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Chemical nitrogen fixation by using molybdenum and tungsten complexes*

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Abstract: Dinitrogen complex *cis*-[$W(N_2)_2(PMe_2Ph)_4$] reacts with an excess of acidic dihydrogen complexes such as *trans*-[$RuCl(\eta^2\text{-}H_2)(dppe)_2$]$BF_4$ (dppe = 1, 2-bis(diphenylphosphino)ethane) at 55 °C under 1 atm of H_2 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 [$Cp^*Ir(\mu\text{–}SH)_3IrCp^*$]Cl ($Cp^* = \eta^5\text{-}C_5Me_5$) 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*-[$M(N_2)_2(dppe)_2$] (M = Mo, W).

INTRODUCTION

Industrial nitrogen fixation from dinitrogen (N_2) and dihydrogen (H_2) 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 N_2 in complexes of the type [$M(N_2)_2(L)_4$] (M = Mo, W; L = tertiary phosphine) because of their possible relevance to biological nitrogen fixation and the rich chemistry of the coordinated N_2 [1]. Although the coordinated N_2 was transformed into ammonia by treatment with inorganic acids such as H_2SO_4 [1,2], H_2 could not be used for the N–H bond formation. We have recently found the ruthenium-assisted protonation of coordinated N_2 on tungsten with H_2 [3]. Treatment of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] with an equilibrium mixture of *trans*-[$RuCl(\eta^2\text{-}H_2)(dppp)_2$]X with p*K*a = 4.4 and [$RuCl(dppp)_2$]X [X = PF_6, BF_4, OTf (Tf = SO_2CF_3); 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 H_2 produced ammonia in 45 ~ 55% yields

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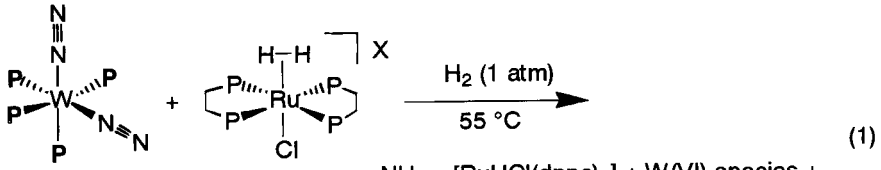
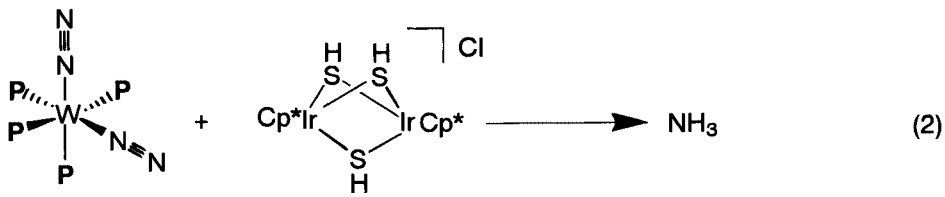
based on the W atom, together with the formation of *trans*-[RuHCl(dppp)$_2$]. Detailed studies on the reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with various Ru(η^2-H$_2$) complexes revealed that the yield of ammonia produced critically depended upon the pK_a value of the employed Ru(η^2-H$_2$) complexes. When *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] was treated with 10 equiv of trans-[RuCl(η^2-H$_2$)(dppe)$_2$]X with pK_a = 6.0 (X = PF$_6$, BF$_4$, OTf) under 1 atm of H$_2$, ammonia was formed in higher yields (up to 80%, eq. 1) compared with the above reaction. If the p*K*a value of a Ru(η^2-H$_2$) complex was increased up to about 10, the yield of ammonia was remarkably decreased. In these reactions, heterolytic cleavage of H$_2$ seems to occur at the Ru center via nucleophilic attack of the coordinated N$_2$ on the coordinated H$_2$, where a proton (H$^+$) is used for the protonation of the coordinated N$_2$ and a hydride (H$^-$) remains at the Ru atom. Treatment of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] or *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo, W) with Ru(η^2-H$_2$) complexes at room temperature led to isolation of intermediate hydrazido(2-) complexes such as *trans*-[W(NNH$_2$)(X)(dppe)$_2$]$^+$ (X = OTf, F) and *trans*-[W(NNH$_2$)(OTf)(PMe$_2$Ph)$_4$]OTf. We presume that further ruthenium-assisted protonation of hydrazido(2-) intermediates such as *trans*-[W(NNH$_2$)(OTf)(PMe$_2$Ph)$_4$]OTf with H$_2$ 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 H$_2$ are effectively used for the catalytic nitrogen fixation from N$_2$ and H$_2$.



