aldehydes and can be reused three times with no loss of activity.

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Executive Summary

The testing of catalyst candidates pentaphenylcyclopentadienylniobium(V)chloride and pentaphenylcyclopentadienylniobium(IV)chloride was not accomplished as there were problems preparing the desired compounds. However, we have prepared the tetraphenylcyclopentadienylniobium(V)chloride and the analogous tantalum compound and characterized them by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The syntheses were accomplished by two different routes: first, the reaction of MCl_5 ($\text{M} = \text{Nb, Ta}$) with $(\text{CH}_3)_3\text{Sn}-\text{HC}_5\text{Ph}_4$ and second; the salt methathesis of LiHC_5Ph_4 with MCl_5 in diethyl ether or dichloromethane. These complexes promote the silylcyanation of butyraldehyde at room temperature at loadings of 1 mole %.

Finally, the determination of drying conditions of high surface area silica gel in preparation for the attachment of niobium complexes has been addressed using a redox stable, NMR sensitive probe, $\text{Zr}(\text{N}(\text{CH}_3)_2)_4$ using both multinuclear CP-MAS NMR spectroscopy and infrared spectroscopy. The use of high temperatures (500°C) and a surface preparation reagent $(\text{Si}(\text{CH}_3)_3)_2\text{Cl}$ prior to reaction with the metal complex appears to provide the most homogeneous surface species. These surface bound complexes can then be derivatized by reaction of the dimethylamido ligands with chiral alcohols to give optically active surface bound catalysts that promote silylcyanation of benzaldehyde.

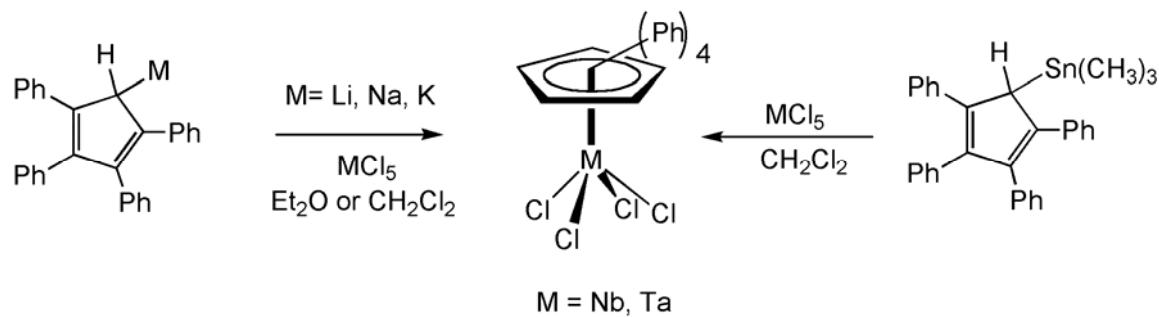
Approach

The approach to achieving the goals of this work is to first synthesize the niobium complexes of the polyaryl-cyclopentadienyl ligand and then proceed towards the goals of preparing derivatives of these and testing their effectiveness as catalysts in [4+2] cycloaddition and polymerization reactions.

Results and Discussion

Group 5 Piano Stools

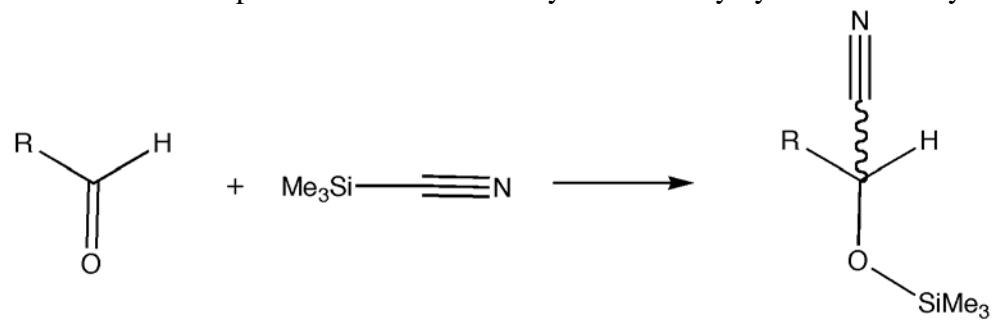
More progress has been made in the second project, that for the synthesis of the Group 5 four legged piano stools. Two routes have been used and are shown below in Scheme 1. Preliminary results show that the tin reagent at the right of the scheme is much more selective than the corresponding silicon reagent that we previously prepared and characterized. However, the use of the lithium reagent at left gives much cleaner reaction than the potassium salt previously used and respectable unoptimized yields are obtained.



Scheme 1. Synthetic routes to four legged piano stools.

These preparations are detailed below; we require some more work before submission of the manuscript.

The niobium complex is an effective catalyst for the silylcyanation of butyraldehyde.



NMR studies show nearly complete conversion at ambient temperatures in 18 hours, at which time no reaction is observed by NMR in the control.

Interaction of trimethyltin-tetraphenylcyclopentadiene with niobium(V)chloride

Preliminary studies, in the form of a NMR-scale reaction mixing a 1:1 molar ratio of niobium pentachloride (21 mg, 0.08 mmol) and trimethyltin-tetraphenylcyclopentadiene (48 mg, 0.09 mmol) in deuterated methylene chloride for 24 hours, indicate that it is possible to synthesize $C_5Ph_4NbCl_4$ using the tin complex as a precursor. Further work must be done to optimize this reaction. 1H -NMR (400 MHz, CD_2Cl_2) CH , δ = 4.71(s); C_6H_5 , δ =6.32-7.32(m).

