Converting Nitrogen to a More Useful Form

Nitrogen-containing organic compounds are important products as well as intermediates for many pharmaceuticals, agrochemicals, and chemicals used in electronics. Air contains plenty of nitrogen, but it is in a form that cannot be used for chemical syntheses: nitrogen gas, a molecule made of two nitrogen atoms, is highly inert.

The main source of nitrogen today involves a detour by way of synthetic ammonia, a process requiring a lot of energy and explosive hydrogen gas under harsh conditions. In order to find synthetic pathways that do not rely on ammonia, scientists are searching for ways to fix atmospheric nitrogen in the form of higher-value organic compounds.

Chemists working with Paul J. Chirik at Cornell University (Ithaca, New York) have now found an interesting new method, which they describe in the journal *Angewandte Chemie*: they have bound nitrogen to carbon dioxide while maintaining the nitrogen–nitrogen bond, forming a hydrazine derivative. The metal hafnium promotes this reaction.

The two nitrogen atoms in a nitrogen molecule are so happy with each other that they have little incentive to enter into chemical bonds with other atoms. Direct formation of a bond between carbon and nitrogen, a requirement for the formation of organonitrogen compounds without resorting to ammonia, is a serious challenge for scientists. The nitrogen has to be “outsmarted”.

While it does not easily enter into chemical bonds with organic substances, molecular nitrogen does have a tendency to form coordination complexes by binding to a metal. When the nitrogen acts as ligand in these complexes, it receives electrons from the metal atom disrupting the strong nitrogen-to-nitrogen triple bond. Chemists often refer to this process as “activating” the nitrogen ligand, as new chemistry is now possible.

Chirik and his co-workers found out that the nitrogen gets activated just right in a hafnocene complex (whose hafnium atoms each have two aromatic five-membered carbon rings as additional ligands), in which the nitrogen molecule is grabbed side-on by two hafnium atoms. Carbon dioxide can then react with the activated nitrogen molecule.

Two carbon dioxide molecules push their way in between the nitrogen and the hafnium. One of the two nitrogen atoms thus forms two strong new bonds to two carbon atoms from the carbon dioxide. One of the nitrogen–nitrogen bonds remains intact. By using an organosilicon compound, the cores of the hafnocene complexes can be released—in the form of a silicon-containing organic hydrazine derivative.

Citation: Paul J. Chirik, Nitrogen–Carbon Bond Formation from N2 and CO2 Promoted by a Hafnocene Dinitrogen Complex Gives Access to a Substituted Hydrazine, *Angewandte Chemie International Edition*, doi: 10.1002/anie.200604099

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