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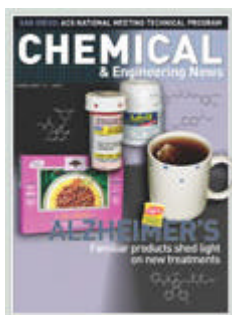
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## Latest News

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## Ammonia Is Ready For A Transfer

### Iridium insertion into N-H bond opens door to catalytic amination reactions

[STEVE RITTER](#)

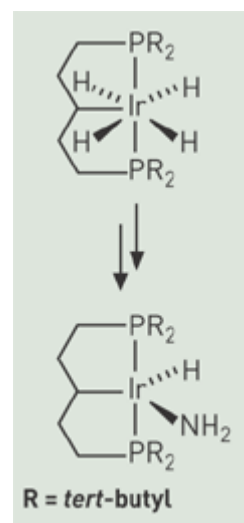
The design and synthesis of an iridium complex that undergoes oxidative addition of ammonia to form an amido hydride derivative appears to have solved one of chemistry's long-standing research challenges: how to activate N-H bonds under mild conditions. This fundamental breakthrough could lead to industrially important catalytic ammonia-transfer processes.

Chemists have known for a century that ammonia forms simple  $M-NH_3$  coordination complexes with most transition metals. Transition-metal complexes also are known to insert into generally unreactive X-H bonds of hydrogen, silanes, boranes, and alkanes (where X = H, Si, B, or C). But no one, until now, had designed a metal-ligand system that is thermodynamically favored to insert into an N-H bond of ammonia.

Graduate student Jing Zhao and chemistry professor [John F. Hartwig](#) at Yale University along with chemistry professor [Alan S. Goldman](#) at Rutgers University, Piscataway, N.J., have accomplished the feat with an iridium complex that contains a tridentate pincer-type ligand [*Science*, **307**, 1080 (2005)]. The key to their success was increasing the electron density on the already electron-rich iridium atom.

Their starting point was a known complex having an aromatic tridentate ligand that can insert into C-H bonds and aniline N-H bonds but reacts with ammonia to give the classical coordination complex. By replacing the aromatic tridentate ligand with an aliphatic version, they boosted electron density on the metal enough to enable it to insert into an N-H bond of ammonia.

The researchers treated the new complex with olefins to form intermediates that dissociate when ammonia is added at room temperature, quickly forming the amido hydride complex. The next step will be to develop procedures to transfer the amido group to substrates. Possibilities include coupling the complex with alkyl or aryl groups to incorporate nitrogen into pharmaceuticals and olefin amination to make nitrogen-



**N-H ACTIVATE**  
Iridium complex quickly inserts into  $NH_3$  at room temperature.

ADAPTED FROM  
*SCIENCE*



Hartwig

YALE UNIVERSITY  
PHOTO

containing monomers, the researchers note.

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