

## **Activation of Atmospheric Small Molecules by Transition Metals**

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## Introduction

Activation of small molecules has been and continues to be of extreme interest to organometallic chemists. This is especially true with activation of inert atmospheric molecules. Some of the most attractive targets for activation include dinitrogen and carbon dioxide. The abundance of both  $\text{CO}_2$  and  $\text{N}_2$  make them quite attractive as chemical feedstocks. Activation and incorporation of carbon dioxide into the chemical feedstock is important for a number of reasons: (1) carbon dioxide is inexpensive; (2) it is generally considered to be nontoxic (3) it is considered a green house gas and controlling the amount present in the atmosphere is desirable as it is believed to be contributing to a rapid change in climate across the earth (global warming). Incorporation of  $\text{CO}_2$  into chemical moieties may provide some balance to the increasing  $\text{CO}_2$  output via fossil fuel combustion.<sup>1</sup>

Introduction of  $\text{N}_2$  into chemical feedstocks is also of significant interest. The abundance and availability of  $\text{N}_2$  makes it attractive from an economic standpoint. Other considerations include the fact that  $\text{N}_2$  is an inert, non-toxic gas. Perhaps what makes activation and functionalization of  $\text{N}_2$  most interesting is the significant role that it holds in biology. It is no secret that chemists and biologists alike yearn to mimic many of the fundamental process that biological systems carry out with such ease. For example, nitrogenases readily fix and functionalize atmospheric  $\text{N}_2$ .<sup>2</sup> The structure for one of these nitrogenases, FeMo cofactor has been determined and well studied; yet, the actual mechanisms by which  $\text{N}_2$  is fixed and reduced to  $\text{NH}_3$  remain unknown. FeMo cofactor, perhaps the most thoroughly studied nitrogenase, has been shown by crystallography to house both iron and molybdenum centers in the active

site. Despite significant research efforts and thorough determination of structure, the mechanism through which  $N_2$  is bound and converted into ammonia has yet to be elucidated.<sup>3</sup>

Despite a lack of complete mechanistic understanding of nitrogenases, work continues on production of  $N_2$  bound metal complexes; it is reported that hundreds of  $N_2$  complexes are known.<sup>3</sup> Few of these complexes have led to any result approaching the significance of the Haber-Bosch process for conversion of  $N_2$  into  $NH_3$ . One notable exception is the discovery of Mo systems with triamidoamine ligands will catalytically reduce  $N_2$  to  $NH_3$  in the presence of a proton source and a strong reductant.<sup>4</sup> Though this system represents a major step toward practical homogeneous conversion of  $N_2$  to  $NH_3$ , the understanding of the mechanism by which this occurs is not completely understood. However, it is likely that this very lack of understanding will continue to drive the synthesis of  $N_2$  bound metal complexes.

$CO_2$  is another example of a plentiful small molecule that is difficult to activate. Despite the abundance of  $CO_2$ , there are a limited number of synthetic processes that take advantage of it as a starting material. It is well known that  $CO_2$  is a thermodynamically inert molecule. It is this thermodynamic stability that makes metal catalysts or reagents necessary for the incorporation of  $CO_2$  into organic molecules.

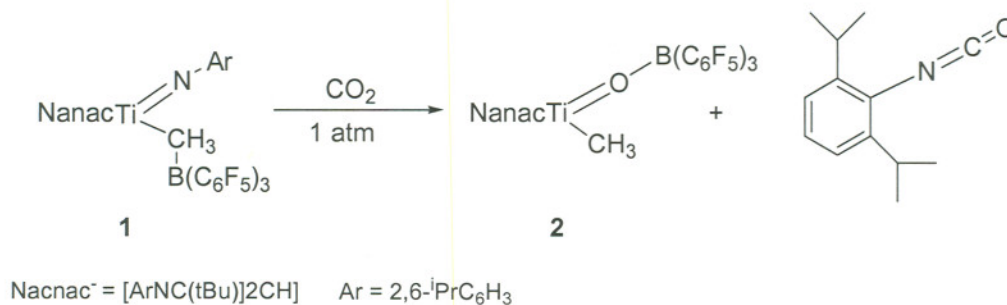
Among the most powerful reactions incorporating  $CO_2$  are catalytic C-C bond forming reactions. The products of such reactions include lactones, pyrones, esters, and carboxylic acids.<sup>6</sup> Cycloadditions involving  $CO_2$  and metal imido species are not

very common. Of those that are known, several result in the formation of N,O bound carbamate complexes or N,N-bound ureates.<sup>6,7,8</sup> Our group has discovered a zwitterionic titanium imido species that undergoes cycloaddition readily with CO<sub>2</sub> and cleanly release organic products such as carbodiimides and isocyanates. Reported herein is the clean utilization of CO<sub>2</sub> in formation of both isocyanates and carbodiimides mediated by a titanium imido-zwitterion, (Nacnac)Ti=NAr(μ-CH<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) **1** (Nacnac<sup>-</sup> = [ArNC(<sup>t</sup>Bu)]<sub>2</sub>CH, Ar = 2,6-<sup>i</sup>PrC<sub>6</sub>H<sub>3</sub>). Formation of isocyanates is the result of ligand metathesis with CO<sub>2</sub>; thus resulting in formation of (Nacnac)Ti=O(μ-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)(CH<sub>3</sub>) **2**.

