

and low e_g B-sites. This quantitative result is supported by a number of studies and arguments at the molecular and electronic level, and suggests that tuning surface electronic features of nanoparticles can lead to highly active catalysts.

The findings of this research differ from earlier work^{4–6} in that it is quantitative and is based on an understanding of electronic structure, specifically the localized e_g electron in an orbital directed towards an O_2 molecule from the surface of the B cations, and explains the origins of the peak catalytic activities associated with high-spin and low-spin electrons. The understanding proposed here leads to generalizations that give a single parameter that identifies those compositions that have great promise for ORR activity. This could allow researchers to take advantage of the large number of possible electrocatalytic systems, including B substitution and partial substitutions. Compositions and structures could then be optimized, perhaps even under the important property constraints necessary for applications, such as ease of synthesis,

cost and durability during operation. It now becomes possible to narrow the focus of the search for new perovskite electrocatalysts.

An experimental aspect of this work that is noteworthy is the methodology for examining electrocatalytic activity. Shao-Horn and colleagues used a thin-film rotating-disc electrode to examine nano-sized electrocatalytic particles. These measurements are on particles of the size expected in operating electrochemical devices that have to optimize oxygen, ion and electron transport and the accessibility of the catalyst surface. Consequently, the experimental measurements are also meaningful for anticipated applications.

As well as having a direct impact on fuel cell development and commercialization, the fundamental nature of this work will have value beyond fuel cells and batteries. For example, the approach could be effective for identifying electrocatalysts for the oxygen evolution reaction, used for high-performance hydrogen-producing water electrolyser, thus storing renewable energy for more efficient use. Another

applicable technology benefiting from this approach is the search for electrocatalysts for reversible alkaline fuel cells, which show promise for energy storage, especially for the large scale, where decoupling power from energy capacity has advantages. Also, tying the understanding of this research into enzymatic catalysis could open a new paradigm in understanding enzyme structure–property relationships, and thus lead to new and exciting technologies for fuels and chemical synthesis. □

Robert Savinell is in the Department of Chemical Engineering at Case Western Reserve University, Cleveland, Ohio, USA.
e-mail: rfs2@case.edu

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NITROGEN FIXATION

Nitrido complexes step up

The discoveries of ruthenium- and iron-nitrido complexes that can be transformed to release ammonia could be important steps towards realizing the catalytic reduction of nitrogen under mild reaction conditions.

Yoshiaki Nishibayashi

The development of nitrogen fixation under mild reaction conditions is one of the most important subjects for chemists. Industrially, ammonia is produced from molecular dinitrogen and dihydrogen by the use of iron-based heterogeneous catalysts. In this reaction system, extreme reaction conditions — high reaction temperatures and high pressures — are required to activate molecular dinitrogen. In sharp contrast to this energy-consuming Haber–Bosch process, biological nitrogen fixation by the nitrogenase enzyme occurs at ambient temperature and pressure. Although a recent X-ray structural model has revealed the active site of nitrogenase¹, where dinitrogen is converted into ammonia, the precise reaction mechanism still remains unclear. It is generally believed that molecular dinitrogen is coordinated and activated at multimetallic sites and converted into ammonia by a sequential process of protonation and reduction.

In both systems (the Haber–Bosch and nitrogenase processes), nitrido intermediates work as key reactive species to form ammonia from molecular dinitrogen. Now, two independent research groups, aiming for the development of efficient industrial catalysts for nitrogen fixation, have reported unusual reactivities of ruthenium- and iron-nitrido complexes.

Writing in *Nature Chemistry*, Holthausen, Schneider and co-workers describe a unique reactivity of a ruthenium-nitrido complex bearing a PNP-type pincer ligand², which is prepared from the reaction of the corresponding ruthenium-chlorido complex with an azide reagent (Fig. 1a). Hydrogenation of the nitrido complex under an atmospheric pressure of molecular dihydrogen at 50 °C for 48 h gives the corresponding ruthenium-hydrido complex together with the formation of ammonia in 80% yield (Fig. 1a). The direct conversion of the nitrido ligand into ammonia is confirmed by the reduction of

the ¹⁵N-labelled nitrido complex. This is the first successful example of hydrogenation of a ruthenium-nitrido complex to form ammonia. This complete hydrogenation of the nitrido complex is in sharp contrast to the previous result by Burger and co-workers, who reported hydrogenation of an iridium-nitrido complex bearing a NNN-type pincer ligand to give the corresponding amido complex, but did not observe formation of ammonia³. The high nucleophilicity of the nitrido moiety is considered to be due to the ruthenium PNP-pincer platform. Furthermore, the final ruthenium-hydrido complex can be converted back into the starting ruthenium-chlorido complex via three steps — dehydrogenation, protonation and deprotonation. As a result, ammonia is pseudo-catalytically produced from azide and molecular dihydrogen in the presence of the ruthenium complex.

