

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

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Year one – July 1, 2004-June 30, 2005

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

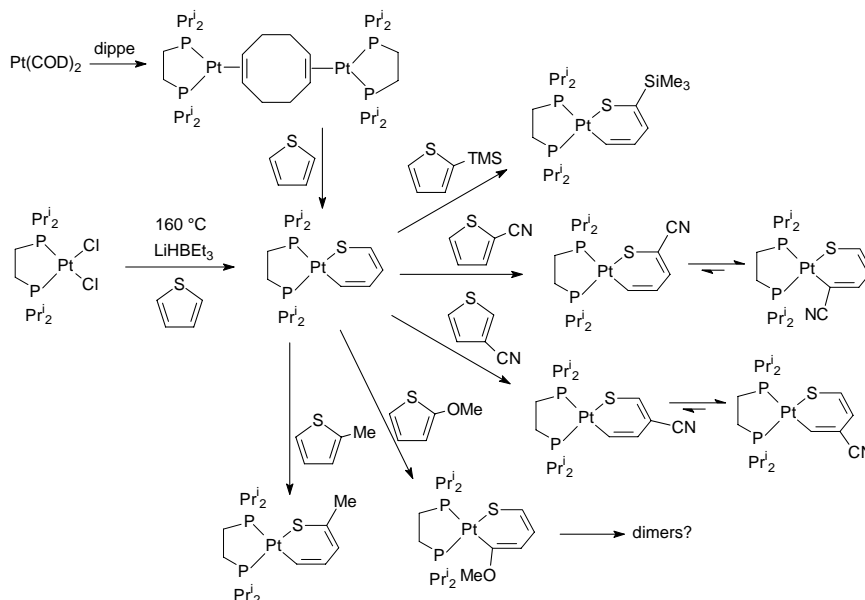
- 1) we will examine new complexes for C–S cleavage reactions. The work will take advantage of the earlier results that indicate that binuclear interactions are essential for the cleavage of both carbon-sulfur bonds.
- 2) we will focus on dibenzothiophene systems that are more difficult to cleave, namely, 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 H₂S. 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 investigated new platinum complexes for C-S bond cleavage. Earlier studies in our laboratory showed that the complex [Pt(dippe)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 [(dippe)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 Pt(COD)₂ as a precursor for the reactive [(dippe)Pt] has been found to provide a reasonable entry point into these compounds. Reaction of Pt(COD)₂ with dippe and thiophene leads to Pt(dippe)(η^2 -C,S-C₄H₄S), **1**. One important side reaction of this method is the formation of platinum colloid, which turns the solution black and decreases the synthetic yield. Recently we have found an improved synthesis which uses the reduction of Pt(dippe)Cl₂ with LiHBEt₃ in the presence of thiophene at elevated temperature to give cleanly the thiophene insertion product.

The thiophene insertion adduct **1** serves as a convenient precursor for other adducts. Heating **1** at 160 °C in the presence of another thiophene leads to exchange. For example, with 2-cyanothiophene a mixture of 2-cyano and 5-cyano ring opened products are obtained. Over the next several weeks, the ratio of products is seen to change dramatically, indicating that there is a kinetic preference for insertion away from the cyano group, but a thermodynamic preference for an α -cyano group. Similar observations are made with other thiophenes.

Scheme 1.

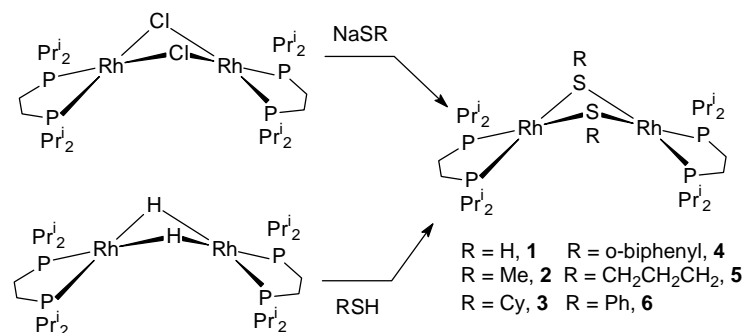


We are trying to understand this reactivity on a fundamental level, in which both steric and electronic effects can be evaluated both in terms of kinetic and thermodynamic selectivity. To assist in the experimental studies, we are also performing DFT calculations on the complexes and the transition states leading to C-S cleavage. In this way, we hope to provide the necessary fundamental insight to understand the reactivity patterns, enabling predictions of future reactivity.

