

Annual Progress Report
National Science Foundation
Grant CHE-0414325

Cleavage and Formation of C–S and C–N Bonds in Heterocyclic Compounds by
Homogeneous Transition Metal Complexes

William D. Jones, P.I.
Department of Chemistry, University of Rochester, Rochester, NY 14627

Year two – July 1, 2005-June 30, 2006

The goal of this project is to advance our understanding of the basic chemistry of and develop new synthetic applications for the cleavage and formation of C-S and C-N bonds in thiophenes and heterocyclic nitrogen containing compounds with transition metal fragments. The studies with sulfur have applications in deep hydrodesulfurization (deep HDS), whereas the work with nitrogen will focus on the use of allylamines for heterocycle synthesis. The work has the following objectives: (1) provide basic information about the requirements for the cleavage of these strong and/or hindered C-X bonds (X = S, N), (2) provide information about the mechanism(s) for C-X bond cleavage, (3) examine structural motifs for the binding of sulfur- and nitrogen-containing organic compounds to metals, (4) understand the chemistry of metal sulfhydryl and sulfido compounds, their interconversion, and their lability, and (5) developing catalytic systems for manipulation of C-S and C-N bonds. New concepts to be explored include the determination of electronic effects on bond cleavage and the use of supported systems for catalysis.

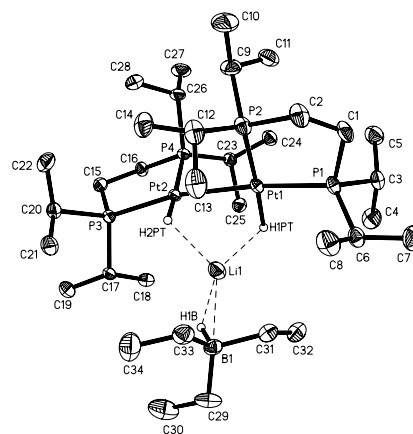
1.a. Proposed Studies: C-S Cleavage

The stated goals of the project are directed at the following focus areas that relate to deep HDS:

- 1) we will examine new complexes for C–S cleavage reactions. The work will take advantage of the earlier results that indicate that binuclear interactions are essential for the cleavage of both carbon-sulfur bonds.
- 2) we will focus on dibenzothiophene systems that are more difficult to cleave, namely, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene.
- 3) the chemistry of μ -sulfido and μ -thiolato complexes will be expanded, as will reactions of the complexes with H_2S . The latter studies relate to the regeneration of the active catalytic species.
- 4) the chemistry of P-N ligands on metals that are active in C–S bond cleavage will be investigated, as these species are more labile than their bisphosphine counterparts.

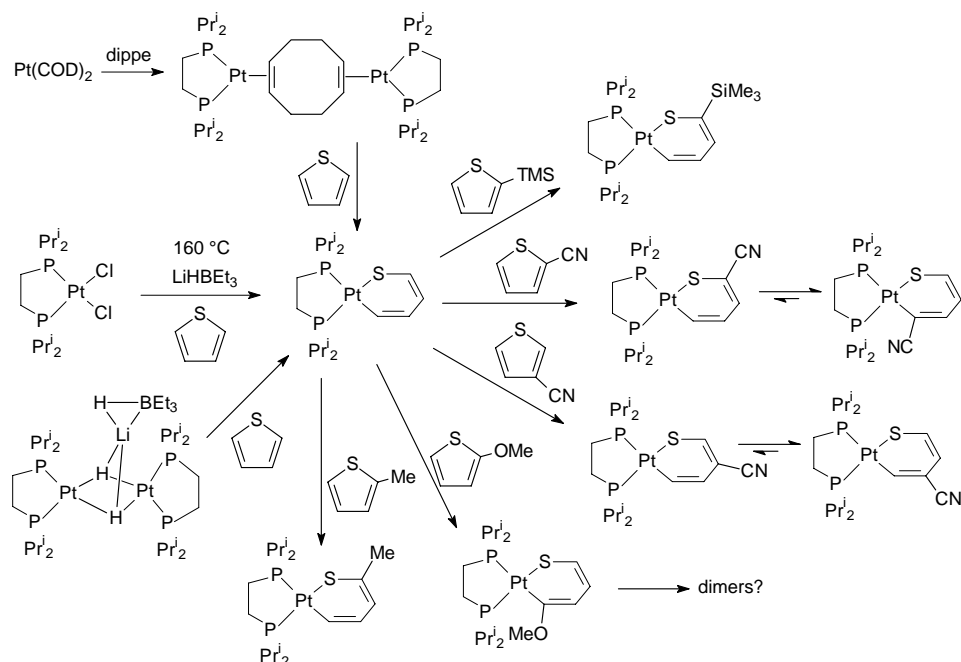
During the first year of this project, we have identified new platinum complexes for C-S bond cleavage. Earlier studies in our laboratory showed that the complex $[\text{Pt}(\text{dippe})\text{H}]_2$ reacts with 4,6-dimethyldibenzothiophene at 120 °C to give the C-S insertion complex, which was characterized by X-ray diffraction. Further reaction with $[(\text{dippe})\text{PtH}]_2$ gives 2,2'-bitolyl in 39% yield. We have extended these activations to a variety of substituted thiophenes as summarized in Scheme 1.