Additionally reported are [PNPNb(CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>)](μ-N<sub>2</sub>), **3**, and [PNPNbCl<sub>2</sub>](μ-N<sub>2</sub>), **4**, (PNP = N[2-P(CHMe<sub>2</sub>)<sub>2</sub>-4-Me-C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>). These complexes are representative of the first necessary steps for activation and functionalization of N<sub>2</sub>. While several examples of N<sub>2</sub> activation by Nb containing complexes are known,<sup>9-13</sup> very little progress has been made in the area of catalytic conversion of N<sub>2</sub> into organic products.<sup>2</sup>

## Results and discussion

### *Scheme 1 - Reaction of (Nacnac)Ti=NAr(μ-CH<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) (**1**) with CO<sub>2</sub>.*

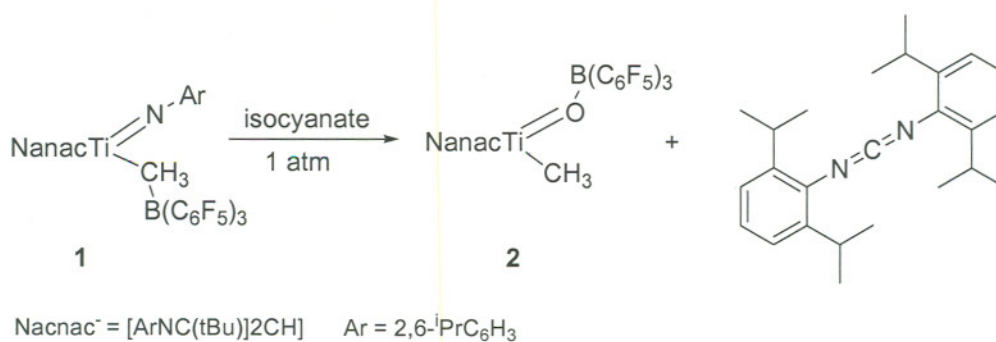


Reaction of complex **1** with 1 atmosphere of carbon dioxide resulted in clean formation of 2,6-diisopropylphenyl isocyanate and  $(\text{Nacnac})\text{Ti}=\text{O}(\mu\text{-B}(\text{C}_6\text{F}_5)_3)(\text{CH}_3)$ ,

**2**. The isocyanate forms via ligand metathesis of  $\text{Ti}=\text{N-Ar}$  motif with  $\text{CO}_2$ .

Formation of **2** rather than an oxo-dimer species can likely be attributed to the presence of the bulky  $\text{B}(\text{C}_6\text{F}_5)_3$ . Crystallographic data shows the formation of a Lewis acid-base adduct between electron deficient B and O. This connective preference over that of **1** is likely due to the strength of the B-O adduct over that of B-C. Leaving the reaction mixture of **2** and diisopropylphenyl isocyanate unseparated for several weeks results in activation of the methine carbon of  $\text{Nacnac}^-$  by the isocyanate carbon. The resulting complex shows what is essentially a tripodal ligand bonded to titanium through the nitrogens of  $\text{Nacnac}^-$  and the oxygen of the isocyanate **5**.

**Scheme 2 - Reaction of 1 with Diisopropylphenyl isocyanate .**

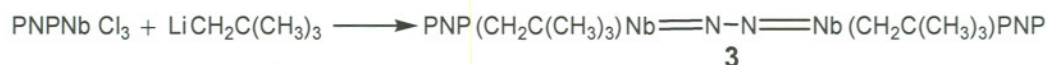


Placing 1 equivalent of diisopropylphenyl isocyanate in a solution of **1** results in gradual formation of bis(2,6-diisopropylphenyl)carbodiimide concomitant with **2**. Ligand metathesis of isocyanate with the  $\text{Ti}=\text{N-Ar}$  fragment results in formation of the carbodiimide. Facile formation of symmetrical carbodiimide via metathesis of

complex **1** can be easily applied to the synthesis of unsymmetrical carbodiimides which have a limited number of practical preparations.<sup>14</sup>

### Activation of N<sub>2</sub>

#### *Scheme 3 – Synthesis of 3*



#### *Scheme 4 – Synthesis of 4*



Activation of N<sub>2</sub> was achieved by placing PNPNbCl<sub>3</sub> in the presence of reductants in an atmosphere of dinitrogen. The formation of **3** was somewhat unexpected. However, the realization that a reducing species such as neopentyl lithium would facilitate activation of N<sub>2</sub> led to attempts with other reductants. The N-N bond length in **3** is 1.286 Å and in **4** it is 1.272 Å. Both of these lengths demonstrate significant reduction of the N-N triple bond suggesting that N<sub>2</sub> has been activated from its molecular form.

Complex **3** shows an EPR spectrum characteristic of a system with one unpaired electron (**fig. 1**) suggesting that each niobium center harbors an unpaired electron with no coupling through the N<sub>2</sub> bridge. Complex **4** has been studied by X-ray diffraction for its connectivity, but has yet to be studied for electronic and magnetic properties.

## Experimental

### *General Considerations*

All Reactions involving **3** and **4** were carried out in a M. Braun Lab Master double-drybox under an atmosphere of purified nitrogen. Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through one column of activated alumina and one of Q-5. Diethyl ether was dried by passage through two columns of activated alumina. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C<sub>6</sub>D<sub>6</sub> and was purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves.

All reactions involving (1) and (2) were were carried out in a M. Braun Lab Master drybox under an atmosphere of purified argon or under high-vacuum standard Schlenk techniques under an argon atmosphere. The drybox contained no coordinating solvents such as diethyl ether or THF. Anhydrous *n*-hexane and pentane were purchased from Aldrich in sure-seal bottles and introduced directly into the drybox. C<sub>6</sub>D<sub>5</sub>Br was purchased from Aldrich, placed under multiple freeze pump thaw cycles and then introduced into the glove box. <sup>19</sup>F NMR, <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. Room-temperature X-band EPR spectra were recorded on a Bruker EMX spectrometer. Acquisition was carried out using an integrated WIN-EPR software package (Bruker). X-ray data were collected on a Bruker SMART6000 diffractometer under N<sub>2</sub>(g) at low temperatures.

