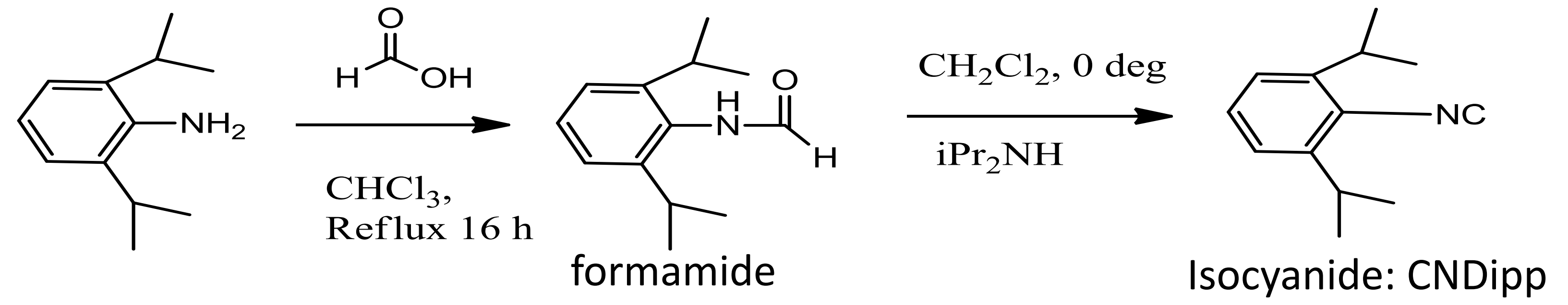
New Chemistry of Hydrocarbon-Stabilized Metal Atom Reagents

Hendro Utama Tjugito UROP, Fall Semester 2012
Mentors: Professor John E. Ellis, Christopher Roberts

