

Final Report for “**Niobium Complexes As Lewis Acid and Radical Catalysts**”

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Abstract

The reaction of lithiumpentaphenylcyclopentadiene ($\text{Li C}_5\text{Ph}_5$) with niobium pentachloride in dichloromethane or toluene produces insoluble red-orange solids whose C/H/Cl analyses are not consistent with $\text{C}_5\text{Ph}_5\text{NbCl}_4$. Addition of an acetonitrile solution of LiC_5Ph_5 with NbCl_5 gives $\text{C}_5\text{Ph}_5\text{NbCl}_4$ observed as a transient product by NMR spectroscopy, which then abstracts H from the acetonitrile solvent to give HC_5Ph_5 and presumably $\text{NbCl}_4\text{CH}_2\text{CN}$. Reversal of the order of addition gives the $\bullet\text{C}_5\text{Ph}_5$ radical as characterized by MS and EPR spectroscopy. Attempts to prepare the trimethylsilyl derivative $\text{Me}_3\text{SiC}_5\text{Ph}_5$ (a less reducing cyclopentadienyl group) were unsuccessful. Reaction was observed only in tetrahydrofuran, producing only $\text{Me}_3\text{SiO}(\text{CH}_2)_4\text{C}_5\text{Ph}_4(m\text{-C}_6\text{H}_4(\text{CH}_3))$ characterized by ^1H , ^{13}C NMR and mass spectroscopy. The trimethylsilyl-tetraphenylcyclopentadienyl derivative, $\text{Me}_3\text{Si}(\text{H})\text{C}_5\text{Ph}_4$, was characterized by ^1H , ^{13}C NMR and mass spectroscopy. This compound reacts with NbCl_5 to give HCl and ClSiMe_3 and a mixture of $\text{HC}_5\text{Ph}_4\text{NbCl}_4$ and $\text{Me}_3\text{SiC}_5\text{Ph}_4\text{NbCl}_4$.

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Introduction.

The objectives of this work are to train students to be proficient in work at research and development positions in energy related positions while they participate in this research project. The project will involve the synthesis of new coordination complexes of niobium(V) coordinated to bulky cyclopentadienyl or other sterically demanding ligands such as amido and alkoxide ligands. The ultimate aim is to develop catalysts that will promote important C-C bond formation reactions under mild conditions using small molecules. The processes will be atom efficient, generating a minimum of byproducts that would need to be disposed or used in other processes. These aims are consistent with the DOE's mission of maintaining a secure energy supply by minimizing energy consumption in such processes.

The first phase of the work was to prepare these complexes. The second was the study of their ability to promote C-C bond formation reactions through Lewis acid catalysis. In view of the limited time of this support, reactions to be studied for this class of catalysts will be limited to the [4+2] cycloaddition,¹ which we have developed methodologies for characterizing the products.²

However, since we found challenges in the synthetic aspect, we have devoted much time to the characterization of the unexpected reaction products and subsequently, the pursuit of alternate synthetic routes.

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. Extended study of the reaction products obtained with acetonitrile solvent revealed that the pentaphenylcyclopentadienide anion underwent two different reaction paths, depending upon order of addition. One gave pentaphenylcyclopentadiene, with a hydrogen atom abstracted from the acetonitrile solvent. The other gave the pentaphenylcyclopentadienyl *radical*. Attempts to prepare a less easily oxidized pentaphenylcyclopentadiene donor, trimethylsilylpentaphenylcyclopentadiene were unsuccessful; however the somewhat less bulky trimethylsilyltetraphenylcyclopentadiene has been prepared. We found this compound to react with niobium pentachloride, although here two reaction paths occur, giving a mixture of the trimethylsilyltetraphenylcyclopentadiene-niobium(V)chloride and tetraphenylcyclopentadiene-niobium(V)chloride which do not readily separate. Alternative preparative routes are being explored in a second grant that was awarded.

Experimental.

General Procedures.