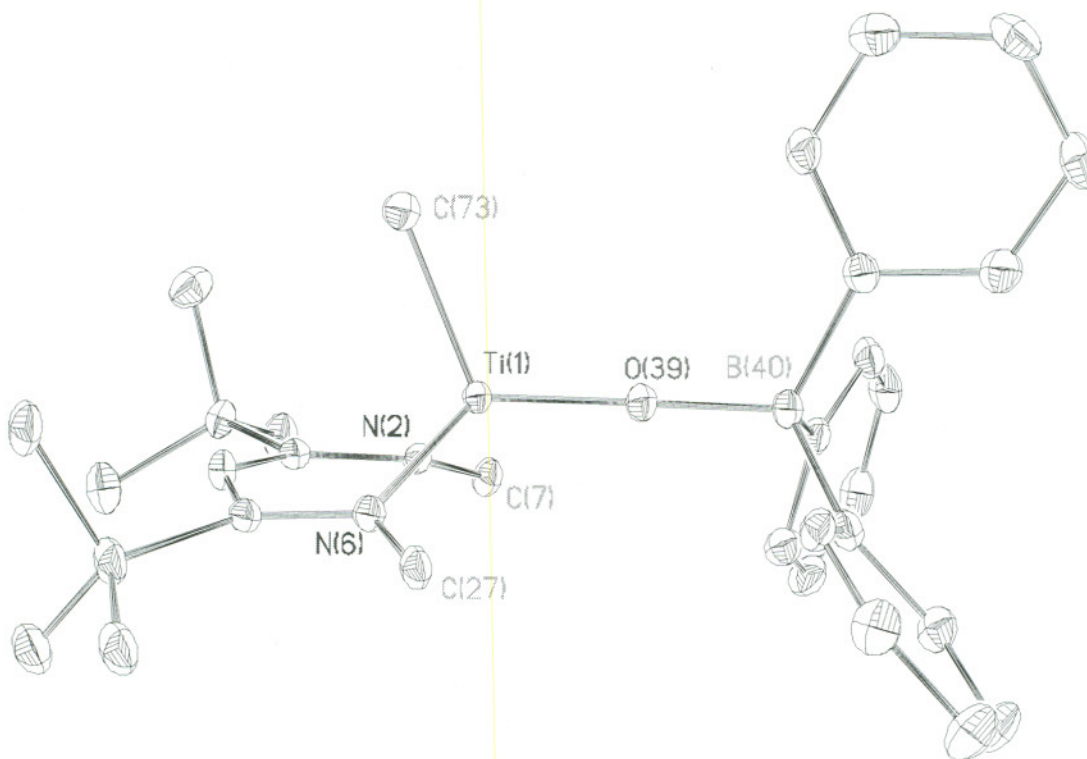
Nacnac<sup>-</sup> (Nacnac<sup>-</sup> = [ArNC(<sup>t</sup>Bu)]<sub>2</sub>CH, Ar = 2,6-<sup>i</sup>PrC<sub>6</sub>H<sub>3</sub>) was prepared according to the literature.<sup>15</sup> Li(PNP) was prepared by slight modification of literature preparation.<sup>16</sup>

### Synthesis of diisopropylphenyl isocyanate and **2** from **1**

Under an atmosphere of argon, a Schlenk flask was charged with **1** (625 mg, 0.572 mmol) dissolved in fluorobenzene and cooled to 77K. The flask was then placed under 1 atmosphere of CO<sub>2</sub>. After 2 hours, the red solution had lightened significantly to a shade of orange. After 2 hours, the flask was reintroduced into the glove box under an atmosphere of argon. To the schlenk flask was added hexane. The solution was then cooled to -35°C. After 2 days, **2** was obtained as yellow powder 344 mg. A second crop of 135 mg was isolated after concentration and cooling of the solution for a total yield 479 mg (0.438 mmol, 76.5 % yield). Concentration of the remaining solution revealed a yellow-green residue. The isocyanate was isolated by dissolving the yellow green residue in hexane followed by filtration. The solution that results is stripped of volatiles to reveal diisopropylphenyl isocyanate as 89 mg (.438 mmol, 75% yield) of a light yellow residue.

**2**: <sup>1</sup>H NMR (23° C, 299MHz, C<sub>6</sub>D<sub>5</sub>Br): δ 7.326 – 6.861 (m – aryl), 6.82 (s – (<sup>t</sup>bu)C-CH-C(<sup>t</sup>Bu)), 2.86 (septet – isopropyl -CH<sub>3</sub>CHCH<sub>3</sub>), 2.12 (septet – isopropyl -CH<sub>3</sub>CHCH<sub>3</sub>), 4.37 (s – Ti-CH<sub>3</sub>), 1.34, 1.169, 1.050, 0.945 (d isopropyl CH<sub>3</sub>), 1.11 (s – <sup>t</sup>Bu). <sup>11</sup>B NMR (23° C, 399MHz, C<sub>6</sub>H<sub>5</sub>F): δ -15.871 (s (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-B-O)

**Diisopropylphenyl isocyanate:**  $^1\text{H}$  NMR (23° C, 299MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.995 – 6.898 (m – aryl 6H), 3.093 (septet – isopropyl  $\text{CH}_3\text{CHCH}_3$  4H), 1.061 (d – isopropyl  $\text{CH}_3$ ). EI  $m/z$ :203.13.



Structure of 2 (Nacnac)Ti=O( $\mu$ -B( $\text{C}_6\text{F}_5$ ) $_3$ )( $\text{CH}_3$ ) - Fluorines and hydrogens not shown for simplicity. C(7) and C(27) – ipso aryl carbons; aryls removed for clarity

Table 1 - Selected distances and angles for 2

Ti(1) – O(39)	1.732 Å
O(39) – B(40)	1.524 Å
Ti(1) – C(73)	2.091 Å
B(40) – O(39) – Ti(1)	172.32°
C(63) – B(40) – (C52)	112.02°

**Synthesis of bis(2,6-diisopropylphenyl)carbodiimide from 1 and diisopropylphenyl isocyanate**

In a glove box under an atmosphere of argon, an NMR tube was charged with a bromobenzene solution of 1 (50 mg, 0.033 mmol) and isocyanate (7 mg, 0.034 mmol). After 72 hours,  $^1\text{H}$  NMR of the mixture revealed peaks characteristic of the titanium-oxo species, 2, and bis(2,6-diisopropylphenyl)carbodiimide. The carbodiimide was separated from the mixture analogously to separation of isocyanate.  $^1\text{H}$  NMR (23° C, 299MHz,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta$  7.395 – 7.041 (m- 3H), 3.65 (septet – 2H), 1.322 (doublet – 12H). EI  $m/z$ : 363.2790