No information on the reactive intermediates is obtained, but a density

functional theory calculation on the hydrogenation of the nitrido complex indicates that heterolytic cleavage of molecular dihydrogen may occur first to form the corresponding N–H and Ru–H bonds in the amido ligand. Sequential activation of two molecules of dihydrogen by Ru–N multiple bonds in the complex may proceed to give the corresponding ammonia complex, which then liberates free ammonia. The proposed reaction pathway is considered to be reasonable, although a substantially higher energy is necessary to promote the first hydrogenation step.

Experimental and theoretical studies on the Haber–Bosch process indicate that the initial splitting of molecular dinitrogen produces the corresponding iron-bound surface nitrido species, and then stepwise hydrogenation of them takes place to form ammonia. As pointed out by Holthausen, Schneider and colleagues, the reduction of a transition-metal–nitrido complex with molecular dihydrogen is considered to be one of the key steps of a model reaction of the Haber–Bosch process to achieve the catalytic reduction of molecular dinitrogen with dihydrogen by using transition-metal–dinitrogen complexes.

Independently, writing in *Science*, Meyer, Smith and co-workers describe the preparation, characterization and reactivity of four-coordinate iron(IV)– and iron(V)–nitrido complexes bearing a tripodal *N*-heterocyclic carbene ligand⁴ (Fig. 1b). The iron(V)–nitrido complex is produced by oxidation of the iron(IV)–nitrido complex, which is itself prepared from the reaction of the corresponding iron(II)–chlorido complex with an azide reagent, with ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate at –78 °C. Although no resonance is observed in the ¹H NMR spectrum of the iron(V)–nitrido complex, its ultraviolet spectrum is distinct from that of the iron(IV)–nitrido complex. The iron(V)–nitrido complex was manipulated at low temperature because the half-life of the iron(V)–nitrido complex is only around 4 h at 25 °C. The X-ray analysis indicates that the iron(V)–nitrido complex has a pseudo-tetrahedral iron centre supported by the tris(imidazol-2-ylidene)borato ligand, containing a significantly shorter Fe–N bond. Iron complexes bearing metal–ligand multiple bonds, such as the iron(V)–nitrido complex, are proposed as key reactive intermediates in the biological synthesis of ammonia (the nitrogenase process). However, no example of the isolation of a thermally stable iron(V)–nitrido complex has so far been reported. This is the first