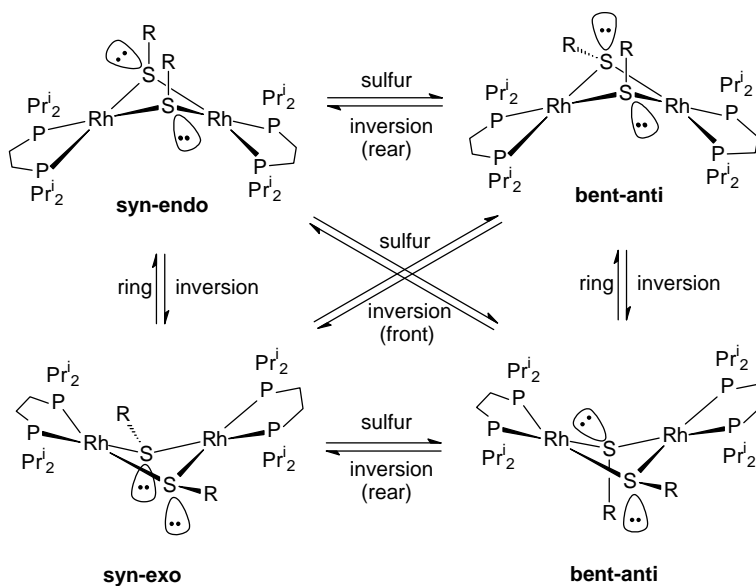
In completing studies since our early NSF grant, we have also investigated several new bis-thiolate complexes of the type $[\text{Rh}(\text{dippe})(\mu\text{-SR})_2]$ where $\text{R} = \text{H}$, methyl, cyclohexyl, *o*-biphenyl, and phenyl, or $(\text{SR})_2 = \text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ (Scheme 2). These complexes have been synthesized and characterized by NMR spectroscopy and single crystal X-ray diffraction. All $[\text{Rh}(\text{dippe})(\mu\text{-SR})_2]$ complexes except $[\text{Rh}(\text{dippe})(\mu\text{-SPh})_2]$ exhibit bent geometries in the solid state, while the orientation of the thiolato substituents changes with increasing steric bulk. ^1H and ^{31}P NMR spectroscopies indicate that both ring inversion and sulfur inversion occur among the members of the series, which allows them to access several isomeric forms when they are in solution (Scheme 3). ^{31}P NMR spectroscopy indicates that sulfur inversion in $[\text{Rh}(\text{dippe})(\mu\text{-SH})_2]$, $[\text{Rh}(\text{dippe})(\mu\text{-Sbiphenyl})_2]$, and $[\text{Rh}(\text{dippe})(\mu\text{-SPh})_2]$ is a nondissociative

process. The barriers for these processes have been determined for several of these substituted derivatives (Table 1), and show that the barrier for ring inversion are much smaller than for inversion at sulfur.¹

Scheme 2:



Scheme 3:

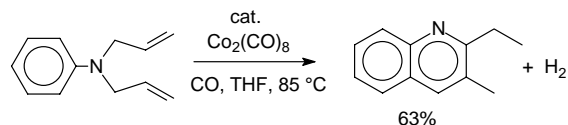


| Complex | Solvent | ΔG^\ddagger Ring Inversion kJ mol ⁻¹ | ΔG^\ddagger Sulfur Inversion kJ mol ⁻¹ |
|--|--------------------------------|--|--|
| [Rh(dippe)-(μ-SH)] ₂ 1 | THF- <i>d</i> ₈ | — | 42.5 |
| [Rh(dippe)-(μ-SCH ₃)] ₂ 2 | toluene- <i>d</i> ₈ | 16.5 | — |
| [Rh(dippe)-(μ-SC ₁₂ H ₉)] ₂ 4 | toluene- <i>d</i> ₈ | 19.7 | 61.4 |
| [Rh(dippe)-(μ-SC ₆ H ₅)] ₂ 6 | THF- <i>d</i> ₈ | — | 32.1 |

¹ "Structural Properties and Inversion Mechanisms of [Rh(dippe)(μ-SR)]₂ Complexes," Steven S. Oster and William D. Jones, *Inorg. Chim. Acta*, **2004**, 357, 1836-1846.

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:



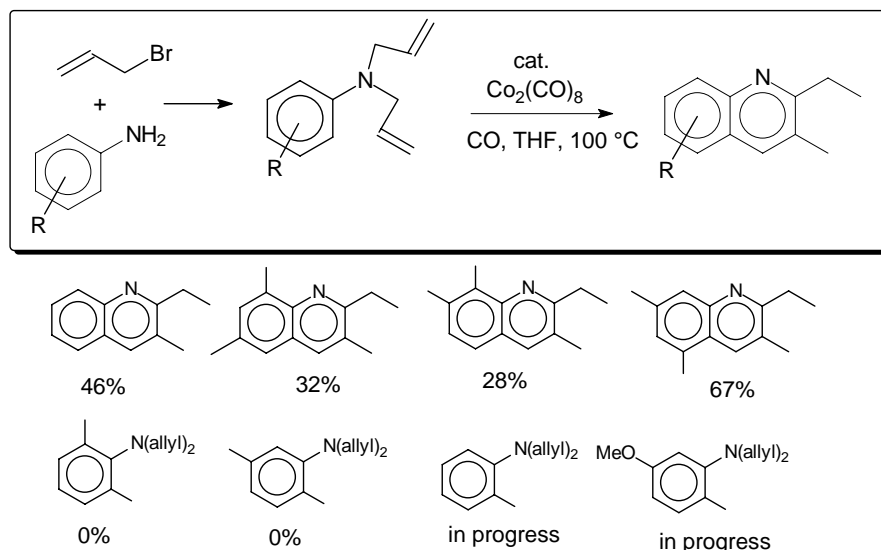
The goals for the project were stated as:

- (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 begun with an expansion of the scope of the reaction.

Quinolines that have been synthesized using this methodology and yields are indicated in Chart 1 below. The combination of the aniline and allylbromide can occur directly in the presence of the cobalt catalyst to give the quinoline.

Chart 1:



We have also now synthesized $(\text{allyl})\text{Co}(\text{CO})_3$, a solid below $-30\text{ }^\circ\text{C}$ that can be recrystallized from cold pentane. The complex reacts with aniline to give quinoline, so that its involvement in C-N cleavage *and reformation* have now been verified. We will proceed to the synthesis of the deuterated analog for the mechanistic crossover experiments described in the proposal.