**Synthesis of  $\text{PNPNbCl}_3$**

50 mg (1 equivalent) of  $\text{NbCl}_4(\text{THF})_2$  was added to a vial and dissolved in toluene. A second vial was charged with 57 mg (1 equivalent) LiPNP dissolved in toluene. Both vials were cooled to  $-35^\circ\text{C}$ . The solution of LiPNP was added dropwise, slowly to the stirring solution of  $\text{NbCl}_4(\text{THF})_2$ . The color change to wine purple was evident immediately. The solution was filtered after 24 hours followed by concentration of solvent and layering with hexanes. Small purple crystals formed on the bottom of the vial within 24 hours of cooling to  $-35^\circ\text{C}$ .

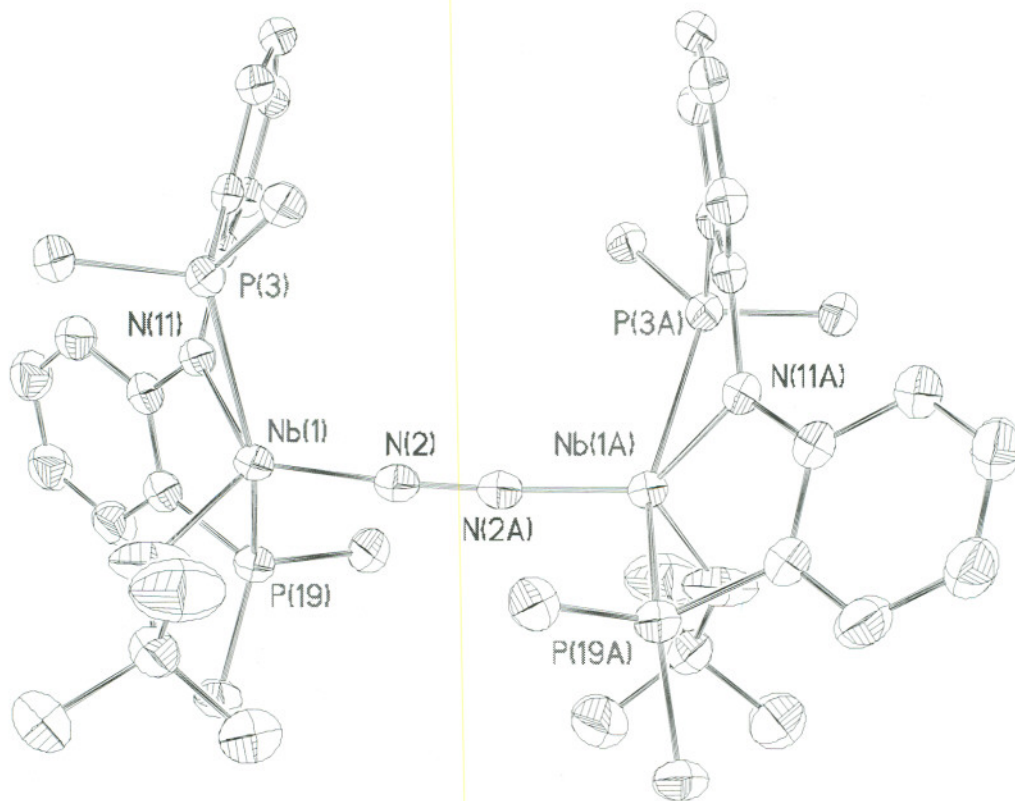
*Characterization incomplete*

EPR: 10 line pattern (figure 2)