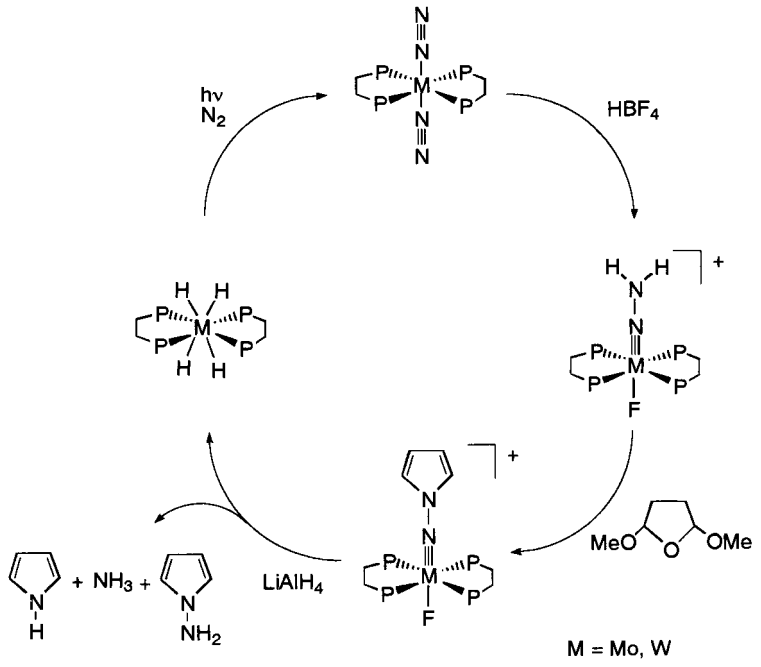
PROTONATION OF COORDINATED DINITROGEN WITH HYDROSULFIDO-BRIDGED DINUCLEAR COMPLEXES

In biological nitrogen fixation, the bridging sulfido ligands in the FeMo-cofactor of nitrogenase is considered to mediate proton transfer to the activated N$_2$ bound to the Mo or Fe metal(s). Although treatment of N$_2$ complexes of the type *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (M = Mo, W) with organic thiols or H$_2$S 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 N$_2$ on the W atom to form ammonia [4]. The reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with 10 equiv of [Cp*Ir(μ-SH)$_3$IrCp*]Cl or [P$_3$Fe(μ-SH)$_3$FeP$_3$]BF$_4$ [P$_3$ = bis(2-diphenylphosphinoethyl)phenylphosphine] in dichloroethane-benzene at 55 °C produced ammonia in moderate yield (eq. 2). When *trans*-[W(N$_2$)$_2$(dppe)$_2$] was employed, the hydrazido(2-) complexes such as *trans*-[WCl(NNH$_2$)(dppe)$_2$]Cl 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.



SYNTHESIS OF NITROGEN HETEROCYCLES FROM DINITROGEN

Dinitrogen complexes of the type *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo, W) are readily converted into the hydrazido(2-) complexes *trans*-$[MX(NNH_2)(dppe)_2]^+$ 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 N_2 [5]. For the synthesis of pyrrole from the coordinated N_2, 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*-$[MF(N\overline{NCH=CHCH=CH})(dppe)_2]$ as the key intermediate. It is noteworthy that the starting N_2 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

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