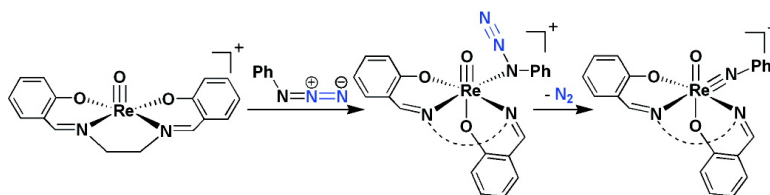


A New Mechanism for the Conversion of Transition Metal Azides to Imido Complexes

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A New Mechanism for the Conversion of Transition Metal Azides to Imido Complexes

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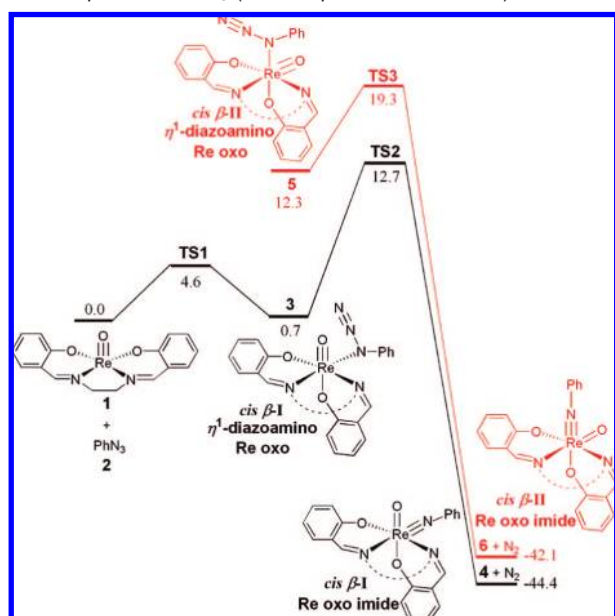
Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received July 2, 2008; E-mail: mbhall@tamu.edu

Transition metal imido complexes ($[M]=NR$) are particularly interesting because of their postulated roles in catalysis, nitrogen fixation, and atom- and group-transfer processes.¹ Coordination of organic azides (RN_3) to the metal complexes^{2–4} followed by elimination of N_2 has been an important preparative route to imido complexes. Very recently, Abu-Omar and co-workers reported a facile synthesis of cationic rhenium(VII) oxo imido complexes from the reaction of oxorhenium(V) and aryl azides under ambient conditions⁵ without thermal or photochemical activation (nitrene capture).⁶ The authors suggest that the reaction proceeds from a terminal η^1 -azide through the Bergman N_2 loss mechanism.⁷ Both Bergman^{7a,b} and Cummins^{7c} groups have isolated terminal η^1 -azido adducts of Ta and V, respectively, observed their thermal decomposition to imido complexes and N_2 , and postulated a four-membered triazametallacyclobutene intermediate. Although this mechanism has reasonable barriers for the Bergman and Cummins systems, it has a huge activation energy ($\Delta H^\ddagger = 52.1$ kcal/mol) for the Re(VII) system.⁸

Here, we report a new mechanism for the conversion of Re azide complexes to the corresponding Re imido complexes by N_2 loss. The entire reaction pathway and relative energy barriers as determined by density functional calculations⁹ (details in the Supporting Information, SI) for each step are presented in Scheme 1, and relevant optimized geometries are shown in Figure 1.

Scheme 1. ΔH (kcal/mol) Diagram for the Reaction of the Rhenium Oxo Complex with PhN_3 (All Re Species Are Cations)^a



^a Free energies and solvation corrections (see SI) uniformly raise the energy of the TS and intermediates with respect to the reactants.

