Dinitrogen (N₂) which makes up about 78% of the earth’s atmosphere is virtually an inert molecule largely due to its strong N-N triple bond (225 kcal mol⁻¹) and non-polarity. Although it is cheap and abundant, effective use of dinitrogen for fine chemical synthesis is fraught with significant challenges, e.g. activation and cleavage of the N-N bond under relatively mild conditions and its subsequent functionalization for the assembly of N-C bond to realize several useful pharmaceuticals, agrochemicals and electronic materials. Ammonia synthesis from dinitrogen and dihydrogen by the Haber–Bosch process produced over 140 million tonnes annually, which sustains approximately 40% of world’s population, is highly energy intensive requiring high temperature and pressure. Dihydrogen used in this process largely comes from the rapidly depleting fossil fuel sources which further delineates the problem. Since there is widespread use of ammonia and ammonia derivatives as fertilizers, there is a strong incentive to develop synthetic methods that assemble nitrogen-element bonds directly from N₂ under mild conditions so as to reduce our dependence on fossil fuels.

The apparent shortcomings of the Haber–Bosch process and the landmark discovery of Allen and Senoff that N₂ could serve as a ligand to a transition metal in the case of [Ru(NH₃)₅(N₂)]⁺ spurred a lot of research activity towards the activation and functionalization of this so-called inert molecule. Shilov and others reported that certain aqueous transition metal mixtures comprising molybdenum precursors mixed with Mg(OH)₂ catalyse N₂ reduction to hydrazine and ammonia in the presence of reducing agents such as sodium amalgam. Chatt and co-workers found that a family of low-valent, phosphine-supported molybdenum and tungsten complexes could bring about a stoichiometric reduction of N₂ to NH₃. The successful isolation and identification of many partially reduced N₂H₃ complexes en route to N₂ reduction to NH₃ at Mo and W centres led to the formulation of the ‘Chatt cycle’ which occupies a central role in N₂ research. In this pathway, dinitrogen bound to the metal is functionalized by addition of strong electrophiles, typically proton donors such as mineral acids. Following these pioneering works, several others made significant contributions relevant to the activation and functionalization of nitrogen molecule.

Activation of the N-N bond of dinitrogen bound to a metal centre and its subsequent functionalization via reactions involving N-H bond or N-C bond formation has been achieved in several instances. Among various metal complexes, zirconocene and hafnocene dinitrogen complexes with the N₂ ligand bridging (μ₂) the two metal centres and bound in a side-on (η²) fashion have been found to exhibit functionalization activity. In all the cases, the N-N bond remained intact. A daunting challenge involving assembly of N-C bond coupled with the cleavage of the N-N bond followed by the elimination of the resulting functionalized compound could prove extremely valuable towards the synthesis of fine and commodity chemicals. In this context, the recent report by Chirik and co-workers assumes significance. Chirik and co-workers have successfully combined N₂ and CO₂ yet another molecule with a strong triple bond (C=O, 257 kcal mol⁻¹) under very mild conditions using a hafnium complex followed by the addition of an acid to obtain an important agrochemical, oxamide which is currently manufactured from fossil fuel sources. The strategy that they employed was to use a 5d metal, hafnium that could elongate the N-N to a very great extent. Reduction of [Hf(Me₂Si(η²-C₅Me₅)(η²-C₅H₅-3-Me)₂)] using excess Na/Hg under a N₂ atmosphere for a week gave an ansa-hafnocene N₂ complex {[Hf(Me₂Si(η²-C₅Me₅)(η²-C₅H₅-3-Me)₂)](μ₂, η², η²-N₂)} (Figure 1) wherein the N-N bond length of 1.457(5) Å is the longest of any group IV metalloocene dinitrogen complex reported to date. Such a great elongation allows for new functionalization chemistry.

Reaction of the dinitrogen complex {[Hh(Me₂Si(η²-C₅Me₅)(η²-C₅H₅-3-Me)₂)](μ₂, η², η²-N₂)} with 4 atm of CO resulted in the cleavage of the N-N bond accompanied by the formation of new N-C bonds and homologation of CO (Scheme 1). The resulting complex obtained in high yield bears an oxamidic ligand (N₂C₅O₂)⁺ which is related to the organic compound oxamide H₂NC(O)C(O)NH₃, a slow releasing fertilizer. The binding of CO to nitrogen rather than the metal as normally expected is rather unusual. The oxamidic complex was thoroughly characterized using multinuclear NMR spectroscopy, IR spectroscopy and X-ray crystallography. Pertinent structural features of this complex

Figure 1. Molecular structure of [(Hf(Me₂Si(η²-C₅Me₅)(η²-C₅H₅-3-Me)₂)](μ₂, η², η²-N₂)].
include the bond lengths of C=N bonds (1.270(3) and 1.275(3) Å), C−O bonds (1.341(3) and 1.339(3) Å) and C−C bond (1.534(3) Å). Elimination of the oxamidide moiety in the form of oxamidide in yields of 90–95% was achieved by the treatment of the hafnium oxamidide complex with excess HCl (Scheme 1). By varying the amount of CO added, other organic derivatives were also obtained.

Cleavage of the N−N triple bond involves a six electron reduction process. Each of the metals in the hafnocene complex contributes two electrons while the incoming CO ligand provides the remaining electron pair. In previous reports of N−N cleavage and/or functionalization, the reducing equivalents were supplied solely by the metal, or by those stored in M−M bonds, or by the proton-coupled electron transfer events as described in the Chatt cycle. In this respect, Chirik’s work is distinctly different. In addition, the initial N2 ligand in earlier examples of group IV complexes that involved N−N bond cleavage coupled with N−C bond assembly was not directly derived from atmospheric nitrogen. In this respect as well, Chirik’s report stands out since the dinitrogen ligand is derived from atmospheric N2.

Thus, a new reaction uncovering the use of cheap and abundant N2 and CO possessing extremely strong triple bonds for the synthesis of important agrochemicals under mild conditions has been discovered. The only hitch of this reaction sequence are that it is stoichiometric rather than catalytic and requires the use of a strong reducing agent like Na/Hg and a long reaction time; however, these will not deter the researchers’ pursuits in realizing one of chemistry’s long standing issues of utilizing N2 as a feedstock for producing fine and commodity chemicals.


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