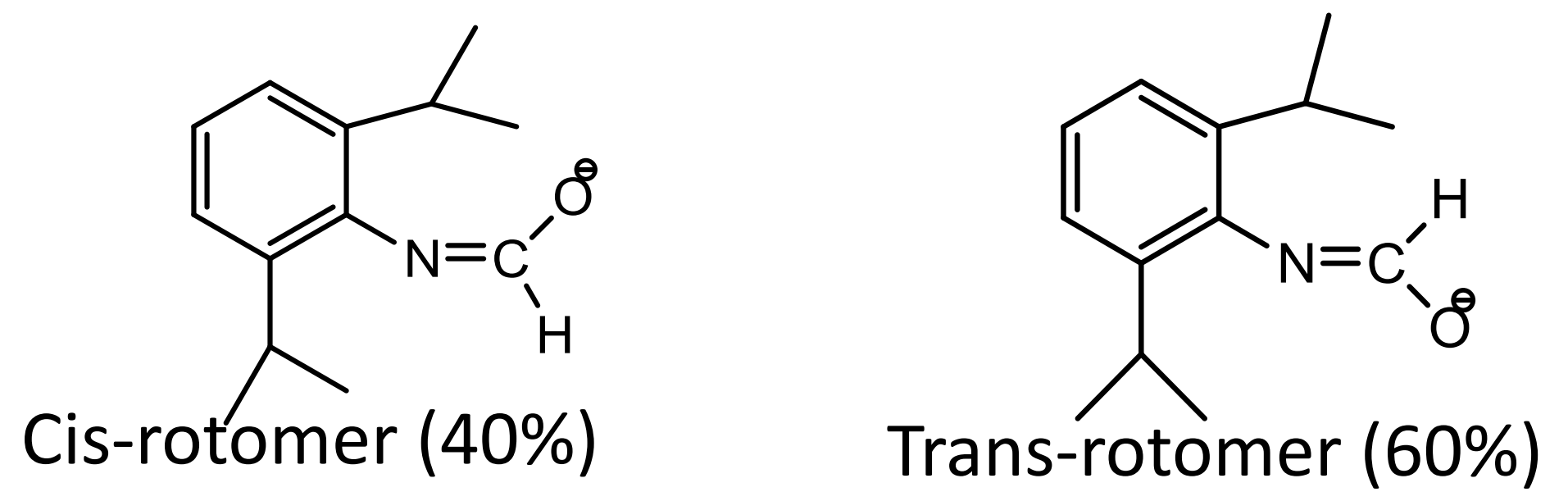
Introduction

Isocyanides have been long thought of as potential surrogates for carbon monoxide due to their standing as isolobal ligands. [1] This had been recognized as many as 50 years ago, but only in 1989 were Warnock and Cooper able to synthesize $[Co(CNXyl)_4]^-$, Xyl = 2,6-dimethylphenyl. This synthesis provided the first evidence that a series of homoleptic isocyanidemetalates, formally analogous to the long known carbonylmetalates, might be possible.[2] Isocyanides provide a largely similar ligand field as compared to carbon monoxide but differ in terms of solubility and steric attributes on the resulting complex. These differences arise due to the R group in the isocyanide (CNR). [3] The Ellis group has explored the chemistry of isocyanide metal complexes, and in 1999, results including the synthesis and isolation of $[Nb(CNXyl)_6]^-$ and structural characterizations of $Cs[Nb(CNXyl)_6]$, $Cs[Ta(CNXyl)_6]$ and $Ta(CNXyl)_6I$ were pusblished.[2] Later in 2007, a method to synthesize $[Ta(CNXyl)_7][BF_4]$ was published. The purpose of this UROP project was to further explore homoleptic isocyanide complexes of tantalum. In particular, the main goal of this project is to synthesize $[Ta(CNDipp)_7][BF_4]$, a previously unknown compound, where CNDipp = 2,6-diisopropylphenylisocyanide.

Synthesis of N-(2,6-diisopropylphenyl)formamide and the 2,6-diisopropylphenylisocyanide



Formamide Rotomer:



Formamide: The synthesis of N-(2,6-diisopropylphenyl)formamide followed the procedure provided by J.M. Chitanda, J.W. Quail and S.R. Foley. [4] Needle-like single crystals of the formamide were obtained using this procedure**.** A yield of 97% was obtained.

Isocyanide: The synthesis of the isocyanide is directed by Professor John Ellis. The desired isocyanide is a colorless and fairly volatile solid. A 73.4% yield of isocyanide is obtained.

The Synthesis of $[Ta(CNDIPP)_7][BF_4]$

$$[Et_4N][Ta(CO)_6] + 2Ag^+BF_4^- + 7CNDIPP \xrightarrow{THF\ at -60\ deg\ to\ 20\ deg} [Ta(CNDipp)_7][BF_4] + 2Ag_{(s)} + 6CO_{(g)} + [Et_4N][BF_4]_{(s)}$$

The synthesis is adapted from JACS 2007, 129,1141-1150. A yield of 80.6% was obtained using this procedure The crystal obtained is needle shaped and deep red in color.

Comparison of the Proton NMR for 2,6-diisopropylphenylisocyanide and $[Ta(CNDIPP)_7][BF_4]$