Experimentally, treatment of the cationic oxorhenium salen complex **1** with phenyl azide **2** leads to the formation of the cationic oxo imido rhenium complexes. Although several geometric isomers are possible (Scheme S1), two *cis* β isomers (*cis* β -I and *cis* β -II) are considered by the experimentalists.⁵ NMR spectroscopy and X-ray crystallography showed that there is stereoselective preference for the *cis* β -I isomer.⁵ The *cis* β -I isomer with the imido *trans* to the imine ligand has been recently reported in $[Mo(O)N^tBu-\{(3,5-tBu_2)_2salpd\}]$, and this geometry was rationalized based on the relative π -donor strengths of the oxo and imido ligands.¹⁰

In contrast to the Bergman N_2 loss mechanism, where the azide coordinates to the metal in an η^1 -terminal mode, we found that in the Abu-Omar's Re system, PhN_3 (**2**) prefers to bind to **1** in an η^1 -diazoamino mode to form **3** (*cis* β -I) and **5** (*cis* β -II), respectively. Forming **3** only requires 4.6 kcal/mol of activation enthalpy. No transition state was located for the direct formation of **5**. Decomposition of **3** or **5** by N_2 loss does not require formation of the cyclic 4-centered intermediates as in Bergman's mechanism. Instead, direct N_2 loss transition states, **TS2** and **TS3**, were located with the activation enthalpies of only 12.7 and 19.3 kcal/mol, respectively. The Re azido intermediate **5** is 11.6 kcal/mol less stable than its geometric isomer **3**, and its N_2 loss transition state **TS3** is 6.6 kcal/mol higher in enthalpy than **TS2** (N_2 loss from **3**). These results suggest that the formation of the *cis* β -I oxo-imido complex **4** is faster than that of *cis* β -II oxo-imido complex **6** by $\sim 10^4$ at room temperature. The overall process of formation of the *cis* β -I oxo-imido isomer, **4**, is exothermic by -44.4 kcal/mol (Scheme 1). Hence, the formation of **4** is facile and the kinetically favored process at room temperature, in agreement with the experiment, where treatment of the cationic oxorhenium salen complex with aryl azide results in the exclusive rapid formation of the *cis* β -I oxo-imido isomer.⁵

Complexes and intermediates **3–6** adopt a distorted octahedral geometry. The Re–N bond (2.409 Å) in **5** is much longer than that in **3** (2.284 Å); the weaker binding between the diazoamino ligand and the Re center in **5** is due to the cost of distorting PhN_3 not being compensated by the Re–N bond in **5** because of the stronger O(salen) *trans* influence that results in **5** having an enthalpy 11.6 kcal/mol higher than that for **3**. **TS2** and **TS3** have noticeably elongated bond lengths for (Re)N–N(\equiv N) (1.535 and 1.464 Å, respectively) from that of **3** (1.258 Å) and **5** (1.260 Å). In **4** and **6**, the Re imido bond is almost linear ($\angle Re-N-C(Ph) = 170^\circ$) and the Re imido, Re–N (1.75 Å) and Re oxo, Re–O (1.70 Å) bond lengths are within the normal range for Re(heteroatom) multiple bonds. The Re oxo bond lengths are moderately longer than that of the starting cationic oxo Re(V) complex (Re–O (1.660 Å))(Figure 1).