All operations were carried out under nitrogen using Schlenk and glovebox (VAC HE-43 with HE-493 DriTrain or VAC Omnilab) techniques, unless stated otherwise. Solvents (toluene, dichloromethane, ether, hexane, pentane) were anhydrous grade from Aldrich and further purified using a Braun SPS-1 and stored over activated molecular sieves 3Å or 4Å in Strauss flasks. THF, Acetonitrile and benzene were dried over activated molecular sieves three times and freeze-pump-thaw degassed three cycles. NMR solvents were either dried by standard methods³ or dried twice over activated molecular sieves and freeze-thaw degassed three cycles. Pentaphenylcyclopentadiene and *mt*-Cp were prepared as in our previous work.^{2,4} Tetraphenylcyclopentadiene was prepared by the method of Cava et. al.⁵ ¹H and ¹³C NMR spectra were recorded at 25°C on a Bruker Aspect 3000 spectrometer at 300 MHz. Air sensitive samples were prepared in Young valve rotationally symmetric tubes using the residual proton resonance as internal standards.

Interaction of lithium metatolyltetraphenylcyclopentadienide *LimtCp* with *NbCl₅* in acetonitrile solution.

- a) Addition of an acetonitrile solution of *LimtCp* to a solution of *NbCl₅* results in an immediate change to a brown color which then fades to light yellow in a matter of minutes. After several hours, a yellow solid precipitates whose NMR is identical to *meta*-tolyltetraphenylcyclopentadiene. When the reaction is carried out in CD₃CN and monitored by ¹H NMR a signal appears at δ 2.09 that diminishes over several hours. When this peak has gone away, the remaining peaks are those for *meta*-tolyltetraphenylcyclopentadiene except the cyclopentadienyl ring proton's signal intensity is nearly zero. The precipitate in the NMR tube is washed with CD₃CN and dried in vacuo. ²H NMR (C₆H₆) δ= 5.1, DC₅Ph₄(*m*-C₆H₄(CH₃)).

- b) Reversing the addition order, injecting an acetonitrile-D₃ solution of NbCl₅ into a solution of *LimtCp* gives a deep purple solution from which a dark purple solid precipitates. The air-sensitive solid is NMR silent and has an ESR signal at 2.003. The filtrate solution produces a green air-sensitive, NMR silent solid upon drying in *vacuo*.

Addition of 5 mL of an acetonitrile solution containing 330 mg *LimtCp* to 5 mL of a bright yellow acetonitrile solution containing 188 mg NbCl₅ results in an immediate color change to deep purple and a black purple solid begins to precipitate nearly immediately. After about 0.5 hour, the supernatant is removed by syringe and the deep purple solid washed three times with 2 mL acetonitrile, which are combined with the supernatant. The solid is dried under *vacuo* for four hours, yielding 214 mg of deep purple solid. Evan's method magnetic susceptibility⁶ of a deep purple solution of this solid in benzene-D₆ gives a magnetic moment of 1.75 μ_B for the given formulation as the radical. ESR spectroscopy in benzene gives a signal at $g = 2.002$. HRMS of this solid give a parent ion at 460.2187 (vs. 460.219 calculated for C₃₆H₂₈). A non-optimized yield of 66% is obtained for the C₃₆H₂₈ radical.

Reaction of potassium metatolyltetraphenylcyclopentadienide with Si(Me)₃Cl in THF to give Si(CH₃)O(CH₂)₄C₅(Ph₄(*m*-C₆H₄CH₃))

To the stirring potassium mt-Cp dienide (1.77g, 3.55 mmol) THF (20 mL) solution was added Si(CH₃)₃Cl (0.6 mL, 4.73 mmol) and warmed up to THF refluxing for 3h. The solvent was removed in *vacuo* by oil diffusion pump. The crude mixture of products was crystallized in heptane to afford the product (1.27g) as an off-white crystalline solid. (MP 36-40 °C) The ¹H NMR at 300 MHz is complex owing to the formation of three isomers whose relative amounts were not determined. ¹H NMR (300MHz, CD₂Cl₂) Si(CH₃)₃; $\delta = 0.1307(s), 0.1295(s)$; Ph-C-H₃, $\delta = 1.919(s), 1.911(s)$; C-H₂, $\delta = 1.58(m), 1.84(m), 2.42(m), 3.51(m)$; C₆H₅, $\delta = 6.7-7.6(m)$. HRMS calc'd. for C₄₃H₄₄OSi (M⁺) 604.3162, found 604.3292.

