

## DFT Study of $\text{Cp}_2\text{Th}$ and $\text{Cp}_2\text{U}$ Catalysts for Pyridine Hydrodenitrogenation

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As our nation's supply of fossil fuels dwindles over the next century, low-quality "dirty" petroleum feedstocks (from tar sands, oil shales, etc.) will serve as a bridge to alternative energy sources. However, these feedstocks typically contain N/S/O-containing hydrocarbons as impurities, and must be "cleaned" prior to burning via HDN, hydrodesulfurization, and/or hydrodeoxygenation. Despite the importance of these industrial processes, they have several drawbacks (e.g., poor selectivity, harsh conditions required, etc.) that have encouraged inorganic chemists to develop better catalysts for each process.

In this paper, we describe the DFT calculations performed for the actinide systems  $\text{Cp}_2\text{Th}$  and  $\text{Cp}_2\text{U}$ . Experimentally, these systems exhibit a rich chemistry towards N-heterocyclic substrates (C-H/C-N activation, ring-opening, dearomatization). Computations are therefore performed to predict how well this chemistry extends to pyridine HDN, as N-heterocycles such as pyridine have been some of the most difficult contaminants to process via conventional HDN routes.

As of 2009, fossil fuels comprised over 80% of US energy consumption [1], despite the global dwindling of fossil fuel reserves. In order to prevent an economic catastrophe, a transition period has been proposed, where abundant, low quality ("dirty") petroleum feedstocks would bridge the gap between fossil fuels and alternative energy sources. These dirty feedstocks, typically tar sands and oil shales, are contaminated with nitrogen (N)-, sulfur (S)-, and oxygen (O)-containing organic impurities that pose environmental hazards after combustion. Once the impurities are removed, the upgraded feedstock may be safely used for fuel.

N-heterocycles such as pyridine are some of the most persistent contaminants in dirty petroleum and are conventionally removed via hydrodenitrogenation (HDN, see Fig. 1), in which the N-heterocycle is reacted with hydrogen over a suitable (typically transition metal) heterogeneous catalyst to remove the nitrogen as ammonia.

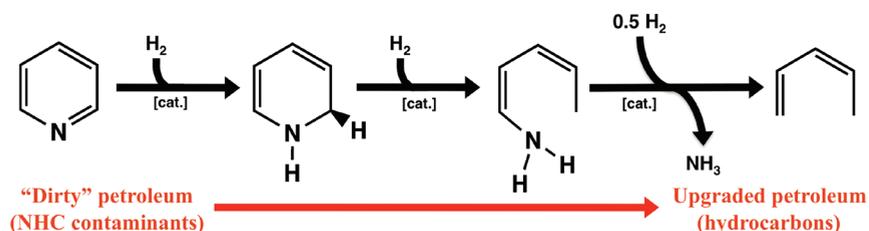
However, due to the drawbacks of current HDN processes (the high pressures and temperatures required, poorly-understood reaction mechanisms, etc.), there has been

renewed interest in homogeneous catalysts, albeit with mixed results; even though potent transition metal catalysts have been discovered, they are only active towards a narrow range of substrates and tend to be stoichiometric as opposed to catalytic.

Fortunately, early actinide catalysts have been more potent towards the strong carbon bonds (C-N and C-H) of N-heterocycles. For instance,  $\text{Cp}^*\text{Th}(\text{Ph})_2$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl; Th = thorium; Ph = phenyl) cleaves the C-N bond of pyridine-N-oxide at room temperature [2]. Additionally, one may tune the product selectivity simply by changing the actinide, as observed in the reaction of  $\text{Cp}^*\text{An}(\text{Me})_2$  (actinide [An] = Th, uranium [U]) with 2-picoline (2-methylpyridine) [3]—for Th and U, the methyl C-H bond and a pyridine C-H bond, respectively, are cleaved.

In the current project, density functional theory (DFT) calculations are performed to predict the mechanism of pyridine C-N cleavage with the putative intermediate  $\text{Cp}_2\text{An}(\text{benzyne})$  ( $\text{Cp}$  = cyclopentadienyl, see Fig. 2). The choice of the latter adduct as catalyst is motivated by the rich chemistry of benzyne. The B3LYP functional is used for all calculations. Geometries are optimized with a double- $\zeta$  basis set and confirmed as either minima or transition states by calculated vibrational frequencies. At each minima, entropies/zero point energies and total electronic energies are calculated with the same double- $\zeta$  and a larger triple- $\zeta$  basis set, respectively, for triple- $f^0$ -quality free energies. All Th

Fig. 1. Idealized HDN process for pyridine.



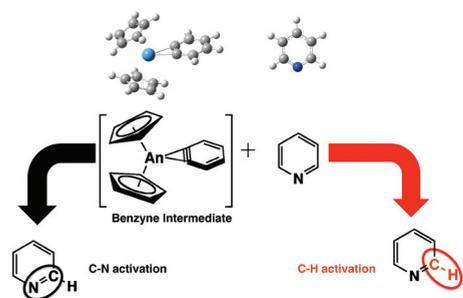


Fig. 2. Initial C-N (black) and C-H (red) activation pathways for pyridine ring opening with  $\text{Cp}_2\text{An}(\text{benzynes})$ .