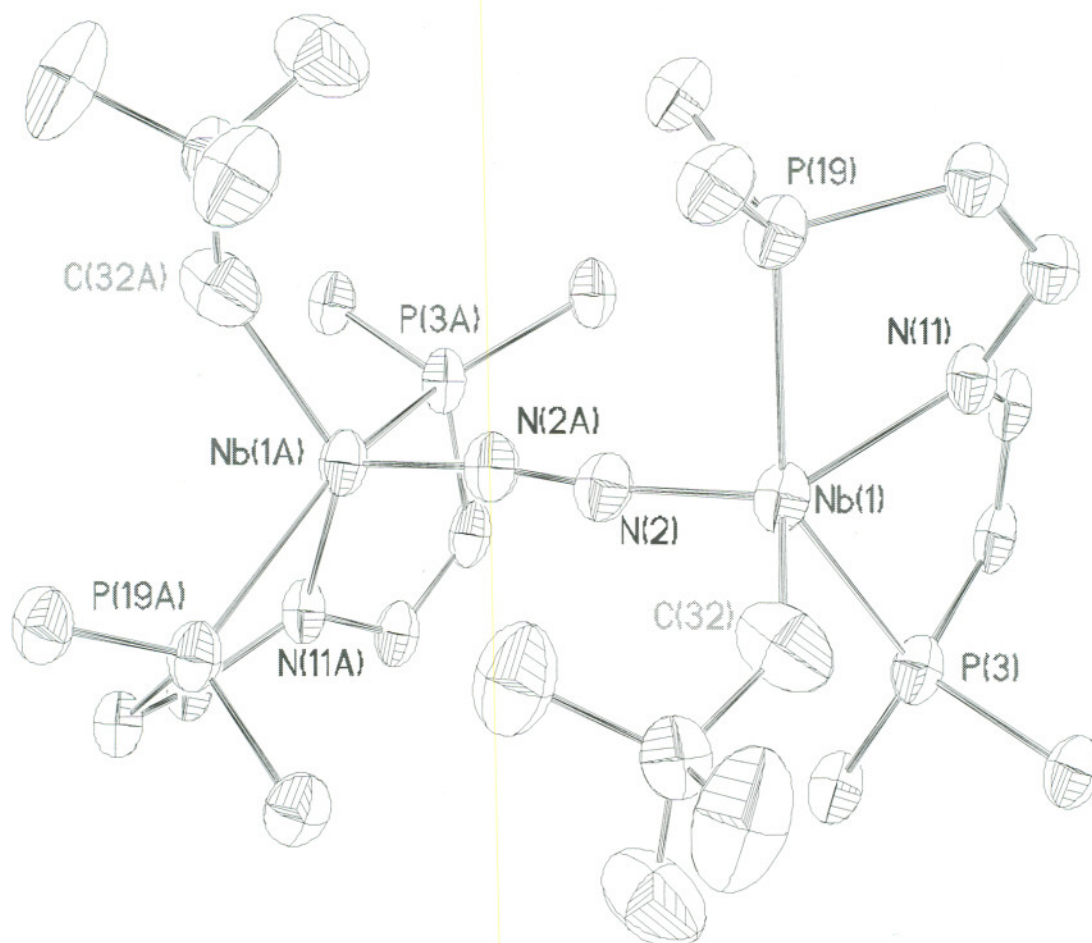
### Synthesis of 3

In a glove box under an atmosphere of  $N_2$ , a toluene solution of  $PNPNbCl_3$  (60 mg, 0.096 mmol) was added to a vial. To a second vial was added a toluene solution of neopentyl lithium (22 mg, 0.29 mmol). Both vials were cooled to  $-35^\circ C$ . To the stirring solution of  $PNPNbCl_3$  was added the solution of neopentyl lithium dropwise. The color of the solution rapidly became green-brown in color. The solution was allowed to come to room temperature and stir for 24 hours. The solvent was removed and the solid was dissolved in pentane and then filtered. To the pentane solution was added a few drops of  $TMS_2O$ . After several days at  $-35^\circ C$ , black crystals were formed along the bottom of the vial.

EPR (10 line pattern).  $^1H$  NMR (Paramagnetic)



Structure of complex 3 – Hydrogens not shown for simplicity; diisopropyl simplified to methyl; tolyl simplified to phenyl. Inversion center about N(2)-N(2A) bond.



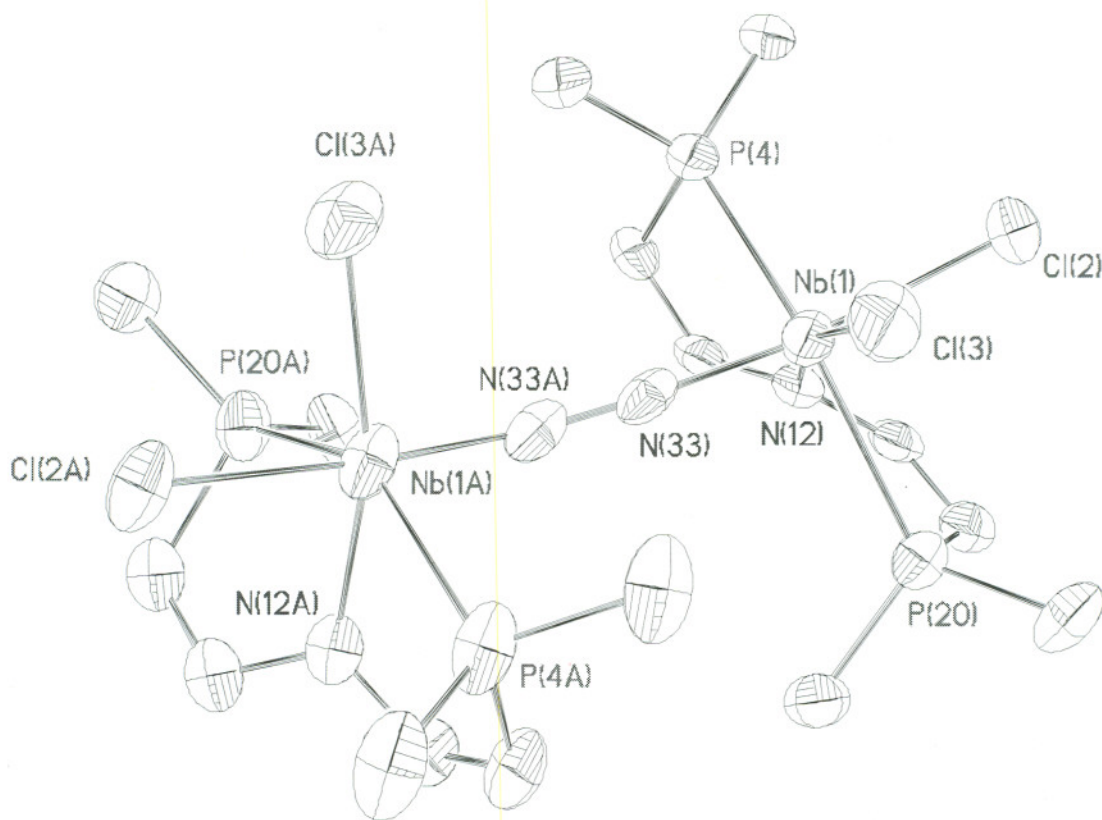
Alternate view of complex 3 – Hydrogens not shown for simplicity; tolyl simplified to ethyl linkage; isopropyl simplified to methyl. Inversion center about N(2)-N(2A) bond.