Interaction of lithium tetraphenylcyclopentadienide with MCl_5 ($M= Nb, Ta$)

Another path to these complexes is the direct salt metathesis reaction of lithiumtetraphenylcyclopentadienide with the group 5 pentachloride complexes of niobium and tantalum in *dichloromethane*. Although this process produces intractable solids in toluene or dichloromethane, in diethyl ether, air and moisture sensitive precipitates are formed which readily dissolve in coordinating solvents such as acetonitrile. The use of longer reaction times results in lower yields; work is in progress to optimize the yields through adjustment of time and temperature.

We are currently completing the characterization of these complexes and then proceed to forming chiral and reduced derivatives.

Trimethylsilylcyanation activity

The tetrachlorotetraphenylcyclopentadienylniobium complex is an effective catalyst for silylcyanation of butyraldehyde. NMR monitoring of a CD_2Cl_2 solution of equimolar trimethylsilyl cyanide and butyraldehyde with 1 mole% $HC_5Ph_4NbCl_4$ shows complete reaction in about 16 hours at room temperature whereas a control shows less than 5% conversion under the same conditions.

Surface Organometallic Complex Lewis Acid catalysts

By monitoring the filtrate solutions of pentaphenylcyclopentadienyl zirconium complexes that had been grafted onto silica gel, it was determined that the cyclopentadienyl ligands were being lost, apparently through protonation. At that time, it was decided to (a) test different drying conditions and (b) limit ligands to oxygen donors, as these are expected to be much less labile. We first examine the effect of drying the silica gel at different temperatures.

Drying silica gel at 3 mtorr at different temperatures was studied by ^{29}Si NMR and IR spectroscopy.

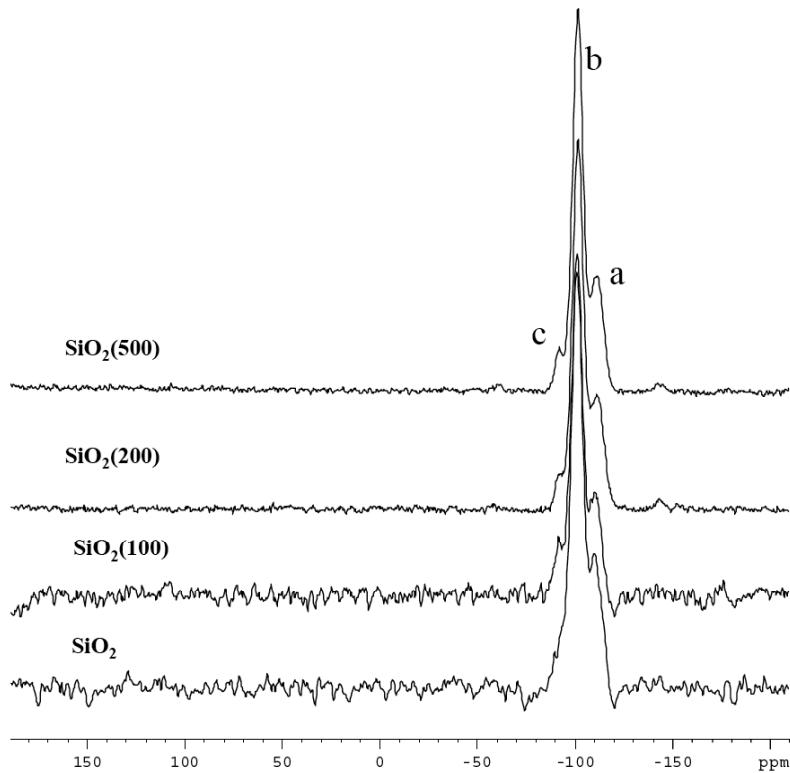


Figure 1. MAS ^{29}Si NMR spectra of silica gel dried at different temperatures

As drying is performed at higher temperature, the MAS ^{29}Si NMR in Figure 1 shows better resolution of the Q2, Q3 and Q4 signals. The ATR FT-IR spectra of these samples in Figure 2 shows a diminishment of the H-bonded O-H groups (broad band ca. 3500 cm^{-1}) and the presence of non-H-banded OH groups (sharp peak ca. 3700 cm^{-1})