Use of $\text{Pt}(\text{COD})_2$ as a precursor for the reactive $[(\text{dippe})\text{Pt}]$ was found to provide an entry point into these compounds. However, competitive decomposition to Pt colloids gave low yields of products. We then discovered that reduction of the dichloride precursor in thiophene solvent gave the platinum(II) thiophene insertion product in good yield. This species could then be heated to 160 °C, at which temperature thiophene is lost and other thiophenes can undergo insertion. More recently, we have discovered a new hydride precursor $[\text{Pt}_2(\text{dippe})_2\text{H}_2\text{LiHBEt}_3]$ that reacts with 2-cyanothiophene *at room temperature* (see figure). This new lithium-bridged platinum dihydride has substantially improved reactivity compared to the parent dimer. Thiophene and 3-methoxythiophene



require slight heating to react. Consequently, these reactions appear to be bimolecular, with different thiophenes reacting at different rates. We are now looking carefully at each step of the reaction, which include thiophene coordination, C–S bond cleavage, and thiophene substitution. We have also noted that a kinetic insertion product is formed that then rearranges to a thermodynamically preferred product. Again, the possibility of bimolecular reaction is being investigated for this rearrangement.

Scheme 1.



We are trying to understand this reactivity on a fundamental level, in which both steric and electronic effects can be evaluated both in terms of kinetic and thermodynamic selectivity. To assist in the experimental studies, we have performed initial DFT calculations on the complexes. We have published the results of a comparison of C–S cleavage in thiophene by Ni, Pd, and Pt. In these complexes, the bonding can be understood in terms of the interaction of the 14-electron d^{10} M(dippe) intermediate with a ring-opened thiophene fragment (Figure 1). The metal HOMO (a $d_{x^2-y^2}$ orbital) donates into the thiophene fragment LUMO, forming the σ -bonding framework for the product. Back donation from the SHOMO and HOMO of the thiophene fragment into the LUMO and SLUMO of the metal fragment orbitals also contributes to the overall bonding in the

adduct. In comparison of Ni vs. Pd vs. Pt, a combination of HOMO donation and LUMO acceptance of electron density combines to give platinum as the most stable insertion product, but palladium as the least stable insertion product (Figure 2).