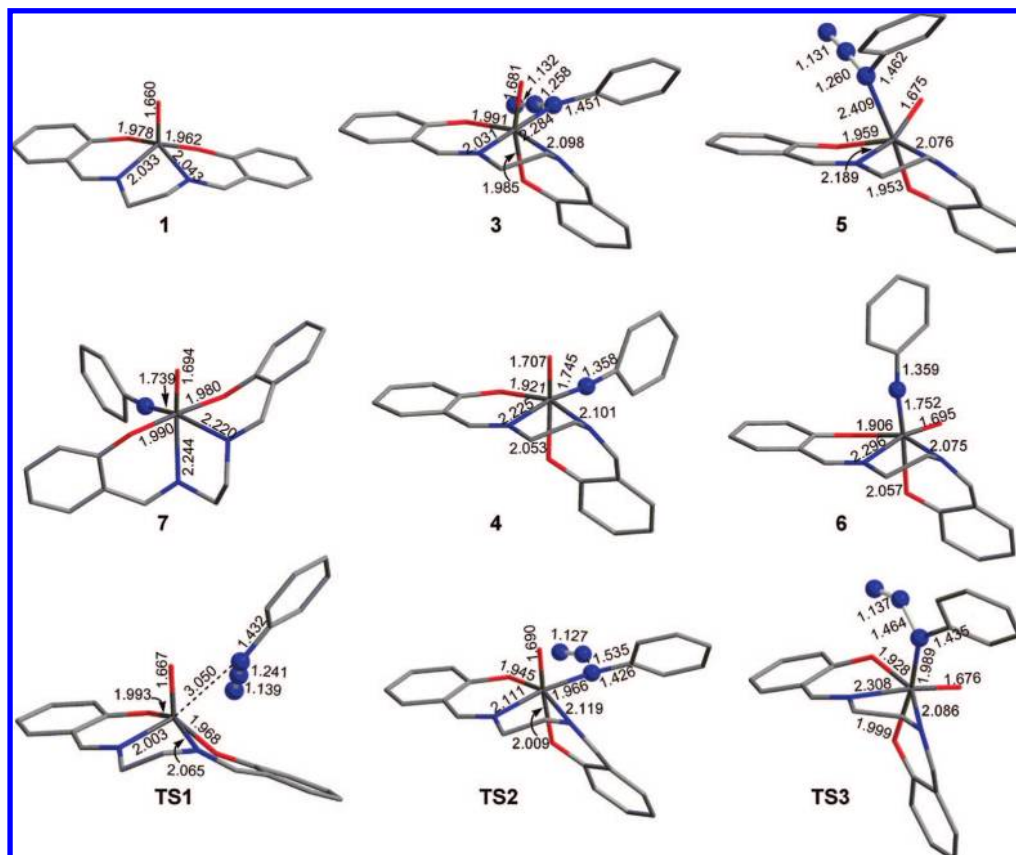


Figure 1. Optimized geometries of relevant reactants, transition states, and products. Bond distances are shown in Å. H atoms were omitted for clarity.

Although the difference in the barriers precludes the formation of the *cis* β -II isomer its thermodynamic stability is quite close to that of the *cis* β -I isomer (2.3 kcal/mol). Because of the similar stability we studied the direct rearrangement from the *cis* β -I isomer (**4**) to the *cis* β -II isomer (**6**) via successive trigonal twists through the *cis* α isomer (**7**), in which the phenoxide ligands of salen are *trans* to each other. In this geometric change, the imido ligand switches from *trans* to imine to *trans* to phenoxide and requires an activation energy of 35.6 kcal/mol. Therefore, the interconversion of **4** and **6** would be quite slow, and if any **6** formed, it would be from the decomposition of the rhenium azide intermediate **5**.

In summary, our calculations demonstrate that the oxo rhenium complex (**1**) reacts with PhN_3 (**2**) through rhenium azide intermediates to produce the *cis* β oxo-imido complex, where *cis* β -I (**4**) is both kinetically and thermodynamically favored over *cis* β -II (**6**). In the new mechanism PhN_3 binds to rhenium in an η^1 -diazoamino mode producing intermediates **3** and **5**. No cyclic 4-centered intermediate or transition state was necessary as the direct N_2 loss¹¹ from **3** and **5** has activation enthalpies of only 12.7 and 19.3 kcal/mol, respectively. Unexpectedly, the azide decomposition via the 4-centered cyclic transition state requires a high activation enthalpy ($\Delta H^\ddagger = 52.1$ kcal/mol). The trigonal twist of *cis* β -I (**4**) to *cis* β -II (**6**) also requires a high activation enthalpy ($\Delta H^\ddagger = 35.6$ kcal/mol). Thus, the distribution of *cis* β -I and *cis* β -II is under kinetic control and in agreement with the experiments; only *cis* β -I was found because the barrier to *cis* β -II is 6.6 kcal/mol higher.

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Supporting Information Available: Complete ref 9, computational details, scheme on stereochemical possibilities for Re oxo-imido complexes, figure for interconversion from **4** to **6**, total energies, thermodynamic data, and coordinates of optimized stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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