Table 2 - Selected Bond Lengths and Angles for 3

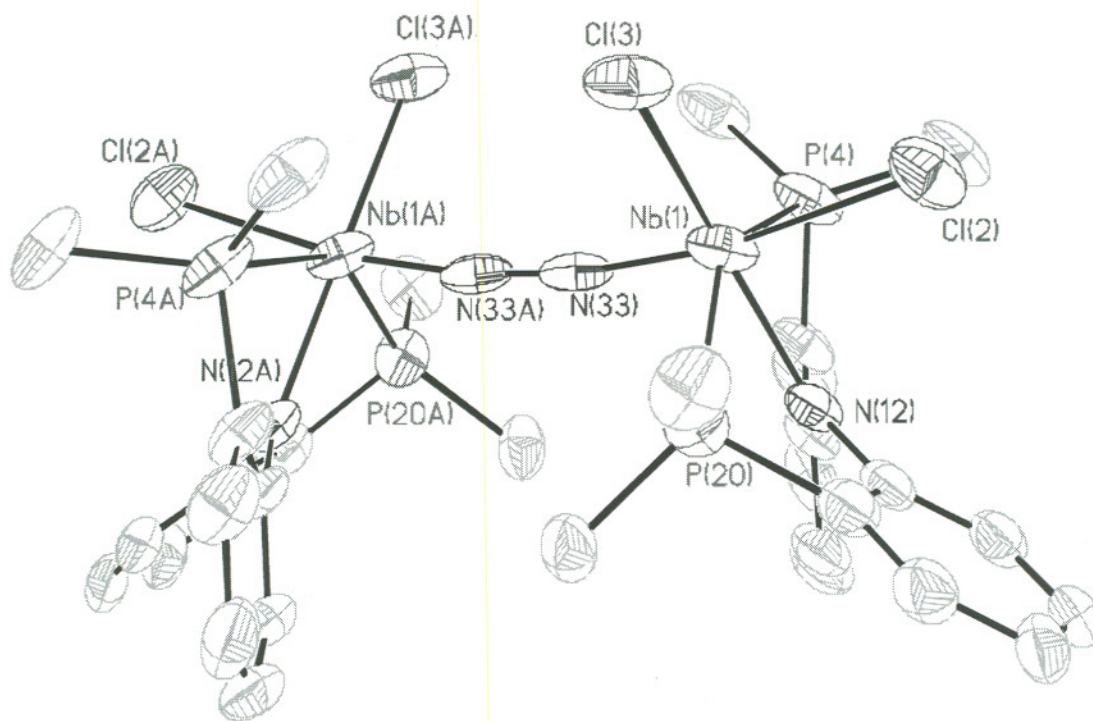
N(2) – N(2A)	1.286 Å
N(2) – Nb(1)	1.837 Å
N(2) – Nb(1) – N(2A)	172.51°
Nb(1) – C(32)	2.102 Å
C(33) – C(32) – Nb(1)	140.16 °

### Synthesis of 4

In a glove box under an atmosphere of  $N_2$ , a vial was charged with 50 mg of  $PNPNbCl_3$  dissolved in THF. To this stirring solution was added 11 mg of  $KC_8$ . The solution rapidly turned brown. After 24 hours, the solvent was removed and the solid was dissolved in  $Et_2O$  and filtered. Black crystals were observed in the vial after the solution was cooled to  $-35^\circ C$  for 2 days.



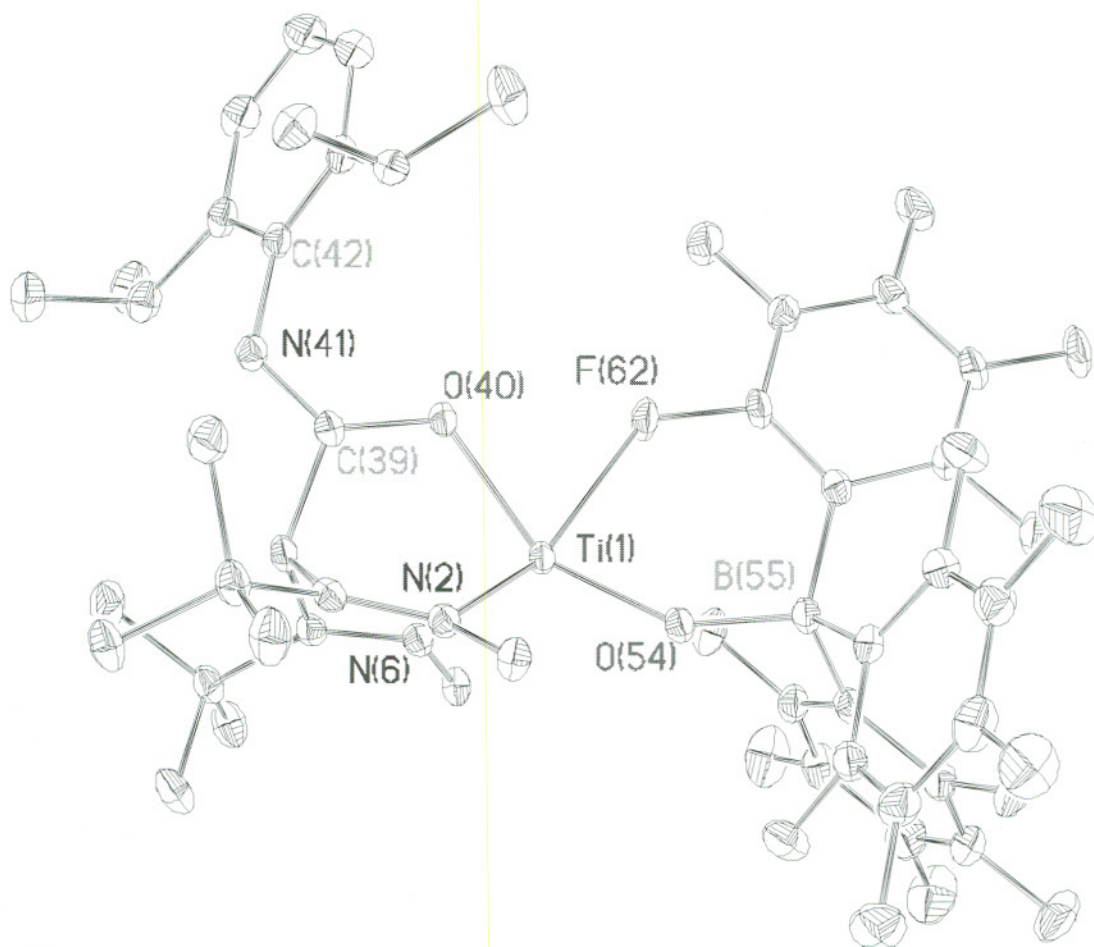
Structure of 4 - Hydrogens omitted for clarity; isopropyl simplified to methyl; tolyl simplified to ethyl linkage. Inversion center about N(33)-N(33A) bond.