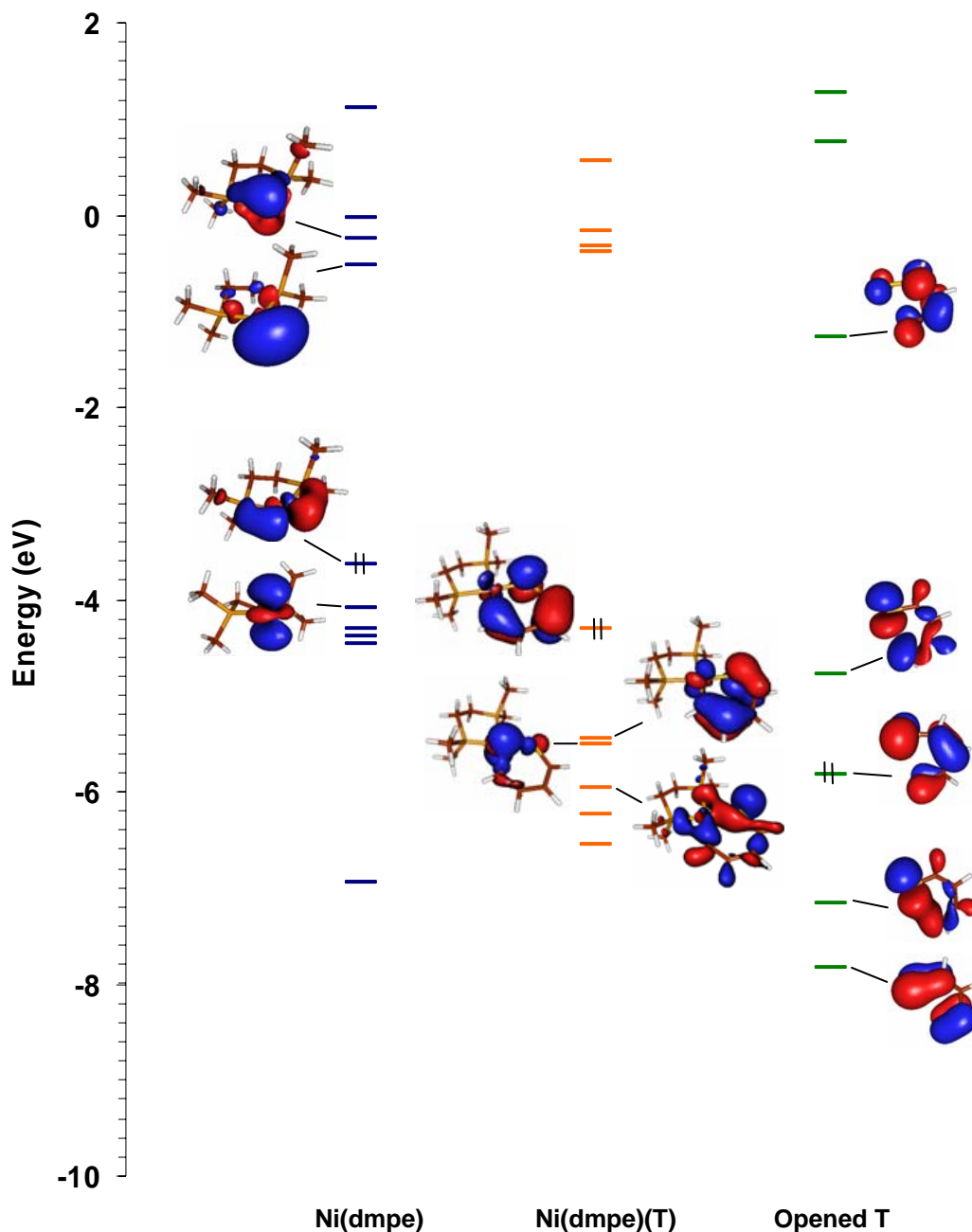


Figure 1. The molecular orbital interaction diagram for Ni(dmpe) with thiophene. Bonding is considered in terms of the interactions between a metal fragment and an opened thiophene fragment, which are shown on the left and right hand sides, respectively. The highest occupied molecular orbitals are marked with an electron pair.