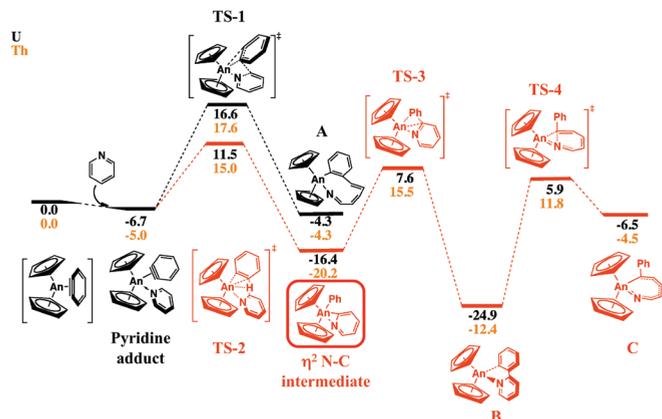


Fig. 3. Free energy diagram (kcal/mol; all energies relative to  $\text{Cp}_2\text{An}(\text{benzynes})$ ) of pyridine C-N (black) and C-H (red) activation pathways for Th (orange) and U (black) systems.

systems are formally  $f^0$  and are therefore singlets whereas triplet ground states were confirmed for all U (formally  $f^2$ ) systems.

Initial pyridine coordination to  $\text{Cp}_2\text{An}(\text{benzynes})$  is slightly favorable for both actinides (Fig. 3). From the pyridine adduct, two reaction mechanisms were considered for each actinide system: (1) initial C-N activation, and (2) initial C-H activation (Fig. 2). In the C-N activation transition state (TS-1), a pyridine C-N bond is broken, while a new C-C bond is formed between pyridine and benzyne, leading to a ring-opened ketimide (A). Although similar chemistry has been reported for  $\text{Cp}^*_2\text{U}(\text{benzynes})$  and  $\text{PhCCPh}$  [4], the calculated pyridine C-H activation transition state (TS-2), in which a pyridine H is transferred to benzyne,

is  $\sim 2\text{-}5$  kcal/mol more favorable, a difference attributable to the relative C-H/C-N bond energies. Our experimental collaborators confirmed this prediction by isolating the next species along the C-H activation pathway, the  $\eta^2$  N-C intermediate [5], calculated to be  $\sim 12\text{-}16$  kcal/mol more stable than ketimide A (Fig. 3). Next, a phenyl migration transition state (TS-3) is found in which the phenyl is transferred from An to pyridine to give intermediate B. Unlike most intermediates in Fig. 3 (An[IV]), the formal oxidation state in B is closer to An(III), owing to a weak An-N

single bond and An-C(Ph) interaction. Finally, a C-N cleavage/ring opening transition state (TS-4) is found, leading to a second ring-opened ketimide (C). Overall, formation of either ketimide (A or C) from  $\text{Cp}_2\text{An}(\text{benzynes})$  is thermodynamically favorable. It is noteworthy that although the barrier for initial pyridine ring opening ( $\sim 23$  kcal/mol, TS-1) is larger than that for C-H activation ( $\sim 18\text{-}20$  kcal/mol, TS-2), the latter pathway includes two additional barriers (TS-3 and TS-4), one of which is larger than that in the former pathway—for Th, phenyl transfer

is least favorable ( $\Delta G^\ddagger = 35.6$  kcal/mol) whereas C-N cleavage is least favorable for U ( $\Delta G^\ddagger = 30.8$  kcal/mol).

In summary, DFT calculations predict two mechanisms for pyridine ring opening catalyzed by  $\text{Cp}_2\text{An}(\text{benzynes})$ . Although the C-H activation pathway is favored at the branching point, higher barriers ( $\sim 31\text{-}36$  kcal/mol) are encountered further along this pathway. Regardless of the operative pathway, a full catalytic cycle requires further processing of the ring-opened ketimide. One possible route involves cleaving the ketimide with  $\text{H}_2$  to give  $\text{Cp}_2\text{AnH}_2$ , which is a potential precursor to  $\text{Cp}_2\text{An}(\text{benzynes})$ , and an 11-carbon (C11) imine (Fig. 4). As an additional benefit, treating the imine with additional hydrogen to release ammonia would give a C11 hydrocarbon, which is within the C10-C15 range found in petroleum-derived diesel [6].

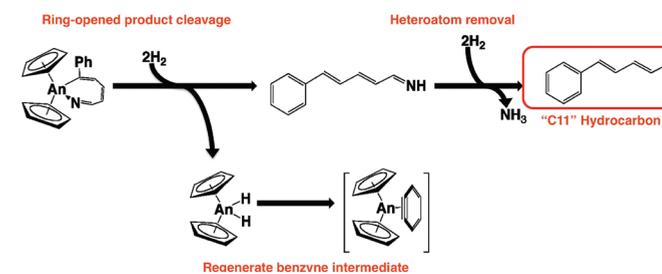


Fig. 4. Possible routes toward a catalytic cycle and N removal from ring-opened products.

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