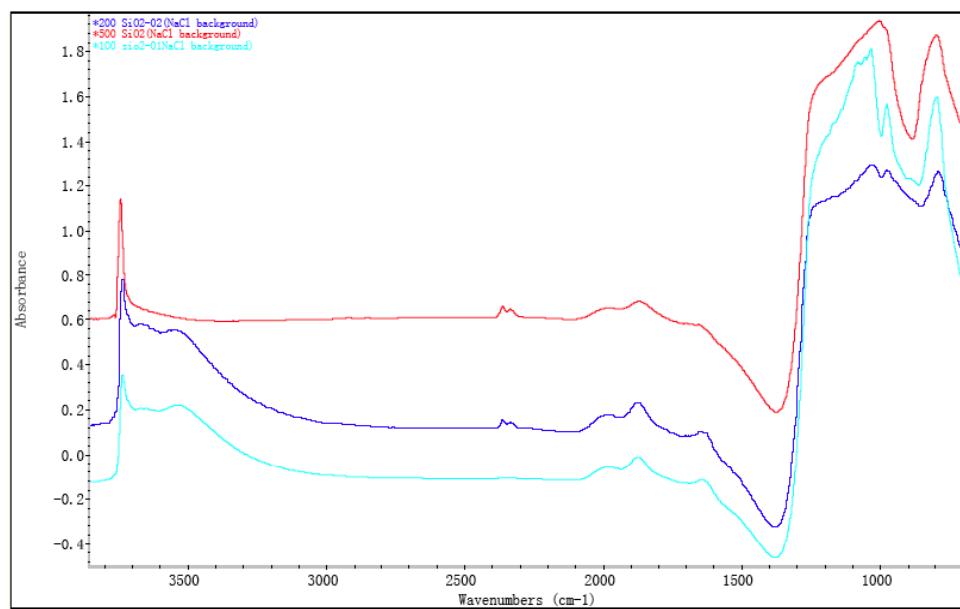


Figure 2. IR absorption spectra of silica gel dried at different temperatures.

The 500° dried silica gel appeared to provide the most homogeneous surface bound zirconium species in reactions with $Zr(NMe_2)_4$. For 100° drying, two signals were observed in the CP-MAS ^{13}C NMR at δ 50 and δ 40 PPM. Drying at 200°C diminished the peak at δ 50 to a shoulder, and 500° drying gave one signal at δ 40.

In our studies we discovered a novel application of trimethyl silyl chloride in treating silica gel. We first contemplated the use of trimethyl silyl chloride as a passivating agent, to remove sites of Brønsted acidity.



The lower two traces in Figure 3 show the reaction of TMSCl after the surface has reacted with $Zr(NMe_2)_4$. The signal for the dimethyl amido groups has split in to a two peaks, one nearly 10 PPM downfield and a signal for the trimethyl silyl group is present at about δ 0. The middle trace (labeled 500 SiO_2 -TMSCl) shows a single peak at δ 0 when TMSCl is reacted with the dried silica gel. The upper two traces show the results of reaction of the silylated silica gel with $Zr(NMe_2)_4$: in both cases a single signal at δ 40 results with only a small signal at 0. The CP-MAS ^{29}Si NMR spectra of these samples are consistent with the ^{13}C NMR:

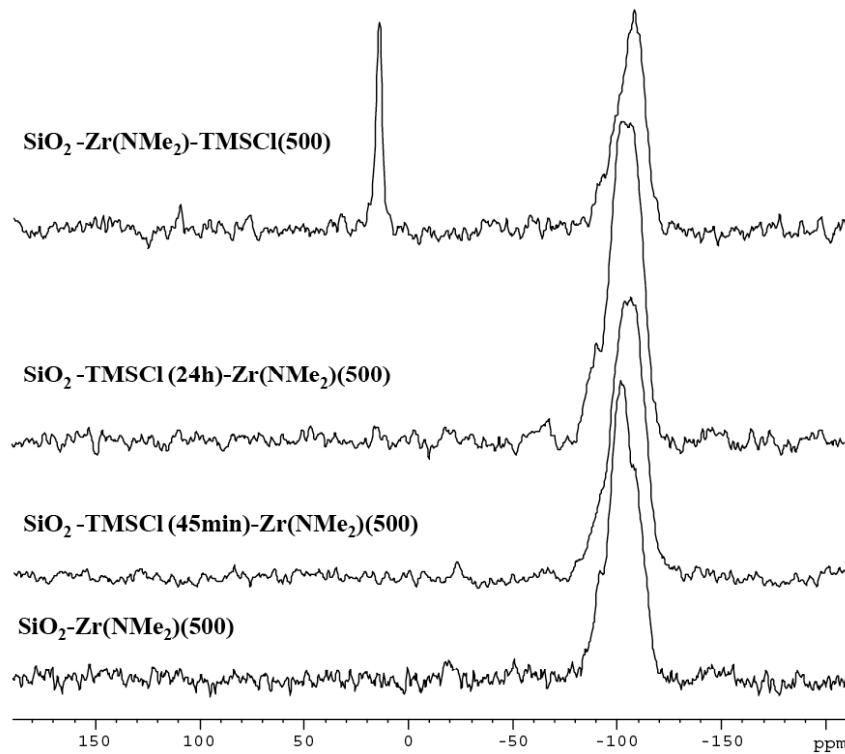


Figure 4 shows the silicon from TMS (near 0 PPM) only when TMSCl is the last reagent to be added. Infrared spectra show that TMSCl is very efficient at reacting with surface hydroxyl groups; Figure 5, trace b shows that OH groups remain after reaction with $Zr(NMe_2)_4$, but subsequent reaction with TMSCl (trace c) removes those OH groups.

However, the reaction of TMSCl after the dimethylamidozirconium reaction changes the coordination sphere of the Zr as noted by changes in the ^{13}C NMR (Figure 3 (500 Si-Zr(NMe₂)-TMSCl) and the IR spectra (Figure 5, traces b and c).