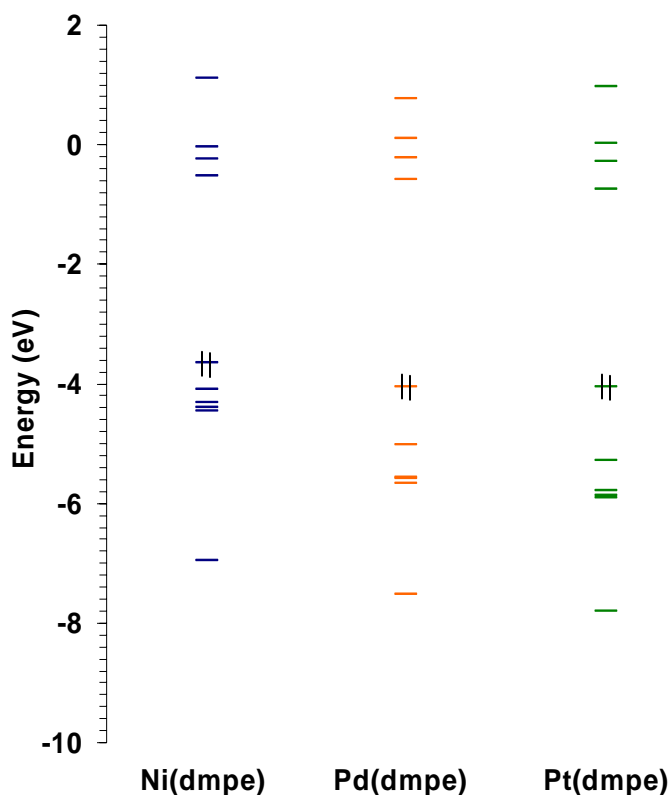
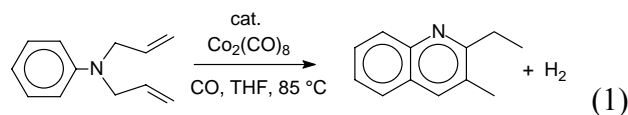


Figure 22. The energies of the molecular orbitals for the metal fragments. The highest occupied molecular orbitals are marked with an electron pair. Nickel is the best donor, but platinum is the best acceptor. Palladium is the worst donor and acceptor.

3.b. Proposed Studies: C–N Cleavage and Formation

Our goals in the synthesis of heterocycles focus on the C–H and C–N cleavage reactions in allylanilines (eq 1):

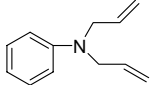
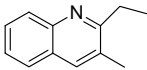
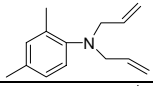
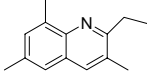
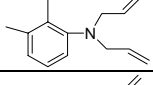
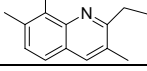
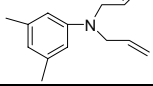
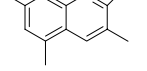
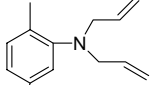
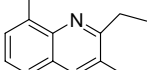
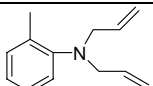
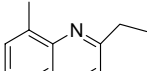
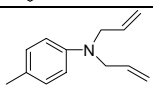
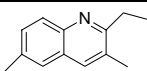
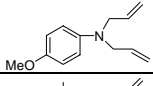
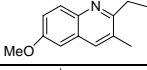
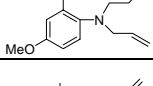
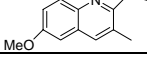
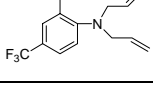
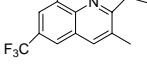


The goals for the project were stated as:

- (1) what is the scope of the reaction, both with respect to allylanilines and imines,
- (2) what is the tolerance for different functional groups,
- (3) are there possibilities for the use of alternate sources of allyl groups,
- (4) can the reduction of the imines be avoided, and
- (5) what is the mechanism of the reaction.

Research progress to date has examined a series of compounds that provide the scope of quinolines that can be synthesized (see Table 1).

Table 1. Isolated yields for the conversion of diallylanilines to quinoline derivatives

Entry	Substrate	Product	Temperature(°C)	Yield(%)
1			105	46
2			105	32
3			105	28
4			105	67
5			105	17
6			120	35
7			120	29
8			105	20
9			120	26
10			120	< 10

We have also investigated the yield of quinoline from diallylaniline as a function of catalyst concentration (Table 2) and solvent (Table 3). From Table 2 we can see that yields are not very different although the reaction time can be reduced with added catalyst. From Table 3 we see that benzene gives the highest yields of product in the shortest times, whereas a nonpolar solvent such as hexane gives low yields even after extended reaction.

