Method found for pulling hydrogen from ammonia for use as clean fuel

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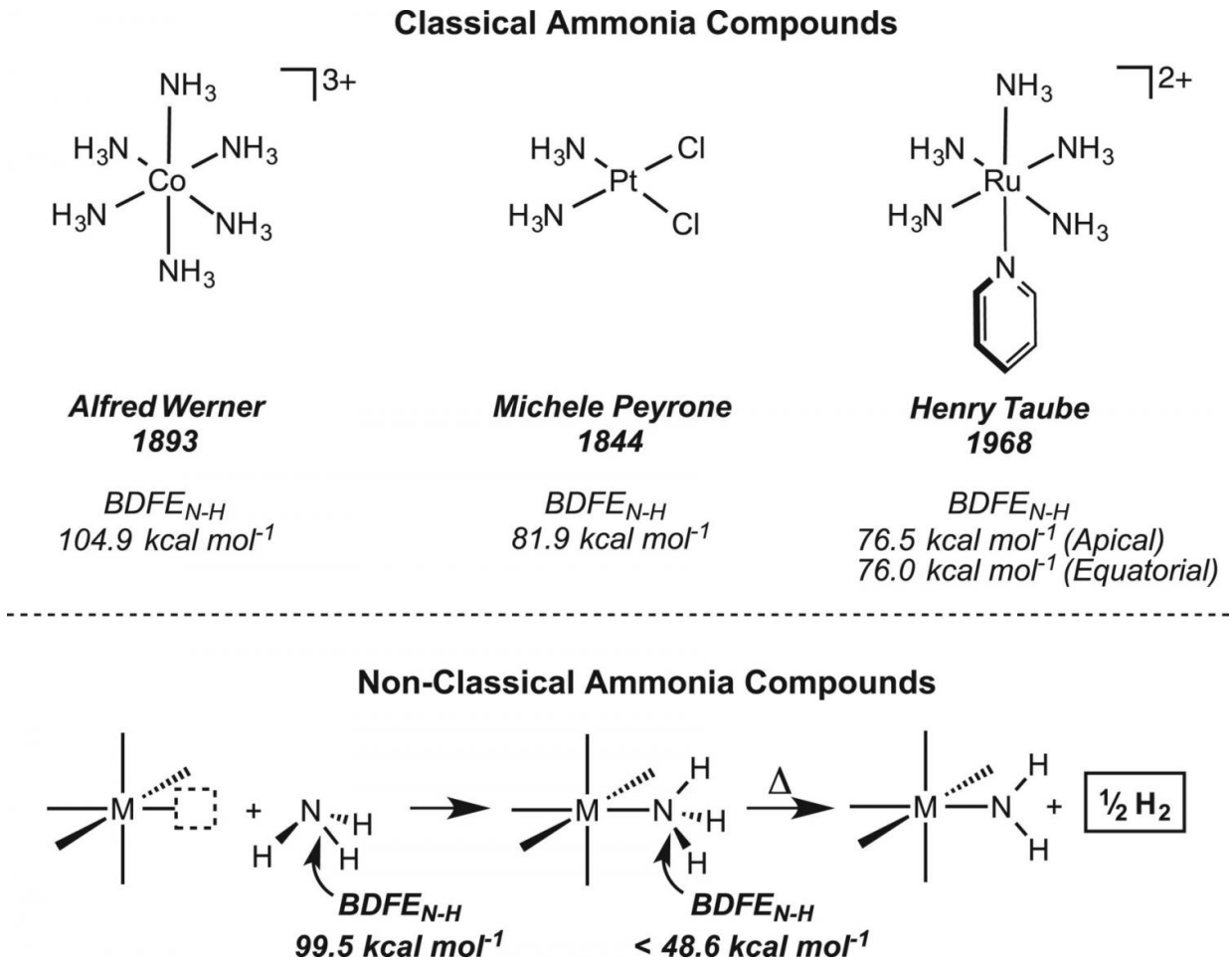

Comparison of classical coordination compounds of ammonia and nonclassical compounds that enable bond weakening by coordination, which in turn enables hydrogen evolution. Credit: (c) *Science* 11 Nov 2016: Vol. 354, Issue 6313, pp. 730-733, DOI: 10.1126/science.aag0246

(Phys.org)—A trio of researchers with Princeton University has found a way to weaken the strong bonds between the nitrogen and hydrogen atoms in ammonia molecules while simultaneously releasing a single hydrogen atom to create hydrogen gas. In their paper published in the journal *Science*, Máté Bezdek, Sheng Guo and Paul Chirik describe the process and the likelihood of using it as a new hydrogen source. Jessica Hoover with West Virginia University offers a Perspective piece on the work done by the team in the same journal issue and also outlines the impact the findings are likely to have on hydrogen energy storage and utilization.

Ammonia has long been used on a large scale to produce both fertilizers and feedstock, and on a smaller scale as a household cleaner, but scientists would also like to use it as a type of fuel, because doing so would offer a new way to create hydrogen gas for use as a clean energy source. But to date, efforts to do so have been stymied by the strong bond that exists between the nitrogen and hydrogen atoms in ammonia molecules. In this new effort, the researchers report that they have found an efficient means for doing so that not only weakens the bond, but also causes the release of one of the hydrogen atoms making it available to bond with another to create hydrogen gas.

The new process involves using an ammonia-bound terpyridine bis(phosphine) molybdenum(I) cation, because as Hoover notes, it is both electron rich and positively charged. In so doing, the nitrogen–hydrogen bond is cleaved homolytically, resulting in a lone hydrogen atom and an M–N bond. The newly freed hydrogen atom is then able to bond with another to form hydrogen gas, which can then be collected, stored and eventually burned to provide energy for a variety of engines.

The work by the team, Hoover also notes, is likely to have an impact both on energy systems (the process is much more efficient than other

methods such as deprotonation or oxidative addition) and on other work that involves synthesizing ammonia, perhaps leading to even more efficient processes.

More information: Coordination-induced weakening of ammonia, water, and hydrazine X–H bonds in a molybdenum complex, *Science* 11 Nov 2016: Vol. 354, Issue 6313, pp. 730-733, DOI: 10.1126/science.aag0246 , science.sciencemag.org/content/354/6313/730

Abstract

Although scores of transition metal complexes incorporating ammonia or water ligands have been characterized over the past century, little is known about how coordination influences the strength of the nitrogen-hydrogen and oxygen-hydrogen bonds. Here we report the synthesis of a molybdenum ammonia complex supported by terpyridine and phosphine ligands that lowers the nitrogen-hydrogen bond dissociation free energy from 99.5 (gas phase) to an experimentally measured value of 45.8 kilocalories per mole (agreeing closely with a value of 45.1 kilocalories per mole calculated by density functional theory). This bond weakening enables spontaneous dihydrogen evolution upon gentle heating, as well as the hydrogenation of styrene. Analogous molybdenum complexes promote dihydrogen evolution from coordinated water and hydrazine. Electrochemical and theoretical studies elucidate the contributions of metal redox potential and ammonia acidity to this effect.