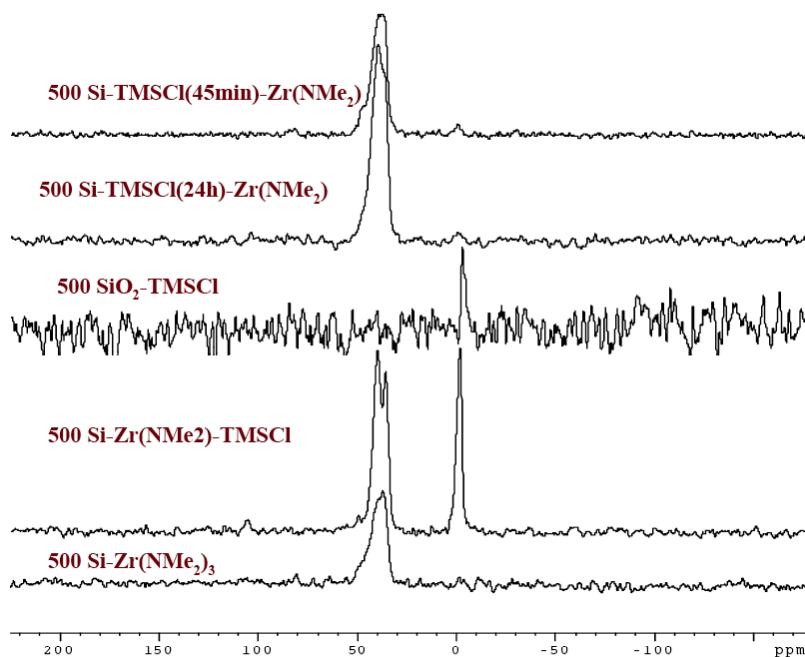
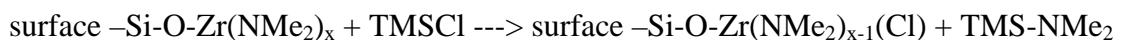


Figure 3. CP-MAS ^{13}C NMR spectra of silica gel reacted with Zr(NMe₂)₄ and TMSCl with different orders of addition.

Since the top three traces in Figure 3 demonstrate that Zr(NMe₂)₄ can react with the surface bound TMS groups (note the formation of one signal at δ 40), we believe that subsequent reaction of TMSCl with surface bound Zr(NMe₂)_x groups results in substitution of Cl for one or more dimethylamido groups.



This is supported by Figure 3, trace $\text{SiO}_2\text{-Zr}(\text{NMe}_2)\text{-TMSCl}$ (where two peaks are observed after TMS-Cl reaction) and

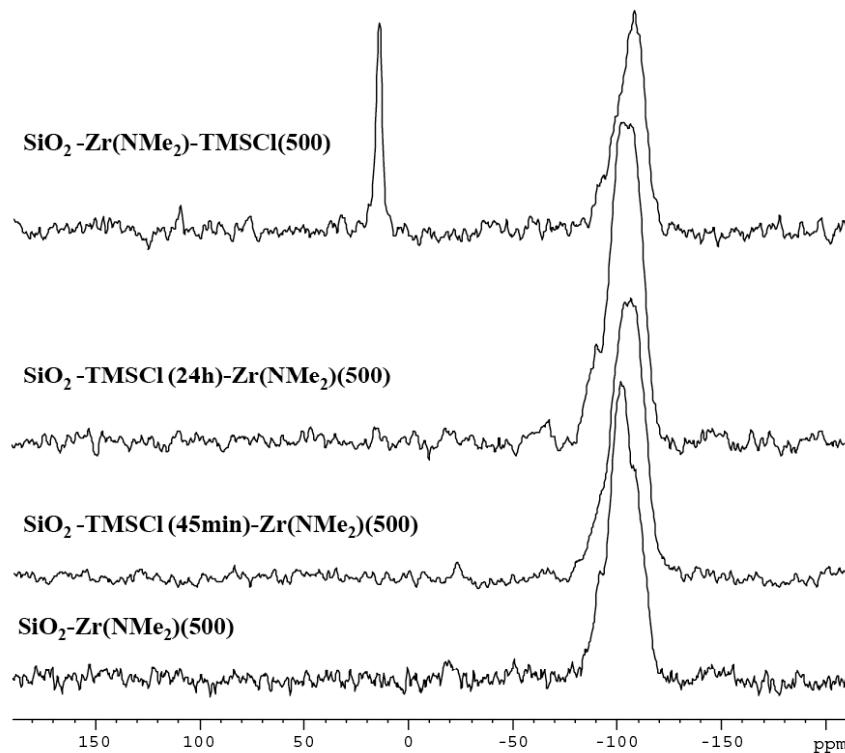


Figure 4, top trace.