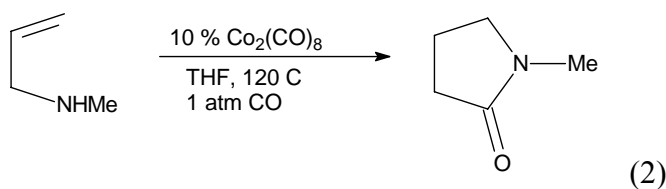
Table 2. Isolated Yields for the Conversion of Diallylaniline to Quinoline Derivatives with Different Amounts of Catalyst

Co ₂ (CO) ₈	Yield	Reaction Time
10%	46%	~ 24 h
20%	49%	8~24 h
50%	53%	< 2 h

Table 3. Isolated Yields for the Conversion of Diallylaniline to Quinoline Derivatives Using Different Solvents

Solvent	Yield	Reaction Time
THF	46%	~ 24 h
Toluene	52.4%	~ 38 h
Benzene	63.1%	~ 21 h
Hexane	34.7%	> 55 h

We have also discovered that simple methylallylamine undergoes cyclization to generate a lactam in greater than 90% yield (eq 2). Other substrates are being synthesized and investigated to determine the scope of this reaction.

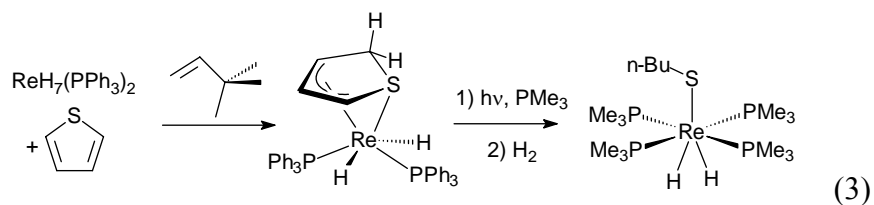


3.c. Broader Significance - New Directions – Hydrogen Storage

I was contacted a month ago by a small start-up company in Seattle called Asemblon. They were interested in some chemistry we had published about 10 years ago describing hydrogenation of thiophene. The CEO of the company (Patrick Quarles) and one of the research chemists (Esmaeel Naeemi) flew out to Rochester in late March to talk about a possible research agreement with the company. The nature of their interest relates to a hydrogen storage/transportation/release system that has substantial potential impact on the 'hydrogen economy'. They have discovered and filed a patent for a process in which a 'special molecule' (a liquid organic compound) when contacted with a metal catalyst produces hydrogen on demand with an acceptable weight efficiency. The use for such a system would permit the generation of hydrogen for use as a fuel without high pressure tanks or large quantities of dangerous gas. In their scheme, the spent molecule would be recycled and re-hydrogenated so that it could return to use as a portable, safe hydrogen source. (see: <http://www.asemblon.com/>)

Their interest in our research stems from our report on the reaction of thiophene to butanethiol, which is similar to what is needed for recycling of their 'special molecule'. We reported two examples of hydrogenation of thiophene to butanethiol (eq 3, 4), and consequently

we will return to a re-examination of this chemistry, and in particular, the hydrogenation of the ‘special molecule’.



This material removed prior to publication.

4. Publications

1. “Bis- μ -2,3,5,6-tetrafluoro-trifluoromethyl-benzenethiolate-bis(3,5-cyclooctadiene)dirhodium(I),” William D. Jones, Juventino Garcia, and Hugo Torrens, *Acta Cryst. E*, **2005**, 61(11), m2204-m2206.
2. “The Synthesis and Structural Properties of $[M(\text{dippe})(\eta^2\text{-C}_4\text{H}_4\text{S})]$ Complexes of Pd and Pt and Comparison with their Ni Analog,” Tülay A. Ateşin, Stephen S. Oster, Karlyn Skugrud, William D. Jones, *Inorg. Chim. Acta*, **2006**, in press.