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, \(\text{Cp}^*\text{Th(Ph)}_2\) (\(\text{Cp}^* = \text{pentamethylcyclopentadienyl; Th} = \text{thorium; Ph} = \text{phenyl}\)) 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 \(\text{Cp}^*\text{An(Me)}_2\) (actinide \(\text{[An]} = \text{Th, uranium [U]}\) 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 \(\text{Cp}_2\text{An(benzyne)}\) (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-ζ and a larger triple-ζ basis set, respectively, for triple-ζ-quality free energies. All Th
systems are formally $f^0$ and are therefore singlets whereas triplet ground states were confirmed for all U (formally $f^3$) systems.

Initial pyridine coordination to Cp$_2$An(benzyne) 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 Cp$_2$U(benzyne) and PhCCPh [4], the calculated pyridine C-H activation transition state (TS-2), in which a pyridine H is transferred to benzyne, is $\sim$2-5 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 $\eta^1$ N-C intermediate [5], calculated to be $\sim$12–16 kcal/mol more stable than ketimide A (Fig. 3). Next, a phenyl migration transition state (TS-3) is found in which the phenyl is transferred from An to pyridine to give intermediate B. Unlike most intermediates in Fig. 3 (An[IV]), the formal oxidation state in B is closer to An(III), owing to a weak An-N single bond and An-C(Ph) interaction. Finally, a C-N cleavage/ring opening transition state (TS-4) is found, leading to a second ring-opened ketimide (C). Overall, formation of either ketimide (A or C) from Cp$_2$An(benzyne) is thermodynamically favorable. It is noteworthy that although the barrier for initial pyridine ring opening ($\sim$23 kcal/mol, TS-1) is larger than that for C-H activation ($\sim$18-20 kcal/mol, TS-2), the latter pathway includes two additional barriers (TS-3 and TS-4), one of which is larger than that in the former pathway—for Th, phenyl transfer is least favorable ($\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 Cp$_2$An(benzyne). Although the C-H activation pathway is favored at the branching point, higher barriers ($\sim$31-36 kcal/mol) are encountered further along this pathway. Regardless of the operative pathway, a full catalytic cycle requires further processing of the ring-opened ketimide. One possible route involves cleaving the ketimide with H$_2$ to give Cp$_2$AnH$_2$, which is a potential precursor to Cp$_2$An(benzyne), 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. 2.** Initial C-N (black) and C-H activation (red) pathways for pyridine ring opening with Cp$_2$An(benzyne).

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

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


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