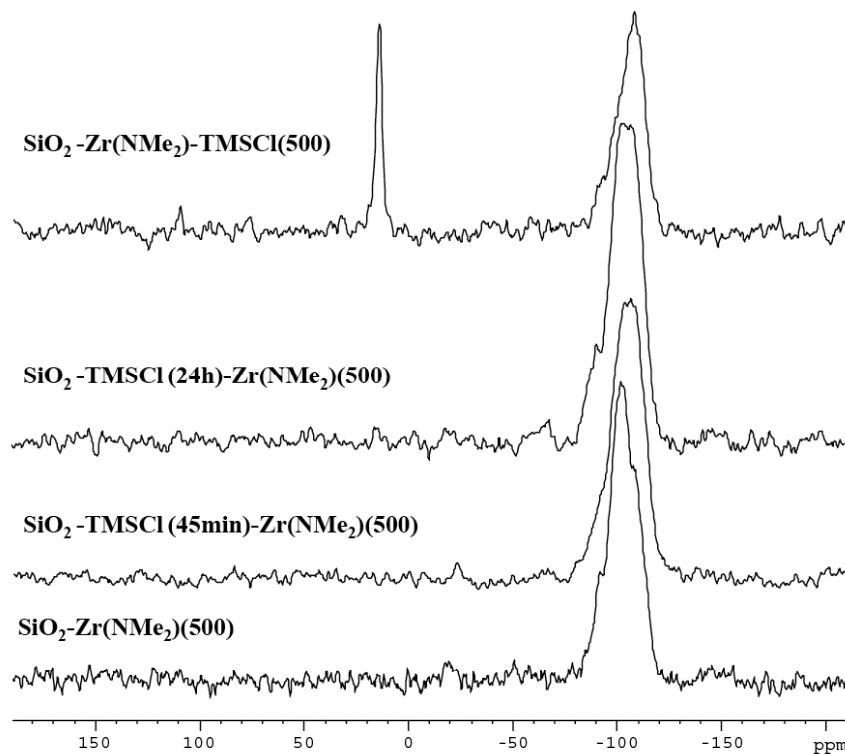


Figure 4. ^{29}Si MAS NMR of silica gel reacted with $\text{Zr}(\text{NMe}_2)_4$ and TMSCl with different orders of addition.

These results suggest that the TMSCl can be used to remove the Brønsted acidic groups and still provide a reactive site for substitution reactions to covalently bond metal complexes to the surface.

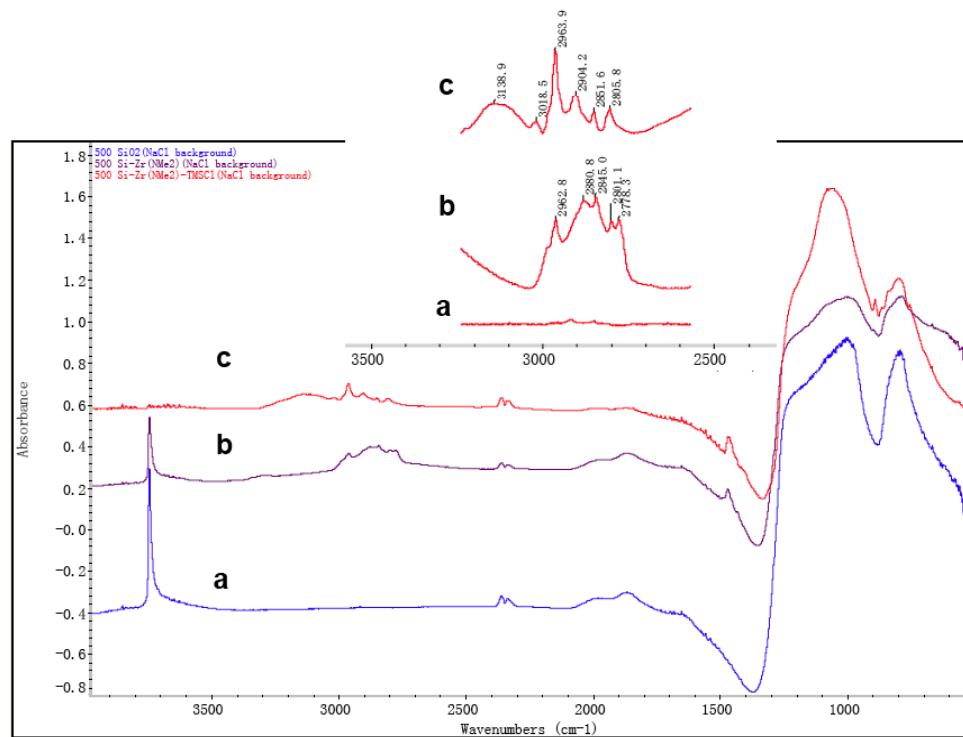


Figure 5. IR absorption spectra of silica gel reacted with $\text{Zr}(\text{NMe}_2)_4$ and TMSCl with different orders of addition: a, dried silica gel; b, silica gel + $\text{Zr}(\text{NMe}_2)_4$; c, silica gel + $\text{Zr}(\text{NMe}_2)_4$ + TMSCl .

We have recently performed C/H/N analysis on a number of these catalysts and are awaiting the results of ICP-MS determination of Zr content to complete the analysis of this data. The data support that reaction proceeds more completely with silica gel dried at the higher temperature. For example, the CHN data are consistent with the tartrate content on the zirconium functionalized systems to be twice as high for 500°C dried silica gel as that for 200°C silica gel.

Silylcyanation of aromatic aldehydes was undertaken to test the efficacy of these catalysts. Aldehydes with activating and deactivating groups were tested and all were converted with the active tartrate and binol catalysts (see Table 1). Chiral column analysis was performed on some of the benzaldehyde reactions and some of those results are in Table 2. These catalysts have been reused three times with no measurable loss of activity. Promising results were observed and further work to elucidate the nature of the active catalysts is in progress.

Table 1. Yields obtained for silylcyanation of benzaldehyde with different catalysts.

