Chemical nitrogen fixation by using molybdenum and tungsten complexes*

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Abstract: Dinitrogen complex cis-[W(N₂)₂(PMe₂Ph)₄] reacts with an excess of acidic dihydrogen complexes such as trans-[RuCl(η²-H₂)(dppe)₂]BF₄ (dppe = 1, 2-bis(diphenylphosphino)ethane) at 55 °C under 1 atm of H₂ to form ammonia in moderate yield. The reaction is presumed to proceed through nucleophilic attack of the remote nitrogen of the coordinated dinitrogen on the dihydrogen ligand. The coordinated dinitrogen is also protonated by treatment with hydrosulfido-bridged dinuclear complexes such as [Cp*Ir(µ−SH)₃IrCp*]Cl (Cp* = η⁵-C₅Me₅) to afford ammonia. On the other hand, the synthetic cycle for the formation of pyrrole and N-aminopyrrole from dinitrogen and 2,5-dimethoxytetrahydrofuran has been established starting from dinitrogen complexes of the type trans-[M(N₂)₂(dppe)₂] (M = Mo, W).

INTRODUCTION

Industrial nitrogen fixation from dinitrogen (N₂) and dihydrogen (H₂) has been carried out for more than 80 years by the use of Fe-based heterogeneous catalysts, but the reaction conditions are extremely severe. In contrast, biological nitrogen fixation occurs at ambient temperature and atmospheric pressure. Thus, one of the most challenging subjects in chemistry is development of a new chemical nitrogen fixation which provides not only ammonia but also organonitrogen compounds from dinitrogen with the aid of specially designed catalysts under mild conditions. Here, we describe our recent study toward this direction.

SYNTHESIS OF AMMONIA BY REACTIONS OF TUNGSTEN DINITROGEN AND RUTHENIUM DIHYDROGEN COMPLEXES UNDER MILD CONDITIONS

We have long been interested in the reactivities of the coordinated N₂ in complexes of the type [M(N₂)₂(L)₄] (M = Mo, W; L = tertiary phosphine) because of their possible relevance to biological nitrogen fixation and the rich chemistry of the coordinated N₂ [1]. Although the coordinated N₂ was transformed into ammonia by treatment with inorganic acids such as H₂SO₄ [1,2], H₂ could not be used for the N−H bond formation. We have recently found the ruthenium-assisted protonation of coordinated N₂ on tungsten with H₂ [3]. Treatment of cis-[W(N₂)₂(PMe₂Ph)₄] with an equilibrium mixture of trans-[RuCl(η²-H₂)(dppp)₂]X with pKa = 4.4 and [RuCl(dppp)₂]X [X = PF₆, BF₄, OTf (Tf = SO₂CF₃); dppp = 1, 3-bis(diphenylphosphino)propane] containing 10 equiv of the Ru atom based on the W atom in benzene-dichloromethane at 55 °C for 24 h under 1 atm of H₂ produced ammonia in 45 ~ 55% yields.

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based on the W atom, together with the formation of trans-[RuHCl(dppe)]2. Detailed studies on the reaction of cis-[W(N2)2(PMe2Ph)4] with various Ru(η2-H2) complexes revealed that the yield of ammonia produced critically depended upon the pK_a value of the employed Ru(η2-H2) complexes. When cis-[W(N2)2(PMe2Ph)4] was treated with 10 equiv of trans-[RuCl(η2-H2)(dppe)]2X with pK_a = 6.0 (X = PF6, BF4, OTf) under 1 atm of H2, ammonia was formed in higher yields (up to 80%, eq. 1) compared with the above reaction. If the pK_a value of a Ru(η2-H2) complex was increased up to about 10, the yield of ammonia was remarkably decreased. In these reactions, heterolytic cleavage of H2 seems to occur at the Ru center via nucleophilic attack of the coordinated N2 on the coordinated H2, where a proton (H^+) is used for the protonation of the coordinated N2 and a hydride (H^-) remains at the Ru atom. Treatment of cis-[W(N2)2(PMe2Ph)4] or trans-[M(N2)2(dppe)] (M = Mo, W) with Ru(η2-H2) complexes at room temperature led to isolation of intermediate hydrazido(2-) complexes such as trans-[W(NNH2)(X)(dppe)2]+ (X = OTf, F) and trans-[W(NNH2)(OTf)(PMe2Ph)4]OTf. We presume that further ruthenium-assisted protonation of hydrazido(2-) intermediates such as trans-[W(NNH2)(OTf)(PMe2Ph)4]OTf with H2 at 55 °C results in the formation of ammonia along with W(VI) species. Our studies are now in progress toward development of bimetallic systems where both the hydrogen atoms of activated H2 are effectively used for the catalytic nitrogen fixation from N2 and H2.