The synthesis of potassium tetraphenylcyclopentadienide (KC₅Ph₄H).

Under N₂ atmosphere, to a stirring KH (31.0 mg, 0.77 mmol) hexane (10 mL) suspension was added tetraphenylcyclopentadiene C₅Ph₄H₂ (286.0 mg, 0.77 mmol) hexane (20 mL) solution. The mixture was refluxing 5 hours under N₂. The mixture filtered through schlenk filter and the solid product was washed twice with 10mL hexane portions and then washed with 10ml pentane. The product then dried in *vacuo* to afford tan power KC₅Ph₄H (302.5mg, yield 96%). ¹H NMR (300 MHz, CD₃CN) CH, $\delta = 6.10$; C₆H₅, $\delta = 6.75-7.15$.

The synthesis of trimethylsilyl-tetraphenylcyclopentadiene C₅Ph₄HSiMe₃ (TMSD)

To the solution of KC₅Ph₄H (2.47g, 6.0mmol) in THF (20 mL) at room temperature was added Si(CH₃)₃Cl (1.0 mL, 7.8mmol). The mixture was stirred for 0.5h and the solvent was removed in *vacuo* to afford a light brown solid. The crude product was recrystallized in pentane to give tan crystals (1.74mg, yield 65%). M.p.123-130°C. ¹H NMR (300MHz,

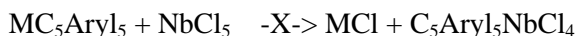
CD₂Cl₂) Si(CH₃)₃ δ= -0.39; C-H, δ= 4.70; C₆H₅, δ=7.05-7.35. ¹³C NMR (300MHz, CD₂Cl₂) δ= -2.4, 54.8, 126.6, 126.7, 127.9, 128.2, 129.7, 130.9, 137.9, 138.0, 142.9, 143.0; HRMS calc'd. for C₃₂H₃₀Si (M⁺) 442.2116, found 442.2107.

Interaction of C₅Ph₄HSiMe₃ with NbCl₅

A yellow dichloromethane solution of C₅Ph₄HSiMe₃ (130 mg in 5 mL) is added to 5 mL yellow dichloromethane solution containing 80 mg of NbCl₅. An immediate color change to dark red occurs upon addition of the first drop. Addition is complete in less than a minute. A strip of damp pH paper placed in the stream of gas coming from a syringe needle inserted into the septum of the reaction flask indicates the presence of an acid in the gas phase. (A similar test where the flask contains only trimethylsilylchloride and dichloromethane shows no change in the same time scale). The solvent is removed in vacuo to give a dark red solid. The trapped volatiles' ¹H NMR spectrum in CD₂Cl₂ show signals for the dichloromethane solvent and trimethylsilylchloride (δ=0.43). ¹H NMR of the red crude in CD₂Cl₂: H-C₅Ph₄NbCl₄, δ= 4.7 (s); HC₅Ph₄NbCl₄, δ= 7.5-6.5, overlapping multiplets); δ= 0.5, tentatively assigned to of SiMe₃C₅Ph₄NbCl₄.

Results and Discussion.

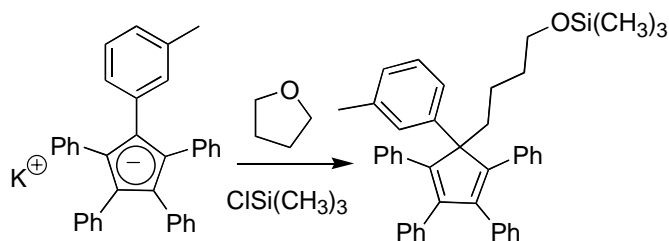
Attempts to directly synthesize penta-arylcyclopentadienylNbCl₄ complexes by salt metathesis reactions were not successful in our hands. A variety of solvents were used, including toluene, dichloromethane, tetrahydrofuran in which insoluble materials were obtained whose analyses were not consistent with the expected formulation. Reaction in acetonitrile gave tractable products.



