

N₂ Activation

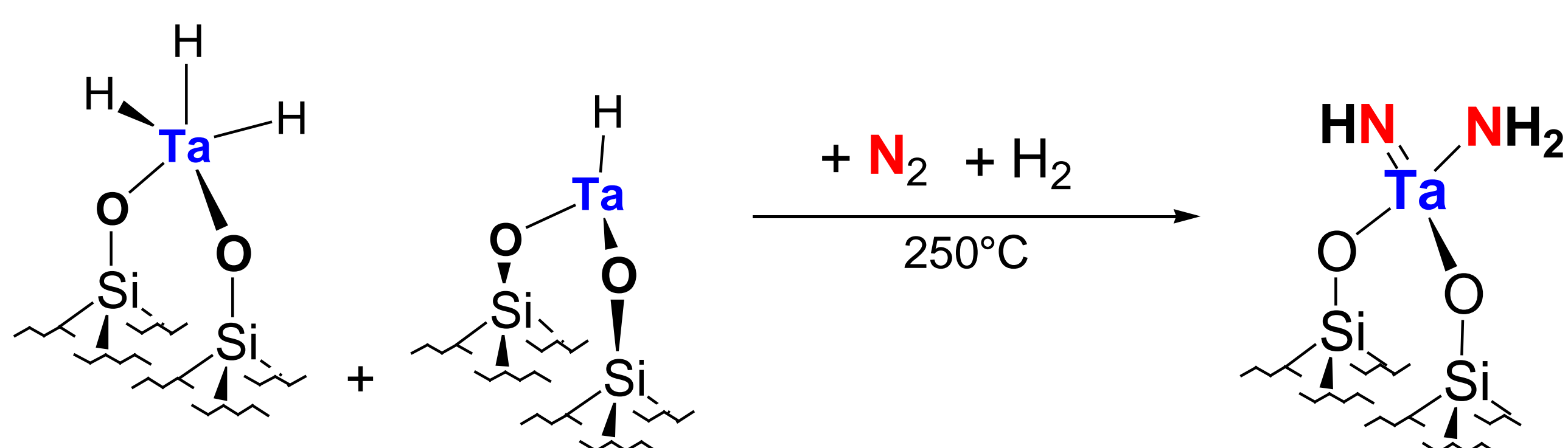
From Dinitrogen Splitting to N-containing Chemicals by Surface Organometallic Chemistry

JCJC 2008

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Starting point: N₂ splitting on an isolated Ta atom

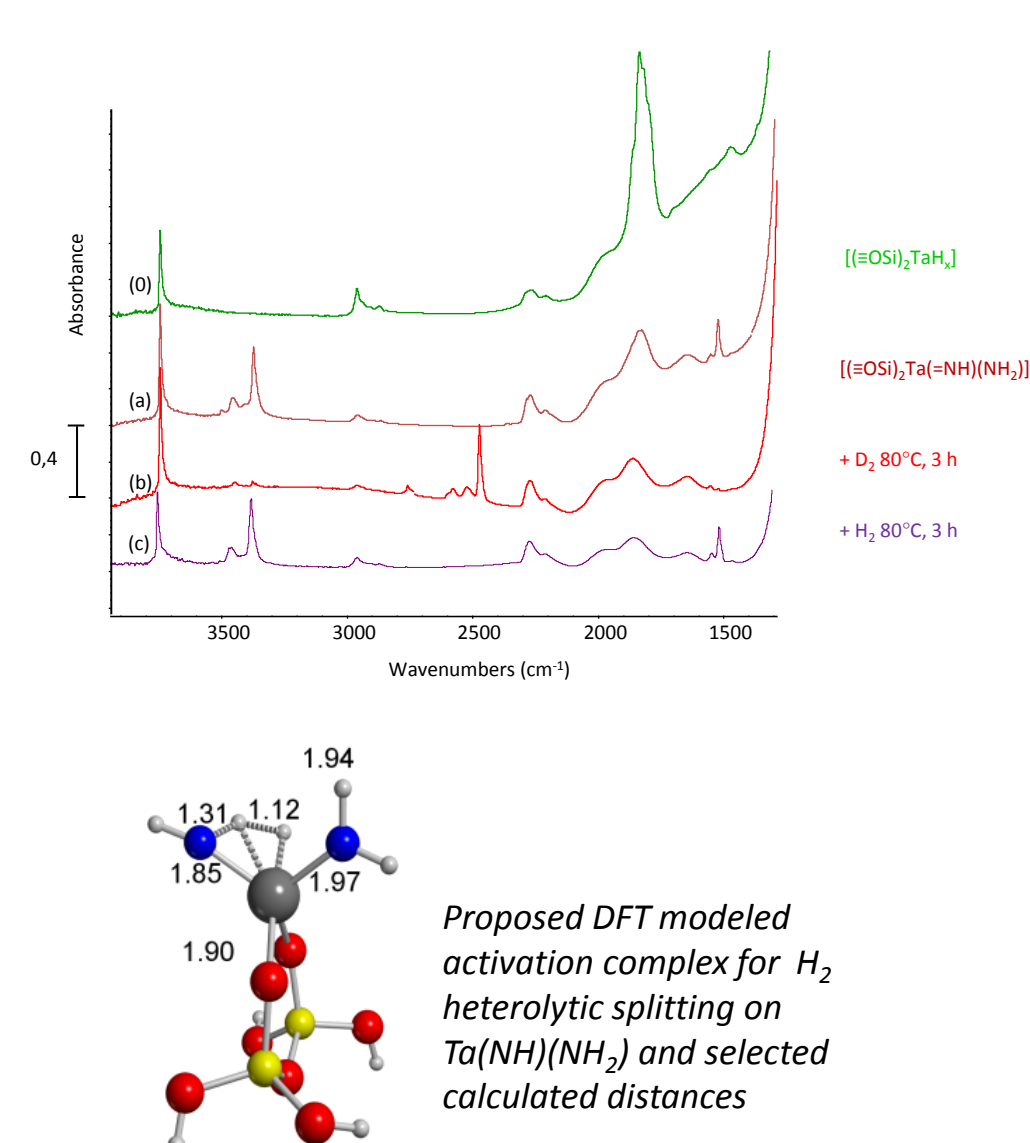
Silica-supported tantalum hydrides, [(≡SiO)₂TaH] and [(≡SiO)₂TaH₃], are able to activate N₂ in a way that has no precedent in either surface, bio- or solution chemistry, since the reaction, which leads to [(≡SiO)₂Ta(NH)(NH₂)], implies H₂ as reductant and an isolated metal atom, while literature precedents are multimetallic or imply sophisticated proton and electron sources: ¹