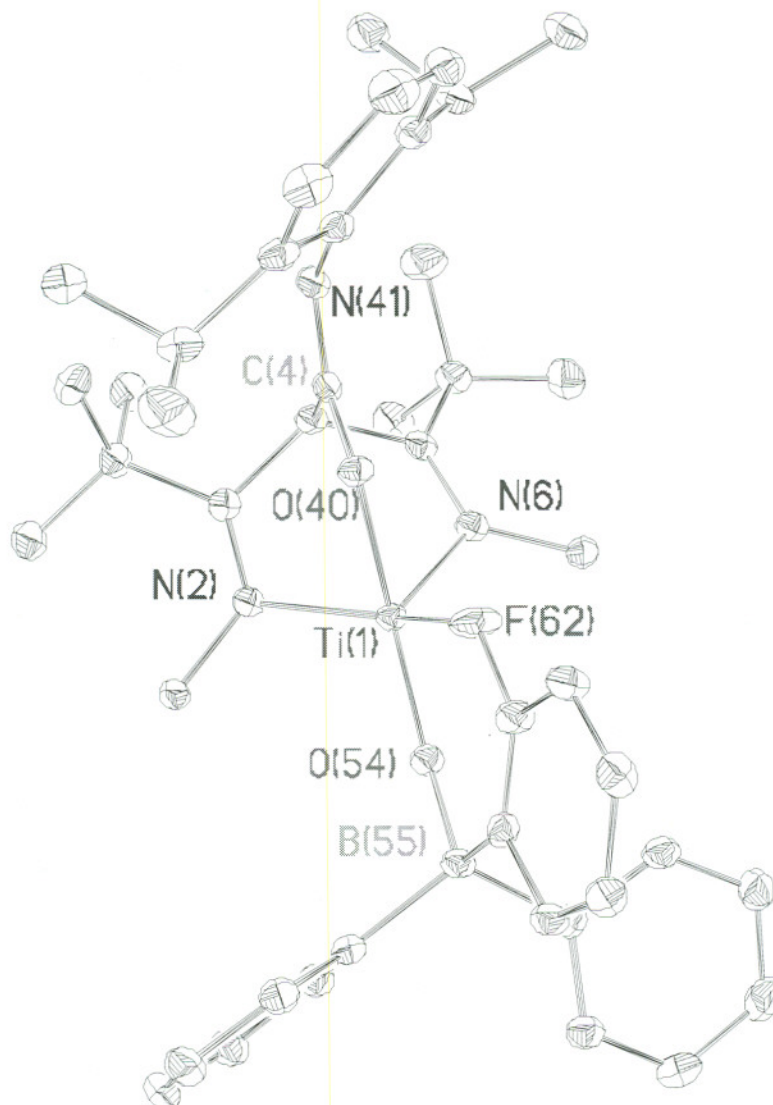
Alternate view of 4 - Hydrogens omitted for clarity. Isopropyl simplified to methyl. Tolly simplified to phenyl.

Table 3 - Selected Bond Lengths and Angles for 4

Nb(1) - N(33)	1.850 Å
N(33) - N(33A)	1.272 Å
Nb(1) - Cl(3)	2.415 Å
Nb(1) - Cl(2)	2.488 Å
N(33A)-N(33)-Nb(1)	172.36 °



Structure of **5** – Hydrogen atoms omitted for clarity. N-C<sub>ipso</sub> shown; N-aryl groups of Nacnac<sup>−</sup> omitted.



Alternate view of 5 - All hydrogens omitted for clarity. All fluorines of  $B(C_6F_5)_3$  except F(62) not shown. N-aryl of Nacnac' omitted for simplicity; N-C<sub>ipso</sub> shown.

Table 3 - Selected Bond Lengths for complex 5

Ti(1) – O(40)	1.968 Å
Ti(1) – O(54)	1.769 Å
Ti(1) – F(62)	2.280 Å
B(55) – O(54)	1.477 Å
Ti(1) – N(2)	2.145 Å
Ti(1) – N(6)	2.139 Å

## Conclusions

We have synthesized a zwitterionic titanium imido complex capable of incorporating CO<sub>2</sub> into isocyanates and carbodiimides. This system is unique from many other metal imido species in that its reactivity with CO<sub>2</sub> results in formation of isocyanates and a non-bridging titanium-oxo complex rather than metal bound carbamates and ureates.

Future work with this complex will be directed at developing an efficient cycle that allows the zwitterionic imido species, *1*, to be regenerated from the titanium-oxo *2* species concomitant with formation of isocyanates or carbodiimides. Development of such a cycle makes *1* potentially viable as a commercial reagent for recycling CO<sub>2</sub> into useful organic products.

