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Chemical nitrogen fixation by molybdenum and tungsten complexes

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Contents

Abstract

Nitrogen heterocycles, such as pyrroles, phthalimidines and pyridines, are synthesized starting from the ligating dinitrogen in Mo and W complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo, W; L = phosphine). Further, ammonia is formed from N_2 and H_2 at 55°C and 1 atm by using a novel Ru/W bimetallic system, where N_2 and H_2 are activated on the W and Ru center, respectively.

Keywords: Dinitrogen; Nitrogen fixation; Heterocycles; Ammonia

1. Introduction

Chemical transformation of molecular nitrogen into nitrogenous compounds, such as ammonia and organonitrogen compounds, at ambient temperature and

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pressure is one of the most challenging subjects in chemistry [1–4]. It is now well-recognized that dinitrogen binds to the electron-rich metal centers surrounded by appropriate ancillary ligands to afford so-called dinitrogen complexes. Among a variety of dinitrogen complexes of transition metals known to date, molybdenum and tungsten dinitrogen complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo, W; L = phosphine), the first of which is *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) prepared by our group in 1969 [5], are quite outstanding because these dinitrogen complexes are readily and on a large scale synthesized by reduction of molybdenum and tungsten halides with magnesium in the presence of phosphine ligands under dinitrogen, and the co-ordinated dinitrogen shows intriguing reactivities leading to the N–H and N–C bond formation and, in some cases, finally resulting in the formation of ammonia, hydrazine, and organonitrogen compounds.

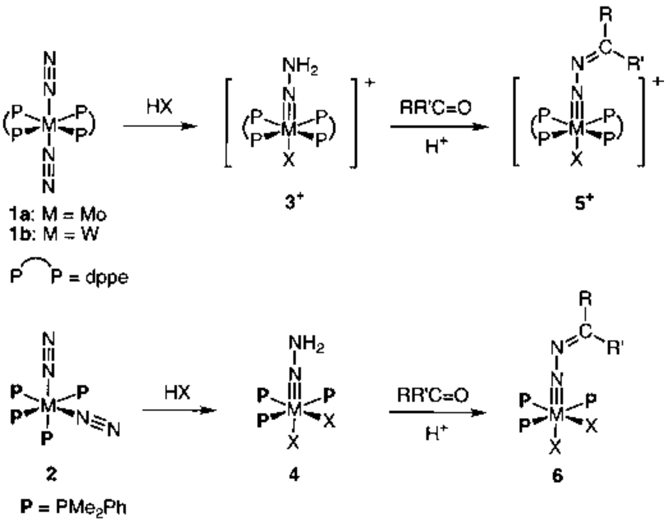
In this article, we wish to summarize recent results of our studies toward the synthesis of nitrogen heterocycles, such as pyrroles and phthalimidines, from dinitrogen by using molybdenum and tungsten complexes. Further, a novel bimetallic approach for nitrogen fixation will be described that has realized the formation of ammonia under mild conditions by ruthenium-assisted protonation of the co-ordinated dinitrogen on tungsten with dihydrogen.

