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## Homogeneous N-H activation of ammonia by iridium and rhodium organometallic complexes

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N-H activation of ammonia by late transition metals is a hot topic. There is an outgrowing interest in the use of cheap ammonia as a substrate to obtain more complex nitrogen-containing molecules of higher value through homogeneous processes. However, this parent molecule is known for its reluctance to undergo homogeneous catalytic functionalization, although recent advances in ligand design have allowed the productive utilization of ammonia in important organic transformations such as allylic amination of  $\text{NH}_3$ , hydroaminomethylation of olefins, reductive amination of unsaturated substrates or alcohol amination with ammonia. Sometimes the key step for triggering the participation of ammonia in homogenous catalysis is intimately related to the N-H bond activation by a transition metal complex. In this scenario two possible mechanisms are possible: the homolytic and the heterolytic splitting. Within this context our research group has been involved in the design and the study of the reactivity of iridium and rhodium complexes with ammonia. The results of this research line has shown that the architecture of the organometallic precursors often determines the mechanism for N-H ammonia activation, which in turn has a strong effect in the electronic nature of the resulting amido complexes. In this line we show interesting examples of methoxy-bridged  $\text{M}(\text{d}^8)$  complexes that activate ammonia by following a heterolytic mechanism that leads to rare amido-bridged di- and trinuclear Ir and Rh complexes. The iridium derivatives are active in the catalytic hydrogen transfer from isopropyl alcohol to ketones. DFT studies indicated that the presence of the amido bridges plays a significant role in the mechanism operative. On the other hand, we found out that the election use of known phosphane complexes containing the diene tetrafluorobenzobarrelene (tfbb) react with ammonia with the formation of a new C-NH<sub>2</sub> bond between NH<sub>3</sub> and the coordinated diene through a direct nucleophilic attack, as confirmed by DFT methods. We also show how subtle changes in the composition of the starting complexes determine the mechanism of N-H activation of ammonia.



## Biography

Miguel A Casado has his expertise in the field of Organometallic Chemistry and currently he has a full time position at the ISQCH in the University of Zaragoza. His current interest is related to the activation of ammonia by iridium and rhodium  $\text{d}^8$  complexes (Project CTQ2015-67366-P). He obtained his PhD from the University of Zaragoza and after two years of Post-doctoral work at the University of Victoria (Canada) and a year at the University of Utrecht (The Netherlands), he came back to Spain, where he is developing his research and teaching in the Department of Inorganic Chemistry at the University of Zaragoza.

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