No.	Catalysts(used 500 °C dried silica gel)	% Yield Benzaldehyde
1	Si-Zr(NMe ₂)-Tartrate	84%
2	Si-Zr(NMe ₂)-Tartrate-TMSCl	73%
3	Si-TMSCl-Zr(NMe ₂)-Tartrate	86%
4	Si-Zr(NMe ₂)-R-Binol	94%
5	Si-Zr(NMe ₂)-R-Binol-TMSCl	94%
6	Si-TMSCl-Zr(NMe ₂)-R-Binol	96%
7	Si-Zr(NMe ₂)-PEA	91%
8	Si-Zr(NMe ₂)-PEA-TMSCl	95%
9	Si-TMSCl-Zr(NMe ₂)-PEA	83%
10	Si-TMSCl-Zr(NMe ₂)-Tartrate-TMSCl	65%
11	Si-C ₅ Ph ₄ Zr(NMe ₂)-PEA-TMSCl	84%
12	Si-C ₅ Ph ₄ Zr(NMe ₂)-Tartrate	76%
13	Si-TMSCl-C ₅ Ph ₄ Zr(NMe ₂)-Tartrate	74%
14	Si-TMSCl-C ₅ Ph ₄ Zr(NMe ₂)-R-Binol	83%

Table 2. Catalysts and ee's for silylcyanation of benzaldehyde. Catalyst preparation indicates order of addition of the components to the 500°C dried silica gel. (TMSCl = Si(CH₃)₃Cl; tartrate = diethyl-*L*-tartrate; R-binol = *R*-binaphthol; PEA = *R*-phenethylalcohol; IP = in progress; NR – no acceleration beyond control.

Catalyst Preparation	Observed ee with benzaldehyde
SiO ₂ -Zr(NMe ₂) ₄	NR
SiO ₂ -TMSCl-Zr(NMe ₂) ₄	NR
SiO ₂ -Zr(NMe ₂) ₄ -TMSCl	NR
SiO ₂ -Zr(NMe ₂) ₄ -tartrate	IP
SiO ₂ -TMSCl-Zr(NMe ₂) ₄ -tartrate	85%
SiO ₂ -Zr(NMe ₂) ₄ -tartrate-TMSCl	IP
SiO ₂ -Zr(NMe ₂) ₄ -R-binol	IP
SiO ₂ -TMSCl-Zr(NMe ₂) ₄ -R-Binol	IP
SiO ₂ -Zr(NMe ₂) ₄ -R-binol-TMS-Cl	IP
SiO ₂ -Zr(NMe ₂) ₄ -PEA	IP
SiO ₂ -TMSCl-Zr(NMe ₂) ₄ -PEA	IP
SiO ₂ -Zr(NMe ₂) ₄ -PEA-TMSCl	74%
SiO ₂ -TMSCl-Zr(NMe ₂) ₄ -tartrate-TMSCl	IP

Conclusions

The synthesis of C₅Ph₄HSnMe₃ as a precursor has been achieved. We expect to complete the characterization in the near future and exploit its anticipated cleaner reactivity in the synthesis of niobium complexes as a higher yield alternative to the silyl compounds. We

are surprised and delighted that the use of ether (which was not effective earlier work with the pentaphenyl derivative) provides access to the desired metal complexes. Both of these routes offer promise to produce the desired compounds for catalyst assessment.

The testing of catalyst candidates based on tetraphenylcyclopentadienyl-niobium(V)chloride has been initiated. This complex shows activity and turnover numbers of at least 100 based on complete reaction at 1 mole% loading. These results were presented at the 233rd ACS National meeting in Chicago, IL and earlier in the year at an undergraduate research symposium hosted by Occidental College by the three students who have been involved in the project (Poster 39, Synthesis and ¹H NMR Characterization of group VB pentahaptocyclopentadienyl transition metal complexes. Danielle Barrios, Tiffany Kwong, Jose B. Lepe, Gordon Tan, Southern California Conference for Undergraduate Research, Occidental College, Los Angeles, CA, November 18, 2006) and most recently at the ACS National meeting in Chicago (#190 "Synthesis and characterization of group 5 pentahaptocyclopentadienyl-transition metal compounds" Wayne Tikkannen, J. Bernardo Lepe*, Danielle T. Barrios*, and Tiffany C. Kwong* 25 March 2007 233rd National Meeting, Chicago, IL). . The preparation and activity of the corresponding Ta complex and chiral derivatives will be investigated using support from other sources.

The supported metal systems have shown significant promise as catalysts since we have been able to prepare active catalysts, some of which exhibit significant enantioselectivity. Some of this work was presented at a regional ACS meeting (#160 "Synthesis, reactivity and characterization of a silica gel supported polyphenyl-cyclopentadienylzirconium(IV) complex, Ziwei Gao*, Veronica Barahona, Luis Gomez, Danielle Barrios, Wayne Tikkannen; ; 61st Northwest Regional Meeting of the American Chemical Society, Reno, NV 27 June 2006). We have since determined that the use of trimethylsilyl chloride is an effective hydroxyl group scavenger and the surface bound TMS group appears to also provide a reasonable leaving group upon reaction with metal amido complexes. Work on this project will also continue using support from other sources.

Experimental.

General procedures.

Silica gel 60 (CAS #63231-67-4, catalog #M9385-9 or #M9385-3, 40 – 63 μ m particle size, 230 – 400 mesh (ASTM), 480 – 540 m^2/g surface area, 0.74 – 0.84 mL/g pore volume, pH 7.0 \pm 0.5) was ordered from Fisher Scientific. $\text{Zr}(\text{NMe}_2)_4$ (CAS #19756-04-8), (+)-(-)-sec-phenethyl alcohol (PEA, CAS #19756-04-8) and Me_3SiCl (TMSCl, CAS #75-77-4) were purchased from Aldrich. (R)-1,1'-bi-(2-naphthol) (R-Binol, 18531-94-7), NbCl_5 , and TaCl_5 was purchases from Alfa Aesar. L(+)-diethyl L-tartrate was purchased from Acros. Solvents (toluene and CH_2Cl_2) were purchased from Aldrich, further purified using an MBRAUN Solvent Purification System, and stored under N_2 over 4 \AA (8-12 mesh) molecular sieves. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories (Woodside, New York). Zr analyses were performed by dissolving a sample of the functionalized silica gel in aqueous HF with a Perkin-Elmer

Corporation Elan DR ICP-MS. ^1H , ^{13}C and ^{29}Si CP/MAS NMR spectra were recorded on a Bruker 600 MHz NMR spectrometer using a 4 mm probe. IR spectra were recorded on a NICOLET 6700 FT-IR spectrometer using CaF_2 and NaCl windows. GC analyses were carried out with SRI8610C using a ZB-5 column (60 m \times 0.53 mm).