2. Synthesis of nitrogen heterocycles from dinitrogen

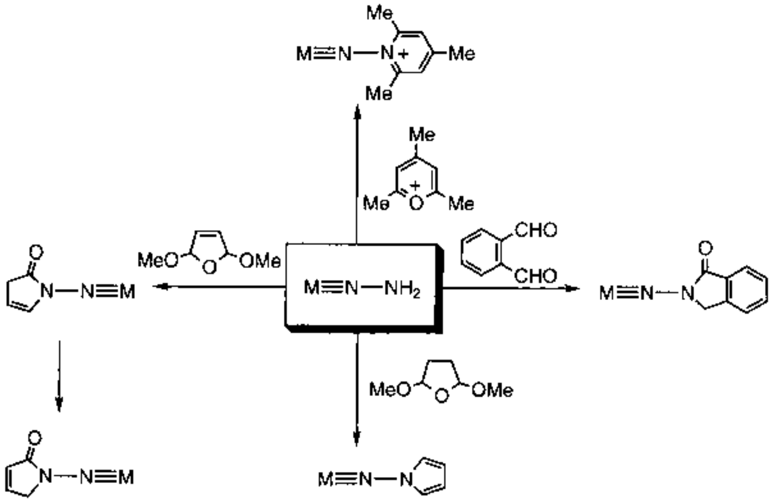
The molybdenum and tungsten dinitrogen complexes, *trans*-$[M(N_2)_2(dppe)_2]$ (**1a**, M = Mo; **1b**, M = W) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**2a**, M = Mo; **2b**, M = W) are readily converted into the hydrazido(2 −) complexes *trans*-$[MX(NNH_2)(dppe)_2]^+$ ($\mathbf{3}^+$) and *cis*, *mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ (**4**), respectively, by protonation of the co-ordinated dinitrogen by acid (HX) [1,4]. The first example of protonation of the co-ordinated dinitrogen to form the hydrazido(2 −) ligand was reported by Chatt and his co-workers in 1972 [6]. Owing to the significant nucleophilicity of the terminal N atom, the hydrazido(2 −) ligands in complexes $\mathbf{3}^+$ and **4** react with aldehydes or ketones ($RR'C=O$) to give the diazoalkane complexes *trans*-$[MX(NNCRR')(dppe)_2]^+$ ($\mathbf{5}^+$) and *cis*, *mer*-$[MX_2(NNCRR')(PMe_2Ph)_3]$ (**6**) (Scheme 1). This provides one of the most versatile methods to achieve the N–C bond formation at the co-ordinated dinitrogen. Thus, the diazoalkane complex **6b** (M = W; R, R′ = Me; X = Br) is obtained by treatment of complex **2b** with aqueous HBr followed by condensation of the resulting hydrazido(2 −) complex **4b** (M = W; X = Br) with acetone. Reaction of complex **6b** with $LiAlH_4$ liberates isopropylamine and ammonia after hydrolysis, whereas treatment of **6b** with HBr gives a mixture of acetone azine and hydrazine [7–9].

Nitrogen heterocycles are widely observed in natural compounds and drugs. The Paal–Knorr synthesis provides a general approach to the heterocyclopentadienes, such as pyrroles [10]. As a typical example, treatment of acetonylacetone with isopropylamine in refluxing acetic acid gives rise to the formation of *N*-methylethyl-2,5-dimethylpyrrole in good yield. Since direct synthesis of nitrogen heterocycles, such as pyrroles from dinitrogen, is of great interest, we have now applied the above condensation reactions of hydrazido(2 −) complexes to the synthesis of nitrogen heterocycles. When complex **3b**$^+$ (M = W; X = F) was treated with acetonylacetone, cyclization at the terminal N atom did not proceed and only monocondensation took place even in the presence of an acid at elevated temperature to give the 5-diazohexan-2-one complex $[\mathrm{WF\{NN{=}C(CH_3)CH_2CH_2COCH_3\}(dppe)_2}]^+$. However, the hydrazido(2 −) ligands in complexes **3**$^+$ and **4** reacted with dialdehydes or their equivalents to form heterocyclic ligands as summarized in Scheme 2.

Reaction of hydrazido(2 −) complexes **4b** (M = W; X = Cl, Br) with phthalaldehyde in the presence of a catalytic amount of aqueous HCl or HBr smoothly proceeded to afford the (phthalimidin-2-yl)imido complexes *cis*, *mer*-$[\mathrm{WX_2(NNCH_2C_6H_4CO)(PMe_2Ph)_3}]$ with a heterocycle containing the terminal N atom of the co-ordinated dinitrogen. However, a similar condensation of the hydrazido(2 −) complex **3b**$^+$ (M = W; X = F) stopped at the stage of the diazoalkane complex *trans*-$[\mathrm{WF(NNCHC_6H_4CHO)(dppe)_2}]^+$, although the latter complex was further converted into the corresponding (phthalimidin-2-yl)imido complex *trans*-$[\mathrm{WF(NNCH_2C_6H_4CO)(dppe)_2}]^+$ by treatment with $\mathrm{AlCl_3}$ in refluxing THF. Reaction of the (phthalimidin-2-yl)imido complex *cis*, *mer*-$[\mathrm{WCl_2(NNCH_2C_6H_4CO)(PMe_2Ph)_3}]$ with HBr liberated 2-aminophthalimidine from the co-ordination sphere in moderate yield, while treatment of the same complex with KOH in THF selectively cleaved the N–N bond to produce phthalimidine. 2,5-Dimethoxy-2,5-dihydrofuran also reacted with the hydrazido(2 −) complexes **3**$^+$ in a similar way. In this condensation reaction, the complexes containing a five-membered lactam structure, *trans*-$[\mathrm{MF(NNCH{=}CHCH_2CO)(dppe)_2}]^+$, were



Scheme 1.