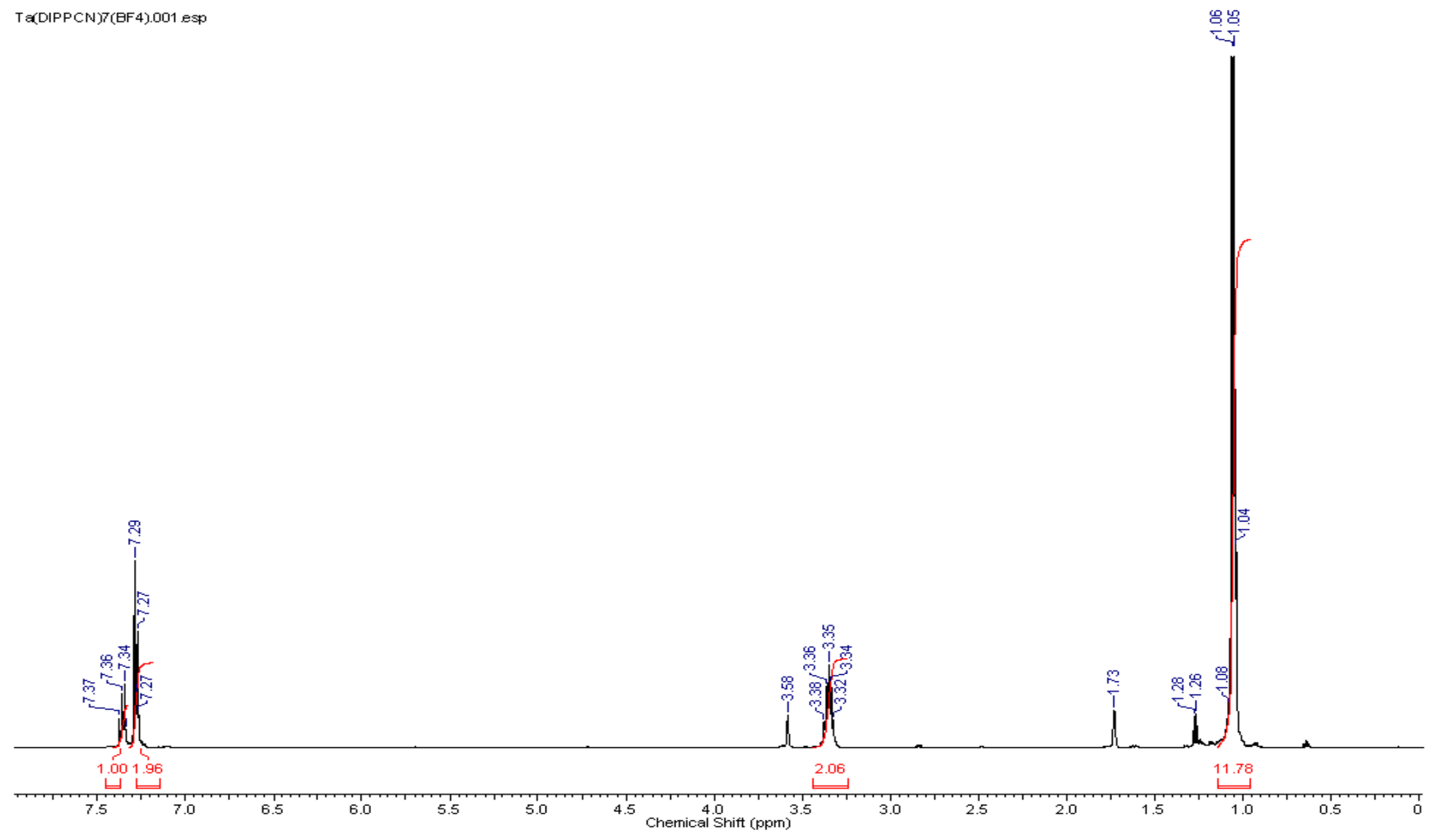