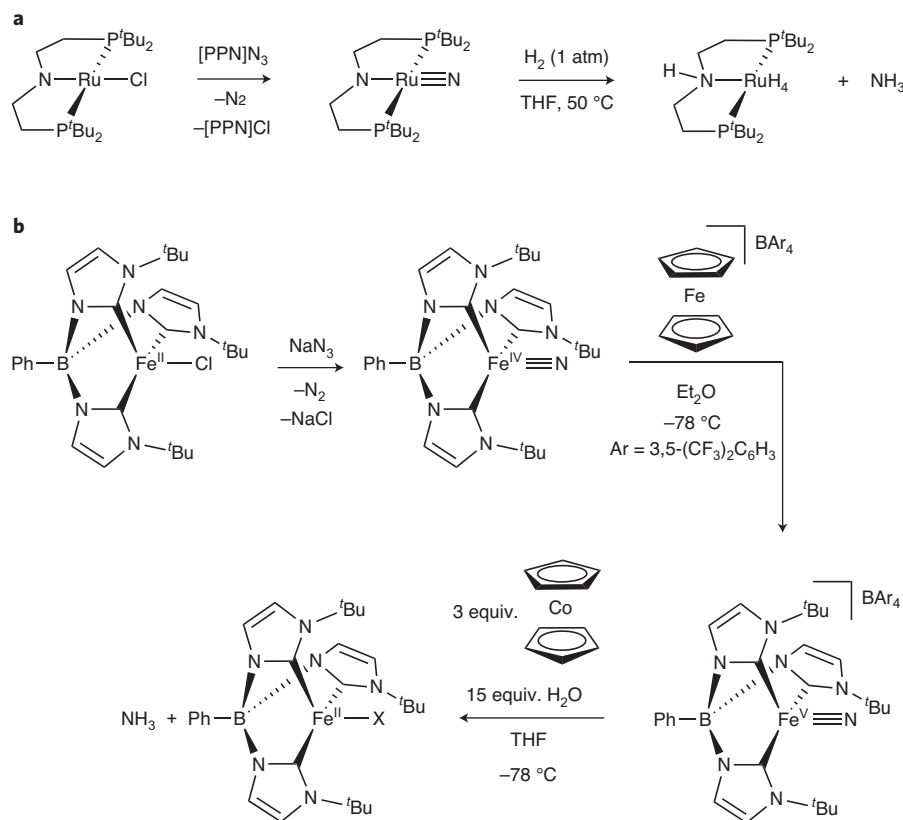


Figure 1 | Unique reactivity of ruthenium- and iron-nitrido complexes. **a**, Hydrogenation of a ruthenium-nitrido complex gives the corresponding ruthenium-hydrido complex with the formation of ammonia. **b**, Reaction of an iron(V)–nitrido complex with cobaltocene as a reducing reagent and water as a proton source gives an uncharacterized iron(II) complex with the formation of ammonia.

successful example of the iron(V)–nitrido complex confirmed by X-ray analysis.

Contrary to the reactivity of the iron(IV)–nitrido complex towards water, where no formation of ammonia is observed at all, the reaction of the iron(V)–nitrido complex with three equivalents of cobaltocene as a reducing reagent and 15 equivalents of water as a proton source at –78 °C in tetrahydrofuran affords ammonia in 89% yield, together with the formation of the iron(II) complex (Fig. 1b). Lower yields of ammonia are obtained when less than three equivalents of cobaltocene are used for the reduction. Generally, nitrido ligands bonded to iron complexes are extremely unreactive, and harsh reaction conditions, such as strong acids, are required for their chemical transformation. This is the first successful example of the formation of ammonia from reduction of nitrido complexes under mild reaction conditions.

Unfortunately, the reaction mechanisms for the formation of ammonia from the iron(V)–nitrido complex has not yet been clarified. The sequential protonation and reduction of the nitrido complex, however, may occur to afford the corresponding

ammonia complex, which liberates free ammonia. In fact, a molybdenum–nitrido complex was isolated as a reactive intermediate in the catalytic transformation of molecular dinitrogen into ammonia by using molybdenum–dinitrogen complexes as a catalyst^{5,6}. In these molybdenum systems, water was not used as a proton source to produce ammonia. As pointed out by Meyer, Smith and colleagues, reduction of the high oxidation state iron(V)–nitrido complex, with water as a proton source and cobaltocene as a reducing agent, is considered to be one of the key steps of a model reaction of the nitrogenase process to achieve the catalytic formation of ammonia from molecular dinitrogen^{5,6}.

To develop a new nitrogen-fixation system for the formation of ammonia from molecular dinitrogen, the present nitrido complexes would have to be prepared from the corresponding dinitrogen complexes. As it stands, both nitrido complexes are only derived from the corresponding chlorido complexes with azide reagents. But both research groups^{2,4} have revealed that it is highly likely that the nitrido species may be a key reactive intermediate

for the conversion of dinitrogen into ammonia, by demonstrating that ammonia is directly obtained from the nitrido species. The reactivity of the transition-metal–nitrido complexes described in their papers shows a real advance towards developing a ‘post-Haber–Bosch process’: a synthetic method for the catalytic formation of ammonia from molecular

dinitrogen under mild reaction conditions. These papers provide essential information for developing a catalytic nitrogen-fixation system by using iron catalysts⁷. □

Yoshiaki Nishibayashi is at the Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan. e-mail: ynishiba@sogo.t.u-tokyo.ac.jp

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ATMOSPHERIC PHOTOCHEMISTRY

Roaming in the dark

The mechanism of NO and O₂ production through the photolysis of the nitrate radical has long proved elusive. Now, theoretical studies help to explain previous experiments, suggesting that two distinct pathways are responsible that both involve ‘roaming dynamics’ on the ‘dark’ excited electronic state.