In superdry acetonitrile, we observed two reaction paths where C₅Aryl₅, where C₅Aryl₅ = C₅Ph₄(*m*-C₆H₄(CH₃)). The path taken is dependent upon order of addition. Addition of a solution the cyclopentadienide anion to a solution NbCl₅ gives an NMR spectrum that suggests initial formation of the desired product. However, a proton abstraction reaction with solvent occurs, giving back HC₅ C₅Ph₄(*m*-C₆H₄(CH₃)) and a presumed Nb(CH₂CN)Cl₄ complex. This is confirmed by reaction in CD₃CN where the deuterated product DC₅Ph₄(*m*-C₆H₄(CH₃)) is recovered and the ²H NMR shows a single resonance at δ= 5.1.

Reversing the order of addition, a deep purple solution is produced that immediately deposits a dark purple solid, the radical, C₅Ph₄(*m*-C₆H₄(CH₃)). The HRMS, ESR spectrum and magnetic susceptibility are all consistent with this formulation. The presumed Nb(IV) byproduct was not characterized. The un-optimized yield obtained was 66%, suggesting that this route may provide a reasonable route to these radicals.

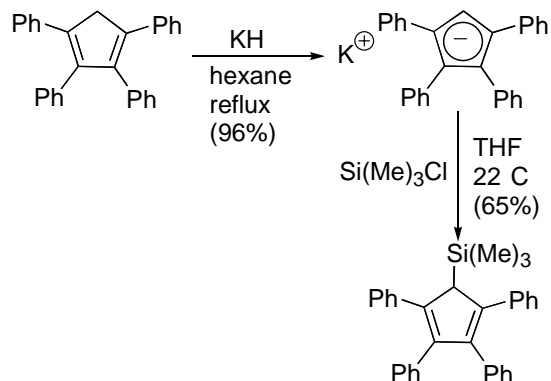
These results suggested that the oxidizing power of the NbCl₅ center might be an obstacle, so developing a less easily reduced cyclopentadienyl transfer agent was the next goal. Trimethylsilylcyclopentadienyl compounds had been used in the preparation of Nb(V) cyclopentadienyl complexes, so synthesis of trimethylsilyl- C₅Ph₄(*m*-C₆H₄(CH₃)) was attempted.



Scheme 1. The Reaction of potassium *mt*-Cp with Si(Me)₃Cl in THF (one product isomer shown).

Efforts to prepare trimethylsilyl-*mt*-Cp by the reaction of potassium *mt*-Cp with Si(Me)₃Cl in a variety of solvents (polar, nonpolar organics and neat TMS-Cl) returned only starting material with the exception of tetrahydrofuran (THF). Removal of solvent in vacuo, followed by addition of toluene and filtration gives an off-white solid. The ¹³C and ¹H NMR spectra as well as HRMS analysis indicate that this compound is the result of ring opening of the THF, cleaving the C-O bond giving a product, one isomer of which is shown in Scheme 1.

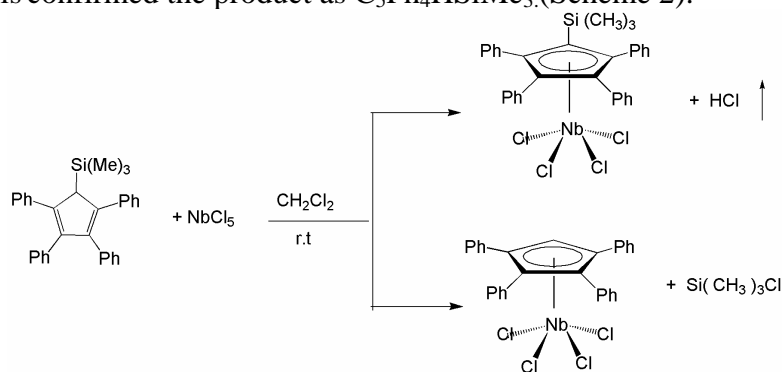
The reason for this unexpected lack of reactivity towards TMS addition may be due to greater steric hindrance of the five phenyl groups compared to the methyl groups on the pentamethylcyclopenta-dienyl ring. Ring opening of THF is known to occur through nucleophilic attack when it is coordinated to a Lewis acid.⁷ Perhaps the THF ring-opening reaction occurs by THF attacking transient SiMe₃-C₅Ph₅ or THF coordination to SiMe₃Cl and subsequent attack by the *mt*-Cp anion to give the ring opened product.