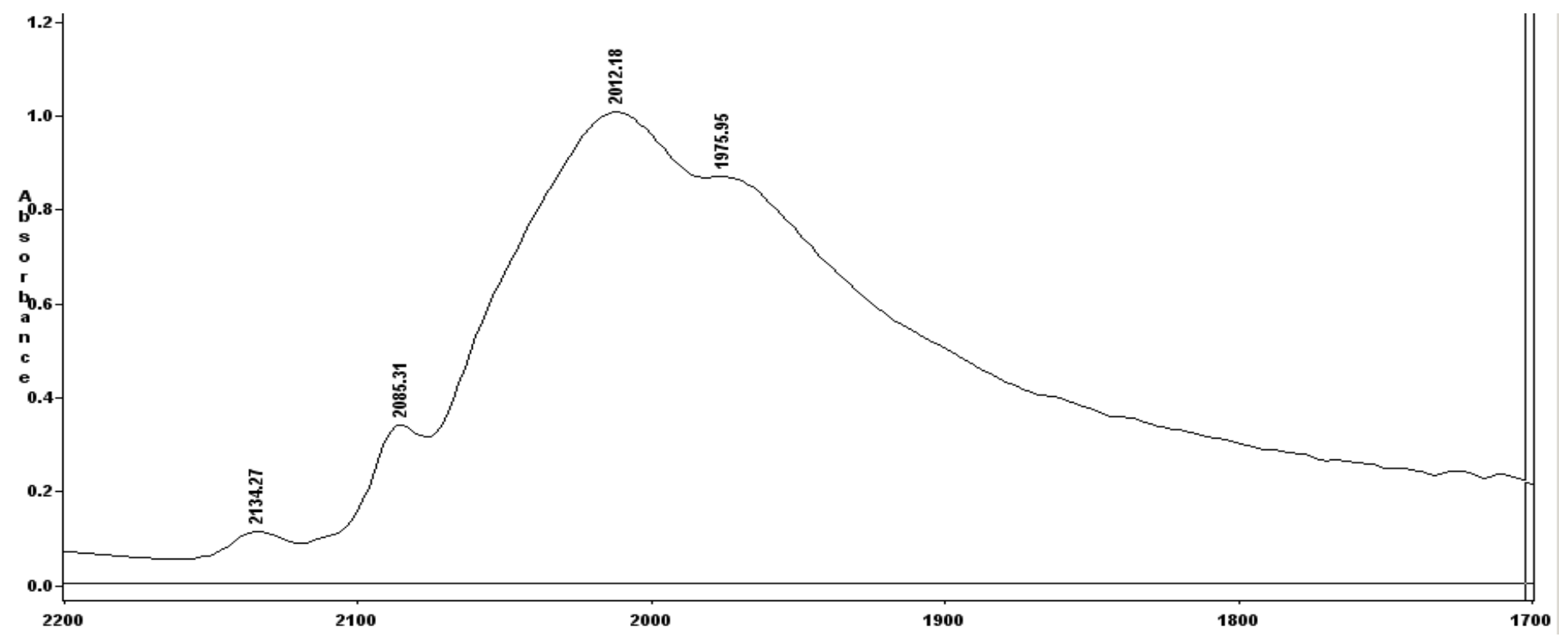