Simon W. North

It has been over a century since the nitrate radical, NO₃, was first observed by optical absorption¹. The strong absorption in the visible region corresponds to excitation to the second excited (‘bright’) state and is used for detection of NO₃ in both atmospheric field studies and in the laboratory. Following absorption, NO₃ rapidly photolyses via two product channels,



Channel 1 leads to the catalytic removal of ozone in the stratosphere (through its reaction with NO), whereas channel 2 is neutral with respect to ozone. Consequently, the quantitative wavelength-dependent branching between these two channels has been the subject of numerous studies. For years the photolysis mechanism was assumed to proceed via a radiationless transition to the electronic ground state followed by either the breaking of a single N–O bond to leave NO₂ (channel 2) or rearrangement to form a traditional three-centre transition state leading to NO and O₂ products (channel 1). Despite theoretical efforts to locate this transition state on the electronic ground state, no states have been identified at energies low enough to play a role in the production of molecular products.

Recent ion-imaging studies have added to the intrigue surrounding the NO + O₂ channel^{2,3}. The experiments show clear evidence that the molecular products are formed by two distinct pathways. The dominant pathway is characterized by highly

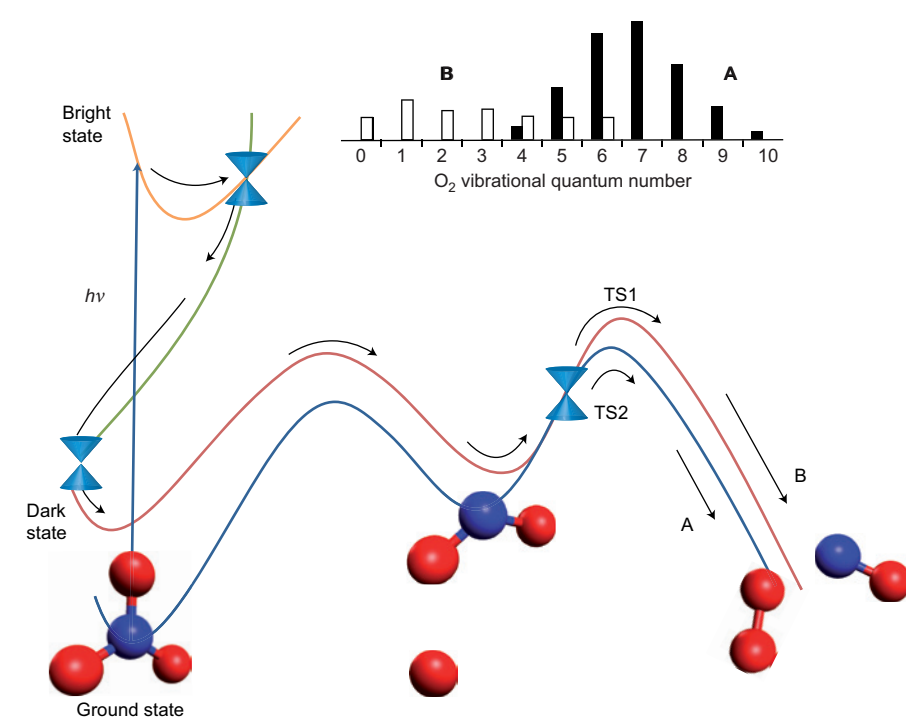


Figure 1 | Schematic energy diagram illustrating how NO and O₂ arise from the visible photolysis of NO₃. Following initial excitation to the bright state (orange), the system accesses the dark state (red), through a conical intersection represented by the connected funnels, where roaming dynamics ultimately leads to two distinct pathways (A and B) to products. The inset highlights the difference in the experimentally determined vibrational energy distribution for both pathways A and B (data from ref. 3); pathway A results in vibrationally hot molecular oxygen. The experimental results are supported by calculations of Maeda, Morokuma and Xiao⁸. Red spheres, oxygen atoms; blue spheres, nitrogen atoms. Figure reproduced with permission from ref. 8, © 2011 ACS.

vibrationally excited O₂ ($\nu = 5\text{--}10$) and rotationally cold NO (pathway A), whereas the second, minor, pathway is characterized by vibrationally cold O₂ ($\nu < 5$) and

rotationally warmer NO (pathway B). The similarity between the energy distribution within the products of these channels and the molecular products resulting from