Scheme 2. Synthesis of Trimethylsilyl-tetraphenylcyclopentadiene (TMS-D)

Suspecting that a less sterically encumbered polyaryl cyclopentadiene would be more amenable to addition of the TMS group, reaction using a tetra-arylcyclopentadiene was attempted and C₅Ph₄HSiMe₃ was successfully synthesized. Tetraphenylcyclopentadiene C₅Ph₄H₂ is readily prepared following a reported procedure.⁵ The highly air and moisture sensitive potassium tetraphenylcyclopentadienide, KC₅Ph₄H, is synthesized by reaction of C₅Ph₄H₂ with KH in dried hexane in 96% yield and characterized by ¹H NMR analysis in “superdry” CD₃CN. Our attempts to make the TMS derivative using diethyl ether, dichloromethane and toluene as solvents gave poor yields. However, reaction of KC₅Ph₄H with SiMe₃Cl in anhydrous THF at room temperature gives a tan crystalline solid after crystallization in pentane in 65% yield. In marked contrast to the

pentaphenylcyclopentadienyl reaction, no ring opening is observed. ^1H NMR analysis and HRMS analysis confirmed the product as $\text{C}_5\text{Ph}_4\text{HSiMe}_3$ (Scheme 2).



Scheme 3. Reaction paths taken upon mixing solutions of NbCl_5 and $\text{C}_5\text{Ph}_4\text{HSiMe}_3$.

The reaction of TMS-D with NbCl_5 does not lead to the clean release of $(\text{CH}_3)_3\text{SiCl}$ and formation of $(\text{C}_5\text{Ph}_4\text{H})\text{NbCl}_4$, rather giving a mixture of products releasing both $(\text{CH}_3)_3\text{SiCl}$ and HCl indicate that these two reaction pathways are operative.

Conclusions

The testing of catalyst candidates pentaphenylcyclopentadienylniobium(V)chloride and pentaphenylcyclopentadienylniobium(IV)chloride was not accomplished as there were problems preparing the desired compounds. Extended study of the reaction products obtained with acetonitrile solvent revealed that the pentaphenylcyclopentadienide anion underwent two different reaction paths, depending upon order of addition. One gave pentaphenylcyclopentadiene, with a hydrogen atom abstracted from the acetonitrile solvent. The other gave the pentaphenylcyclopentadienyl *radical*. Attempts to prepare a less easily oxidized pentaphenylcyclopentadiene donor, trimethylsilylpentaphenylcyclopentadiene were unsuccessful; the somewhat less bulky trimethylsilyltetraphenylcyclopentadiene has been prepared as an alternative reagent. We found this latter compound to react with niobium pentachloride, although here two reaction paths occur, giving a mixture of the trimethylsilyltetraphenylcyclopentadiene-niobium(V)chloride and tetraphenylcyclopentadiene-niobium(V)chloride which do not readily separate.

We are currently pursuing the use of $\text{C}_5\text{Ph}_4\text{HSnMe}_3$ in the synthesis of niobium complexes as a higher yield alternative to the silyl compounds with less potential to go astray in the metallation steps. We are also investigating the use of the less oxidizing TaCl_5 to prepare the tantalum analogues to the niobium complexes we have been pursuing. Preliminary results in the formation of $\text{C}_5\text{Ph}_4\text{H}(\text{Sn}(\text{CH}_3)_3)$ are promising. After preparing the complexes from the latter compound, we can proceed with investigation of the potential of these complexes as Lewis acid and radical catalysts.

References.

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List of acronyms and abbreviations

ESR	electron spin resonance
<i>LimtCp</i>	lithium meta-tolyltetraphenylcyclopentadienide
HRMS	high resolution mass spectrum
NMR	nuclear magnetic resonance
THF	tetrahydrofuran
TMSD	trimethylsilyl-tetraphenylcyclopentadiene