

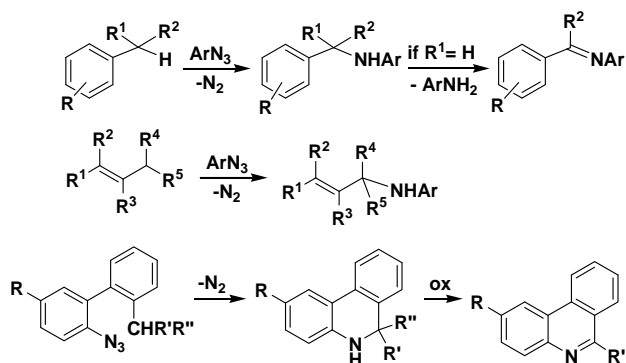
## Ruthenium Porphyrin Complexes: Powerful Catalysts For Hydrocarbon Atom-Efficient Aminations

Emma Gallo

Università degli Studi di Milano – Chemistry Department  
Via Golgi 19 – 20133 Milano (Italy)

The direct amination of hydrocarbons is a reaction of great synthetic interest because of the biological and pharmaceutical relevance of aza-derivatives. For several years we have studied these reactions by using aryl azides as nitrogen sources and metallo porphyrins as catalysts [1]. In particular, we have investigated the catalytic activity of the  $16e^-$  species  $Ru(\text{porphyrin})(CO)$  in hydrocarbon aminations.

Ruthenium porphyrins show a good catalytic activity in the amination of both benzylic and allylic C-H bonds [2]. Moreover, they also promote the intramolecular amination of biaryl azides yielding dihydrophenanthridine and phenanthridine derivatives [3] (Scheme 1).



Scheme 1

In order to investigate the reaction mechanism, the reactivity of  $Ru(\text{TPP})CO$  (TPP = dianion of tetraphenyl porphyrin) towards aryl azides was studied. We have recently isolated and fully characterised the ruthenium (VI) bis-imido complex  $Ru^{VI}(\text{TPP})(NAr)_2$  (Ar = 3,5-( $CF_3$ ) $_2C_6H_3$ ) [4], which showed a good catalytic activity in the amination reactions reported in scheme 1. The molecular structure of the bis-imido intermediate was determined by X-ray analysis (figure 1).

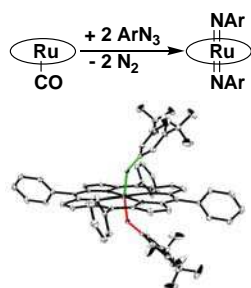
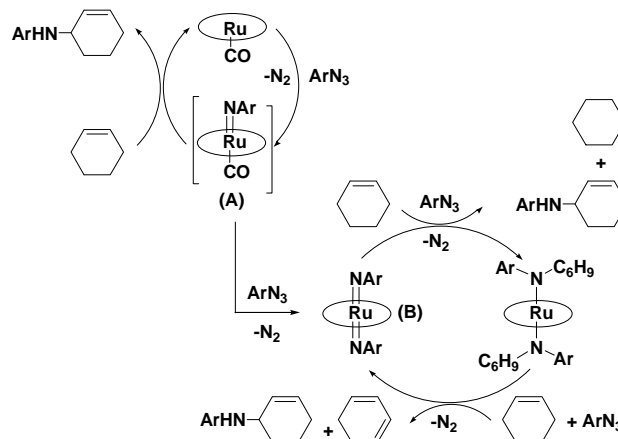


Figure 1

To rationalise the role of the azido molecule and the influence of different substituents on it, kinetic studies were performed relative to the allylic-type amination of cyclohexene [5].

It was found that mono and bis-imido species of formulae  $Ru^{IV}(\text{TPP})(NAr)CO$  (**A**) and  $Ru^{VI}(\text{TPP})(NAr)_2$  (**B**) are generated upon loss of  $N_2$  from the azide. The data confirm the importance of the azide substituent, but also of the olefin concentration as a key governing parameter.



Scheme 2

A differentiating role must also be played by the presence/absence of the CO ligand, since it affects the energies of the ruthenium  $d_{\pi}$  orbitals, which transfer their electrons and form imido ligands. Since all the efforts to trap and characterise by X-ray the mono-imido complex **A** failed, a computational study was carried out to outline possible profiles for the double azide activation leading to the products **A** and **B**.

Transition states were detected and the energies involved in the mechanism will be presented together with the necessary structural rearrangements. Results relative to the amination of allylic substrates indicated that a five-coordinated species “ $Ru(\text{TPP})NAr$ ” is formed during the organic transformation and that it represents the *catalytic key point* of the reaction. The intermediate “ $Ru(\text{TPP})NAr$ ” is almost equally stable in the singlet and triplet states. The diradical character of the triplet state is responsible for the homolytic activation of a C-H bond with the stepwise formation of the allylic amine. Conversely, “ $Ru(\text{TPP})NAr$ ” in its singlet state is involved in the synthesis of bis-imido derivative (**B**).

In summary, experimental data indicated the involvement of several ruthenium intermediates in the C-H allylic amination and we strongly believe that the reaction mechanism comprehension can contribute to planning new and more efficient synthetic procedure in the future.

### References:

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