Figure 1: Proton NMR of $[Ta(CNDIPP)_7][BF_4]$

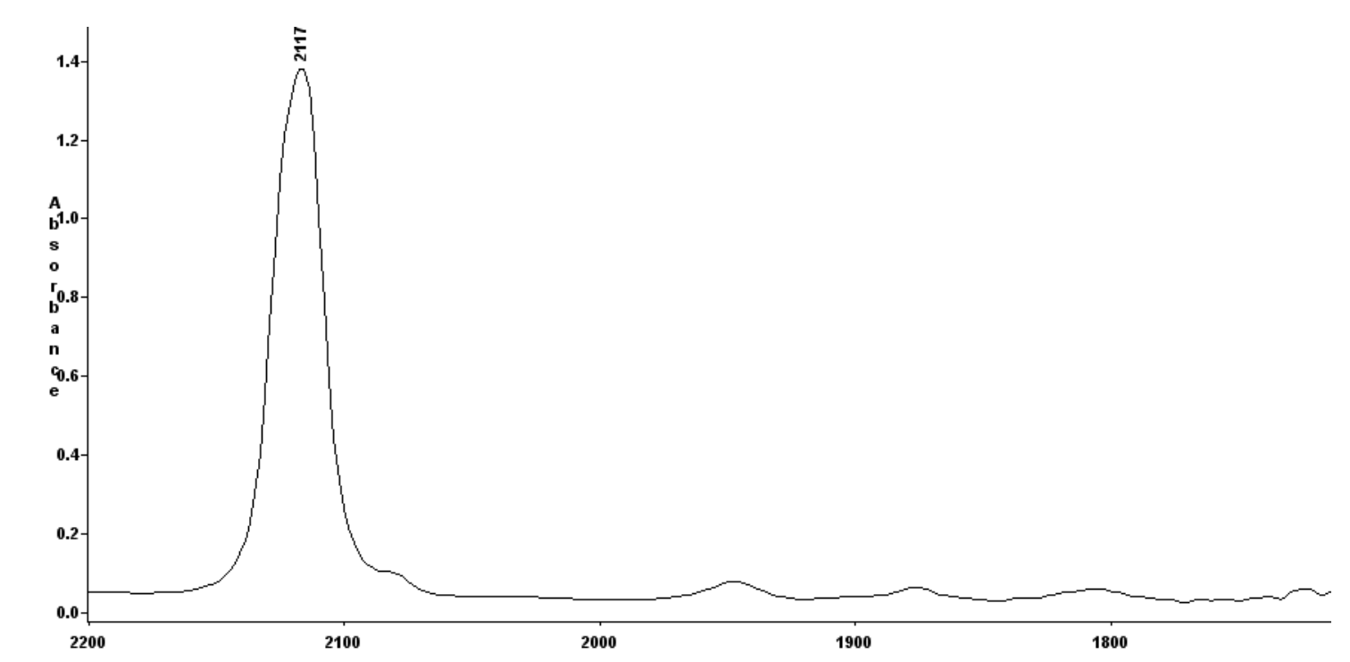
^1H NMR Tantalum complex: Methyl protons, doublet at 1.04 ppm. Methinine protons δ 3.35, septet. Aromatic H, δ 7.27, doublet, and δ 7.343 triplet.