[1] « Dinitrogen Dissociation on an Isolated Surface Tantalum Atom. » P. Avenier, M. Taoufik,* A. Lesage, X. Solans-Monfort, A. Baudouin, A. de Mallmann, L. Veyre, J.-M. Basset,* O. Eisenstein, L. Emsley, E. A. Quadrelli,* **SCIENCE** 2007, 317, 1056-1060

Achievement 2: H₂ heterolytic splitting across Ta-amido bonds

Heterolytic splitting, a crucial elementary step in several catalytic mechanisms such as Noyori-type asymmetric hydrogen transfer, has been clearly observed and modeled for one of the first on a surface on our Ta-N bonds (see IR evidence on the side).³



[3] « H/D exchange on silica-grafted tantalum(V) imido amido [(≡SiO)₂Ta^V(NH)(NH₂)] synthesized from either ammonia or dinitrogen: IR and DFT evidence for heterolytic splitting of D₂. » P. Avenier, X. Solans-Monfort, L. Veyre, F. Renili, J.-M. Basset, O. Eisenstein,* M. Taoufik, E. A. Quadrelli.* **TOP. CATAL** (Special Issue: Nitrides, Oxynitrides and Nitrogen containing Materials), **52**:1482–1491 (2009).

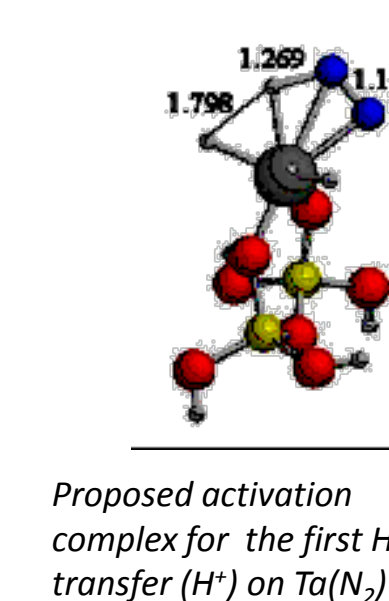
Outlook: Combined N₂ (or NH₃) and alkane activation will be tested to explore direct amine synthesis.⁵

[5] « Ammonia and Dinitrogen Activation by Surface Organometallic Chemistry » C. Chow, M. Taoufik, and E. A. Quadrelli,* **EUR. J. INORG. CHEM.**, (9), 1349–1359 (2011).

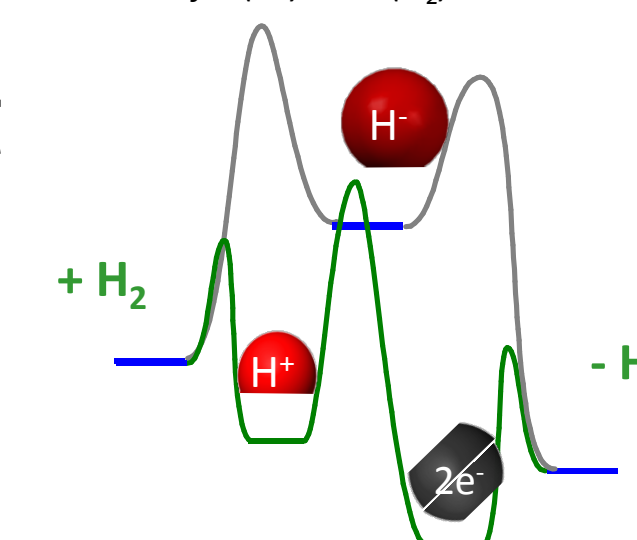
Achievement 1: Unique mechanism unraveled