All air- and moisture-sensitive compounds were transferred using standard vacuum line, Schlenk, or cannula techniques under dry, deoxygenated argon or in a drybox under an argon atmosphere, further purified by passage through activated molecular sieves (4 \AA).

Preparation of LiHC_5Ph_4

Under N_2 atmosphere, to a boiling solution of tetraphenylcyclopentadiene $\text{C}_5\text{Ph}_4\text{H}_2$ (503.0 mg, 1.36 mmol) in anhydrous toluene (40 mL), a solution of 2.5 M N-butyl lithium was added (.75 mL, 1.88 mmol) slowly. A milky white paste forms and changes color from white to pink. The mixture was left stirring under gentle reflux for 24 hrs under N_2 . The color of the mixture at the end of this period goes back to white. The mixture was then filtered through Schlenk filter and the solid product was washed three times with 5 mL portions of pentane. The product then dried in vacuo to afford a white powder $\text{LiC}_5\text{Ph}_4\text{H}$ (432.0 mg, yield 85%). ^1H NMR (300 MHz, CD_3CN) CH , δ =6.10 (s, 1H); C_6H_5 , δ =6.75-7.15 (m, 20H).

The synthesis of trimethyltin-tetraphenylcyclopentadiene $\text{C}_5\text{Ph}_4\text{HSnMe}_3$ (TMSnD)

Diethyl ether (40 mL) was added to trimethyltin chloride (1.98 g, 9.92 mmol) and lithium tetraphenylcyclopentadienide (3.44 g, 9.14 mmol), yielding a turbid yellow mixture that was stirred for 24 hours. The mixture was subsequently gravity-filtered in order to remove LiCl . The resultant yellow solution was then dried in vacuo to afford the yellow solid $\text{C}_5\text{Ph}_4\text{HSnMe}_3$ (2.65 g, unoptimized yield 53.7%). ^1H -NMR (400 MHz, C_6D_6) $\text{Sn}-(\text{CH}_3)_3$, δ =-0.194 (s), $^2\text{J}_{\text{Sn}-\text{H}}=52.5$ Hz; CH , δ =5.05 (s), $^2\text{J}_{\text{Sn}-\text{H}}=89.1$ Hz; C_6H_5 , δ =6.90-7.31 (m). ^{13}C -NMR (400 MHz, C_6D_6) δ =-8.62, 1.34, 14.24, 32.2, 55.72, 126.45, 126.56, 130.28, 131.29, 137.26, 138.57, 139.91

The synthesis of tetraphenylcyclopentadiene-niobium(V)chloride $\text{C}_5\text{Ph}_4\text{HNbCl}_4$ Preliminary studies, in the form of a NMR-scale reaction mixing a 1:1 molar ratio of niobium pentachloride (21 mg, 0.08 mmol) and trimethyltin-tetraphenylcyclopentadiene (48 mg, 0.09 mmol) in deuterated methylene chloride for 24 hours, indicate that it is possible to synthesize $\text{C}_5\text{Ph}_4\text{HNbCl}_4$ using the tin complex as a precursor. Further work must be done to optimize this reaction. ^1H -NMR (400 MHz, CD_2Cl_2) CH , δ =4.71 (s); C_6H_5 , δ =6.32-7.32 (m).

Interaction of NbCl_5 with LiHC_5Ph_4 to give tetraphenylcyclopentadiene-niobium(V)chloride

In the glovebox, a mixture of NbCl_5 (375 mg, 139 mmol) and LiHC_5Ph_4 (508 mg, 1.35 mmol) were placed in a Schlenk flask. A volume of 20 mL of dry diethyl ether was added to the mixture and it was left stirring at room temperature for 4 hrs. The resulting solid was then Schlenk filtered and the product was dried in vacuo overnight to yield a purple powder (375 mg, 46% unoptimized yield). ^1H in CD_2Cl_2 ; HC_5Ph_5 ; δ 4.74 (s, 1 H); C_6H_5 ;

δ 6.48 (m), 6.72 (m), 7.00 (m), 7.10 (m), 7.32 (m), 7.38 (m) (20 H). $^{13}\text{C}\{\text{H}\}$ NMR in C_6D_6 ; peaks obscured by solvent from δ 126.7 to δ 134.6; other resonances at δ 136.3, 136.6, 136.9, and 137.3, 143.7(s), 144.6, 145.1, 145.7.

Interaction of TaCl_5 with LiHC_5Ph_4

Inside a glovebox, a mixture of TaCl_5 (469 mg, 131 mmol) and LiHC_5Ph_4 (480 mg, 1.27 mmol) were placed in a Schlenk flask. A volume of 20 mL of dry diethyl ether was added to the mixture and it was left stirring at room temperature for 4 hrs. The resulting solid was then filtered through a Schlenk flask and the product was dried in vacuo overnight to yield a purple colored powder (442 mg, 50% unoptimized yield). ^1H in CD_2Cl_2 ; HC_5Ph_5 ; δ 4.68 (s, 1 H); C_6H_5 ; δ 6.48 (m), 6.72 (m), 7.00 (m), 7.10 (m), 7.32 (m), 7.38 (m) (20 H).