^1H NMR Ligand complex in $CDCl_3$: Methyl protons, doublet at 1.30 ppm. Methinine protons δ 3.21, septet. Aromatic H, δ 7.17, doublet, and δ 7.342 triplet. The Proton NMR for the ligand is similar to figure 1.

Comparison of the IR for 2,6-diisopropylphenylisocyanide and $[Ta(CNDIPP)_7][BF_4]$



IR (Tantalum compound): strong peak at 2012.18 cm^{-1} due to CN stretch is observed.



Free ligand IR: sharp and strong peak at 2117.07 cm^{-1} due to CN stretch is observed. Medium sharp peak at 2245 cm^{-1} thought to be a degradation product of isocyanide in $CDCl_3$

X-ray crystal structure of $[Ta(CNDIPP)_7][BF_4]$

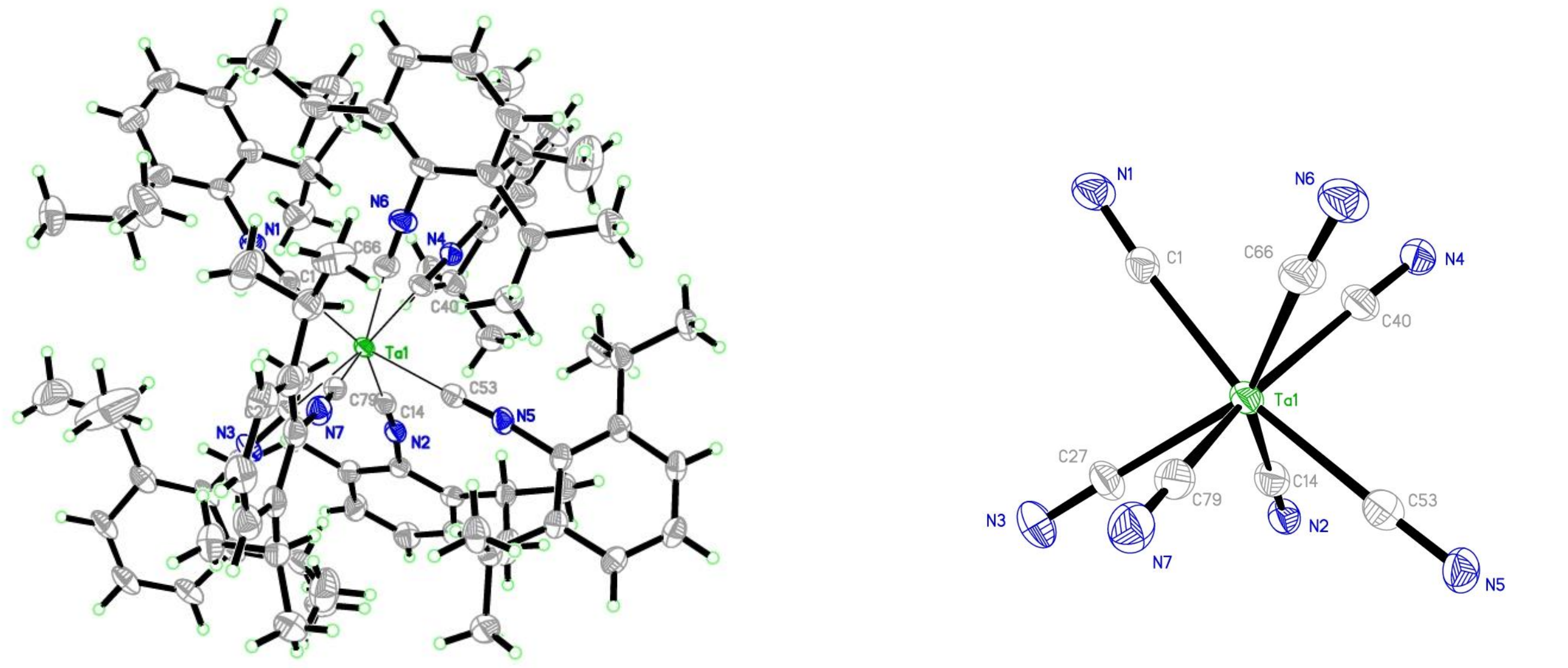


Figure 2: ORTEP of the cation of $[Ta(CNDIPP)_7][BF_4]$ with thermal ellipsoids draw at 30% probability (left) and ORTEP of the same cation showing only the metal center and isocyanide functional groups (right).

Results and Discussion: NMR and IR

The isocyanide CN stretching frequency region show intense absorptions at about 2012 cm^{-1}. The positions of the absorptions are very similar to the previously reported $[Ta(CNXyl)_7][BF_4]$. The IR frequency absorptions for the CN in the metal complex is shifted by approximately 100cm $^{-1}$ relative to the free CNDipp which absorbs at 2117cm^{-1} in $CDCl_3$. This difference in wavenumber indicates that the metals in these complexes effectively participate in backbonding to the coordinated isocyanides.

The data by the infrared spectra is supported by the carbon-13 NMR. The signal of 184.256ppm is observed and occurs at approximately 16 ppm downfield of the corresponding absorption for free CNDipp (168.508ppm). This shift provides convincing evidence there is σ-donation from the isocyanide to the metal complex.

The ^1H NMR of the metal complex is similar to the ^1H NMR of the free isocyanide. This indicates that the metal complex is pretty pure, suggesting that $[Ta(CNDipp)_7][BF_4]$ is the only product formed.
Finally, the crystal structure suggested the desired compound is obtained.

Further work

The physical and chemical properties of this metal complex have not been studied. Further research which includes investigating the chemical reactivity of this metal complex could be carried out.

References

1. Ditri, T. B.; Fox, B. J.; Moore, C. E. ; Rheingold, A. L.; Figueroa, J. S.; *Inorg. Chem*. **2009**, *48,* 8362.
2. Barybin, M. V.; Brennessel, W. W.; Eucera, B. E. ; Minyaev, M. E.; Sussman, V. J.; Young Jr., V. G.; Ellis, J. E.; *J. Am. Chem. Soc.* **2007**, *129,* 1141.
3. Fox, B. J.; Sun, Q. Y.; DiPasquale, A. G.; Fox, A. R.; Rheingold, A. L.; *Inorg. Chem*. **2008**, *47*, 9010.
4. Chitanda, J. M.; Quail, J.W.; Foley, S.R.; *Acta Cryst.* **2008**, *E64*, o1728.