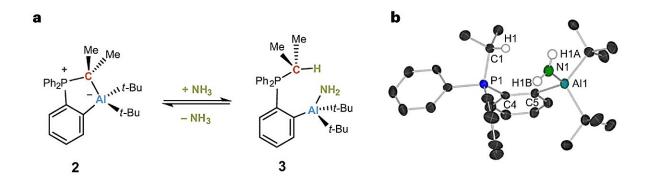


New ammonia reaction could offer a sustainable source of nitrogen

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a, The reversible reaction of the aluminium–carbon-based ambiphile 2 with NH₃ in benzene at RT. b, The molecular structure of 3 in the solid state (ellipsoids drawn at the 30% probability level). The hydrogen atoms (except the NH₂ and ylidic protons) are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 = 1.8237(12), N1–A11 = 1.8494(12), C5–A11 = 2.0766(12); C5–N1–A11 = 110.97(5). Credit: *Nature Chemistry* (2023). DOI: 10.1038/s41557-023-01340-9

A big goal in chemistry is to find a simple way to produce amines from ammonia and unsaturated hydrocarbons. Catalytic addition to activate and transfer ammonia would not give rise to any waste. Hence, the process would be sustainable.

Researchers from Karlsruhe Institute of Technology (KIT) have now come closer to reaching this goal. They have developed a system for



activation and catalytic transfer of <u>ammonia</u>, which is not based on <u>transition metals</u>, but on a compound of main group elements. <u>The</u> <u>results</u> are reported in *Nature Chemistry*.

The ammonia molecule (NH_3) , a compound of nitrogen and hydrogen, is one of the most frequently produced chemicals worldwide and it is also used for the production of many other nitrogen-containing compounds.

If amines could be produced by the simple addition of ammonia to unsaturated hydrocarbons, this would be a major breakthrough in chemistry, because amines, the organic derivatives of ammonia, are in high demand as <u>building blocks</u> of agricultural and pharmaceutical chemicals as well as of detergent substances, dyes, lubricants, and coatings. Moreover, amines are used as catalysts in the production of polyurethanes. And <u>amines</u> are applied in gas scrubbers at refineries and power plants.

By breaking the strong bond between nitrogen and hydrogen, i.e., activation, the ammonia molecule may be transferred at least theoretically to other molecules, such as unsaturated hydrocarbons. Transfer of ammonia to ethylene, an important substance in <u>chemical</u> industry, for instance, would give rise to ethylamine. This addition is referred to as hydroamination by chemists. However, ammonia and ethylene do not react with each other easily. A catalyst is required for the reaction to take place.

Conventional catalysts based on transition metals, however, react with ammonia and become inactive. "Hydroamination of non-activated alkenes with ammonia, hence, is considered a big challenge or the holy grail of catalysis," says Professor Frank Breher, head of a research group at the Division of Molecular Chemistry of KIT's Institute for Inorganic Chemistry (AOC).



Activation and catalytic transfer of ammonia

In cooperation with researchers from Paderborn University and Complutense University of Madrid, Professor Frank Breher and Dr. Felix Krämer from AOC have now come much closer to reaching this challenging goal. "We have developed a system for the activation of ammonia, which is not based on transition metals, but on main group elements. The 'atom-economic' process of activation and subsequent transfer of ammonia do not give rise to any waste, which is of particular interest in terms of sustainability," Breher says.

The team produced a so-called frustrated Lewis pair (FLP) that consists of an acid as electron pair acceptor and a base as electron pair donor. Usually, both react with each other and produce an adduct. If adduct formation is prevented or at least limited, a frustrated situation results and the molecule readily reacts with small molecules, such as ammonia.

"It is crucial to dampen reactivity such that the reaction with <u>small</u> <u>molecules</u> is reversible. Only then will it be possible to use such an FLP in catalysis. We were the first to achieve this with ammonia as a substrate," Breher reports.

The FLP was found to easily react with non-aqueous ammonia in a thermoneutral way and to reversibly split the nitrogen-hydrogen bond of ammonia at room temperature. For the first time, the researchers present NH_3 transfer reactions catalyzed by a catalyst based on main group elements.

"So far, we have converted activated substrates only and no unsaturated hydrocarbons. But we have come much closer to the reaction of our dreams," Breher says. "We expect that our first proof of principle will initiate further work on the use of N-H-activated ammonia as an easily available and sustainable source of nitrogen."



More information: Felix Krämer et al, A crystalline aluminium–carbon-based ambiphile capable of activation and catalytic transfer of ammonia in non-aqueous media, *Nature Chemistry* (2023). DOI: 10.1038/s41557-023-01340-9

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