Silylcyanation studies

In the glove box, a solution was prepared from 2 mL of CD_2Cl_2 , 16 mmole each of trimethylsilylcyanide and butyraldehyde. The solution was split into rotary symmetric (young valve) NMR tubes and to one tube 5. mg (8 μmole) of $\text{HC}_5\text{Ph}_4\text{NbCl}_4$ was added. ^1H NMR spectra were obtained at 1 hour intervals over the next 24 hours in a Bruker AM 400 spectrometer at ambient temperature (23°C). After 18 hours, conversion was complete in the sample containing the niobium complex.

Dehydration of silica gel.

Silica gel 60 was put inside a large quartz tube, having a quartz frit at one end, which was connected with a small water-collecting system via liquid nitrogen (Fig. 1). The loaded tube was then placed inside a tube furnace, where after reaching a homogeneous temperature zone. It was cautiously evacuated, ultimately reaching about 6×10^{-3} torr. Gradually, the tube furnace having three separate silica gel samples were primarily heated up at a rate of 1 °C/min until reaching 100 °C for the first, 200 °C for the second and 500 °C for the third, where sample **SiO₂(100)** maintained a temperature of 100 °C for 24h, sample **SiO₂(200)** of 200 °C for 10h and sample **SiO₂(500)** of 500 °C for 16h. After this heating process, the furnace was allowed to cool slowly under dynamic vacuum where each individual sample was cooled and transferred to an argon glove box.

TMS-modified silica gel

The procedure for TMS-modified silica is as follows: 1.5 g of dehydrated silica with a toluene solution of TMSCl (2.1 mL) was stirred at room temperature overnight. The solvent was removed under vacuum and gave the product **TMSCl-SiO₂(100)**. **TMSCl-SiO₂(200)** and **TMSCl-SiO₂(500)** were prepared with an identical procedure as **TMSCl-SiO₂(100)**.

Preparation of dimethylamidozirconium functionalized silica gel

In the glove box, dehydrated silica (2.0 g), a stir bar and $\text{Zr}(\text{NMe}_2)_4$ (567 mg, 2.1 mmol) were transferred into a Schlenk flask. On the Schlenk line, 20 mL anhydrous toluene was syringed into the flask under N_2 flow and the mixture was stirred for 24 h at room temperature. The suspension was transferred into a Schlemk filter under N_2 flow and then

filtered. The silica collected on the filter was washed with 8×4.0 mL of toluene and dried in vacuum at room temperature overnight. **Zr(NMe₂)_n-SiO₂(100)** was obtained and transferred to the glove box. **Zr(NMe₂)_n-SiO₂(200)** and **Zr(NMe₂)_n-SiO₂(500)** were synthesized with an identical procedure as **Zr(NMe₂)_n-SiO₂(100)**.

Preparation of (R)-1,1'-bi-(2-naphthol) derivatives

In the glove box, **Zr(NMe₂)_n-SiO₂(100)** (2.0 g) and R-Binol (608 mg, 2.1 mmol) were transferred into a clean Schlenk flask fitted with a stir bar. On the Schlenk line, 20 mL anhydrous toluene was syringed into the flask under N₂ flow and the mixture was stirred for 24 h at room temperature. The suspension was transferred into a Schlemk filter under N₂ flow and then filtered. The solid collected on the filter was washed with 8×4.0 mL of toluene and dried in vacuum at room temperature overnight. **Zr(NMe₂)_n-R-Binol-SiO₂(100)** was obtained and transferred to the glove box. **Zr(NMe₂)_n-R-Binol-SiO₂(200)** and **Zr(NMe₂)_n-R-Binol-SiO₂(500)** were synthesized with an identical procedure as **Zr(NMe₂)_n-R-Binol-SiO₂(100)**.

Preparation of L(+)-diethyl L-tartrate derivative

Using the same procedure of **Zr(NMe₂)_n-R-Binol-SiO₂(200)**, a suspension of **Zr(NMe₂)_n-SiO₂ (200)** (2.0 g) and L(+)-diethyl L-tartrate (2.1 mmol) were mixed in 20 mL of toluene to yield the silicon-containing analogue of **Zr(NMe₂)_n-Tartrate-SiO₂(200)** and **Zr(NMe₂)_n-Tartrate-SiO₂ (500)**.

Preparation of (+)-(-)-sec-phenethyl alcohol derivative

Using the same procedure of **Zr(NMe₂)_n-R-Binol-SiO₂(500)**, a suspension of **Zr(NMe₂)_n-SiO₂ (500)** (2.0 g) and (+)-(-)-sec-phenethyl alcohol (0.6 mmol) were mixed in 10 mL of toluene to yield the silicon-containing analogue of **Zr(NMe₂)_n-PEA-SiO₂(500)**.

Schedule Status:

The project fell behind schedule as we had not produced catalyst candidates. We are now characterizing these precursor tetraphenylcyclopentadienyl-tetrachloro niobium and tantalum complexes and will prepare chiral derivatives in the immediate future. With support from other agencies, their characterization as catalysts will be investigated after the budget period expires.

Cost Status:

At the end of the period covered by this report, funds were 100% expended.