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\text{NH}_3 + [\text{RuHCl(dppe)}]_2 + \text{W(VI) species} + \ldots
\]

\[(P = \text{PMe}_2\text{Ph}, P = \text{dppe}, X = \text{PF}_6, \text{BF}_4, \text{OTf})\]

**PROTONATION OF COORDINATED DINITROGEN WITH HYDROSULFIDO-BRIDGED DINUCLEAR COMPLEXES**

In biological nitrogen fixation, the bridging sulfido ligands in the FeMo-cofactor of nitrogenase is considered to mediate proton transfer to the activated N2 bound to the Mo or Fe metal(s). Although treatment of N2 complexes of the type cis-[M(N2)2(PMe2Ph)4] (M = Mo, W) with organic thiols or H2S does not lead to the N–H bond formation, we have now found that the proton on the bridging sulfur in hydrosulfido-bridged dinuclear compounds of iridium and iron is transferred to coordinated N2 on the W atom to form ammonia [4]. The reaction of cis-[W(N2)2(PMe2Ph)4] with 10 equiv of [Cp*Ir(µ-SH)2IrCp*]Cl or [P,F,Fe(µ-SH)2FeP3]BF4 [P3 = bis(2-diphenylphosphinoethyl)phenylphosphine] in dichloroethane-benzene at 55 °C produced ammonia in moderate yield (eq. 2). When trans-[W(N2)2(dppe)]2 was employed, the hydrazido(2-) complexes such as trans-[WCl(NNH2)(dppe)]2Cl were isolated in high yields. Whether such proton transfer occurs in nitrogenase is still completely open to conjecture, however, this type of model system will provide valuable information about the mechanism of biological nitrogen fixation.

\[
\text{NH}_3
\]

\[\text{eq. } 2\]

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SYNTHESIS OF NITROGEN HETEROCYCLES FROM DINITROGEN

Dinitrogen complexes of the type trans-[M(N₂)₂(dppe)₂] (M = Mo, W) are readily converted into the hydrazido(2-) complexes trans-[MX(NNH₂)(dppe)₂]⁺ by treatment with acid HX, which further condense with aldehydes or ketones (RR’C=O) to form the diazoalkane complexes trans-[MX(NNCRR’)(dppe)₂]⁺. This provides one of the most versatile methods to achieve the N–C bond formation at the coordinated N₂ [5]. For the synthesis of pyrrole from the coordinated N₂, 2,5-dimethoxytetrahydrofuran, a cyclic acetal of succinaldehyde, was employed in the condensation reaction. The overall synthetic cycle for the formation of pyrrole and N-aminopyrrole from dinitrogen and 2,5-dimethoxytetrahydrofuran is shown in Scheme 1, which includes the pyrrolylimido complexes trans-[MF(NNCH=CHCH=CH)(dppe)₂] as the key intermediate. It is noteworthy that the starting N₂ complexes can be regenerated in the final step after releasing the nitrogen heterocyles from the coordination sphere of the metal [6]. Furthermore, in sharp contrast to free pyrrole, the pyrrole ring derived from the coordinated dinitrogen undergoes electrophilic substitutions exclusively at the β-position owing to the steric effect of the dppe ligands around the metal.

Scheme 1

REFERENCES