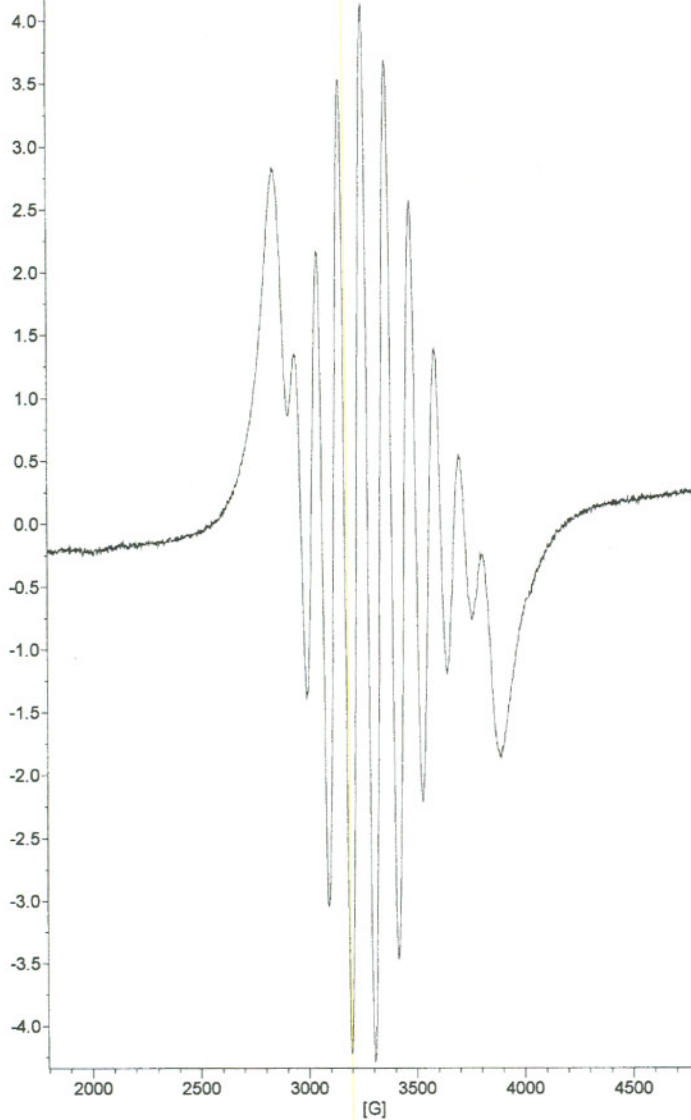
We have also synthesized two dinuclear N<sub>2</sub> bridging complexes that have activated dinitrogen. Future work for these complexes will include attempts to cleave the N-N bond to form the terminal nitride species. The next pursuit involves functionalization at the nitrogens. Successful functionalization of the N-N bridge will allow us to pursue a catalytic process in which the parent PNPbCl<sub>3</sub> complex can be regenerated.

Figure 1 – EPR Spectrum of 3

WinEPR Acquisition

FileName: C:\EPR DATA\Uriah\PNPNbN2NbPNP.par

Date: 04/08/2005 Time: 16:35


$$PNPNb = N - N = NOPNP$$
[\*10<sup>3</sup>]

## Parameter List

Operator: Bruker BioSpin GmbH  
Resonator: c:\hs0408.cal  
Acq. Date: 04/08/2005  
# of Scans: 2

## Field

Center Field: 3300.000 G  
Sweep Width: 3000.000 G  
Resolution: 2048 points

## Microwave

Frequency: 9.354 GHz  
Power: 0.634 mW

## Receiver

Receiver Gain: 1.00e+004  
Phase: 0.00 deg  
Harmonic: 1  
Mod. Frequency: 100.00 kHz  
Mod. Amplitude: 12.00 G

## Signal Channel

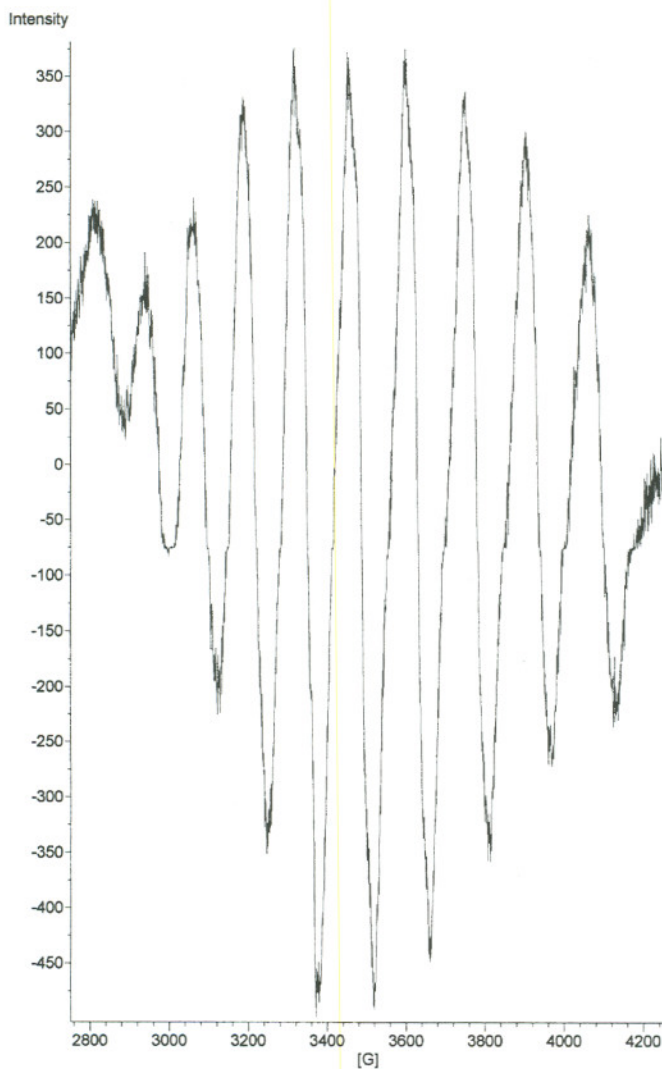
Conversion: 81.920 ms  
Time Constant: 20.480 ms  
Sweep Time: 167.772 s

Figure 2 – EPR Spectrum of  $\text{PNPNbCl}_3$ 

WinEPR Acquisition

Date: 04/08/2005 Time: 16:42

FileName: C:\EPR DATA\Uriah\nb2.par

 $\text{PNPNbCl}_3$ 

## Parameter List

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Resonator: c:\hs0408.cal  
Acq. Date: 03/08/2005  
# of Scans: 1

## Field

Center Field: 3500.000 G  
Sweep Width: 1500.000 G  
Resolution: 2048 points

## Microwave

Frequency: 9.439 GHz  
Power: 0.201 mW

## Receiver

Receiver Gain: 1.00e+004  
Phase: 0.00 deg  
Harmonic: 1  
Mod. Frequency: 100.00 kHz  
Mod. Amplitude: 10.00 G

## Signal Channel

Conversion: 81.920 ms  
Time Constant: 20.480 ms  
Sweep Time: 167.772 s

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