Thanks to novel experimental evidence and to DFT study performed by O. Eisenstein (Institut Gerhardt de Chimie Moléculaire et des Matériaux de Montpellier) and X. Solans-Monfort (U. Autònoma de Barcelona), a pathway is proposed² with two major mechanistic originalities:

- Ta(H₂) adducts play a crucial role: they allow the low-energy transfer of a proton to the nitrogen-based ligands by heterolytic splitting of H₂ across Ta-N₂H_x.

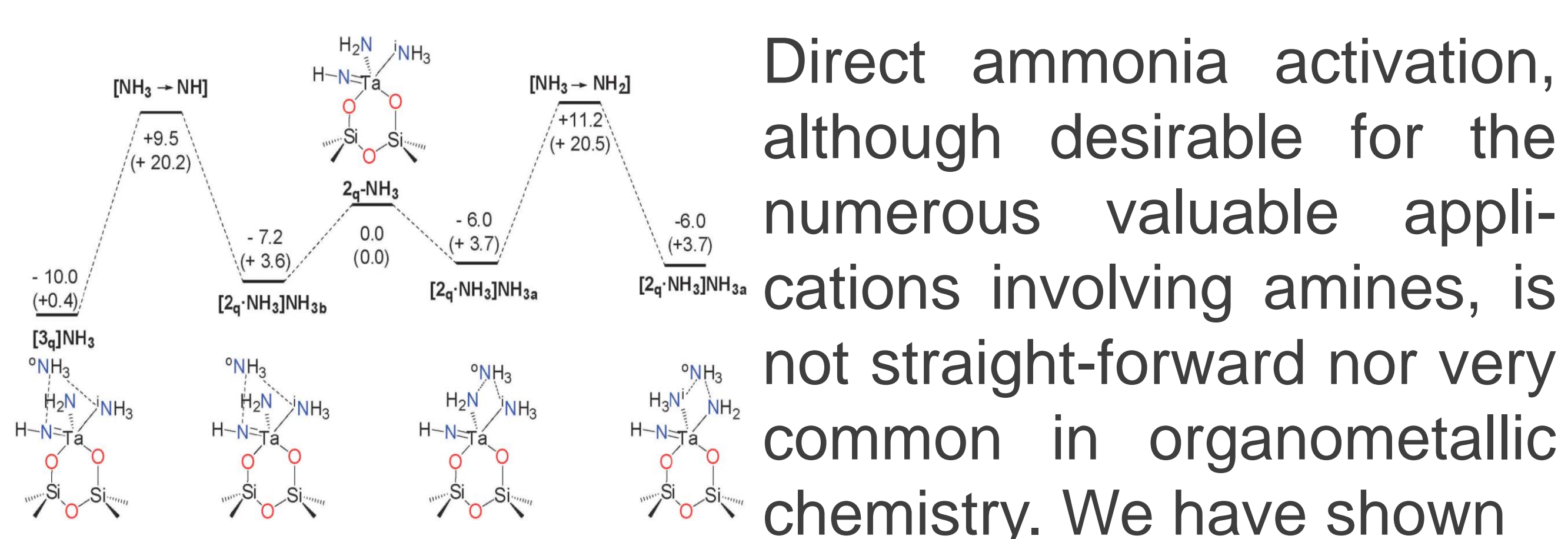


- Supra-stoichiometric H₂ assists the last hydride transfer by lowering its activation barrier without itself being consumed during the process.



[2] « Successive heterolytic cleavages of H₂ achieve N₂ splitting on silica-supported tantalum hydrides. A DFT proposed mechanism. » X. Solans-Monfort,* C. Chow, E. Gouré, Y. Kaya, M. Taoufik, J.-M. Basset,* E. A. Quadrelli* and O. Eisenstein* **INORG CHEM.**, 51(13), 7237-7249 (2012)

Achievement 3: NH₃ Activation



Direct ammonia activation, although desirable for the numerous valuable applications involving amines, is not straight-forward nor very common in organometallic chemistry. We have shown that [(≡SiO)₂Ta(NH)(NH₂)] activates NH₃, and that mechanistically such activation is favoured by 6-member intermediates formed with excess NH₃.⁴

[4] « Heterolytic cleavage of ammonia N-H bond by bifunctional activation in silica-grafted Ta(V) imido amido surface complex. Importance of the outer sphere NH₃ assistance » E. Gouré, P. Avenier, X. Solans-Monfort, L. Veyre, A. Baudouin, Y. Kaya, M. Taoufik, J.-M. Basset, O. Eisenstein,* and E. A. Quadrelli.* **NEW J CHEM.** **35**, 1011-1019 (2011) ****hot paper****

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