Scheme 2.

initially formed as the kinetic product, which gradually isomerized to the thermodynamically more stable complexes *trans*-[MF(NNCH$_2$CH=CHCO)(dppe)$_2$]$^+$ [11,13].

For the synthesis of pyrroles, 2,5-dimethoxytetrahydrofuran, a cyclic acetal of succinaldehyde, was employed in the condensation reactions. Hydrazido(2 −) complexes **3**$^+$ (M = Mo, W; X = F, Cl) and **4b** (X = Cl, Br) condensed with 2,5-dimethoxytetrahydrofuran to afford pyrrolylimido complexes of the type *trans*-[MX(NNCH=CHCH=CH)-(dppe)$_2$]$^+$ (**7**$^+$) and *cis*, *mer*-[WX$_2$(NNCH=CHCH=CH)-(PMe$_2$Ph)$_3$] (**8b**), respectively, which have a pyrrole ring containing the terminal nitrogen of the original dinitrogen ligand. The reactions proceeded at r.t. by acid catalysis via stepwise condensations at the terminal nitrogen, the first step being the formation of 4-diazobutanal complexes containing the MNN=CHCH$_2$CH$_2$-CHO moiety. The molecular structures of the pyrrolylimido complexes **7b**$^+$PF$_6$ (M = W; X = F) and **8b** (X = Br) were determined by X-ray analysis. The ORTEP drawing and space filling view of complex **7b**$^+$PF$_6$ are shown in Fig. 1. The geometry around the tungsten is distorted octahedron with the (1-pyrrolyl)imido ligand and the fluoride atom in *trans* positions. The space filling view clearly shows that the pyrrole ring is surrounded by a fence or embedded in a pocket made by the phenyl groups of the dppe ligands around the metal. Thus, the α-position of the pyrrole ring is completely protected by the phenyl groups, while the β-position sticks out of the hindered region.

Pyrrole, a highly electron-rich heteroaromatic compound, readily undergoes electrophilic substitution reactions that take place exclusively at the α-position due to the stability of the transient pyrrolium ions. In contrast, the pyrrole ring in complex $\mathbf{7}^+$ is expected to undergo electrophilic substitutions at the β-position owing to the steric effect of the dppe ligands (vide supra). This unique reactivity of the pyrrole ring derived from the co-ordinated dinitrogen has been actually demonstrated by using various electrophiles as shown in Scheme 3. Exclusive β-bromination, cyanation, sulfonation, formylation and acylation have been achieved by treatment of complex $\mathbf{7b}^+$ with *N*-bromosuccinimide (NBS), chlorosulfonyl isocyanate (CSI) and DMF, SO_3-pyridine complex, [CHCl=NMe$_2$]Cl followed

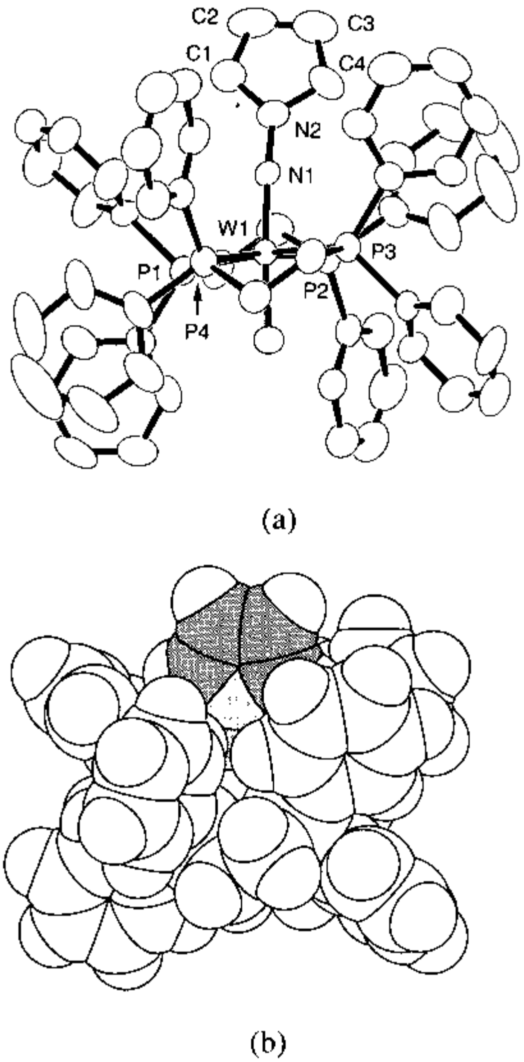
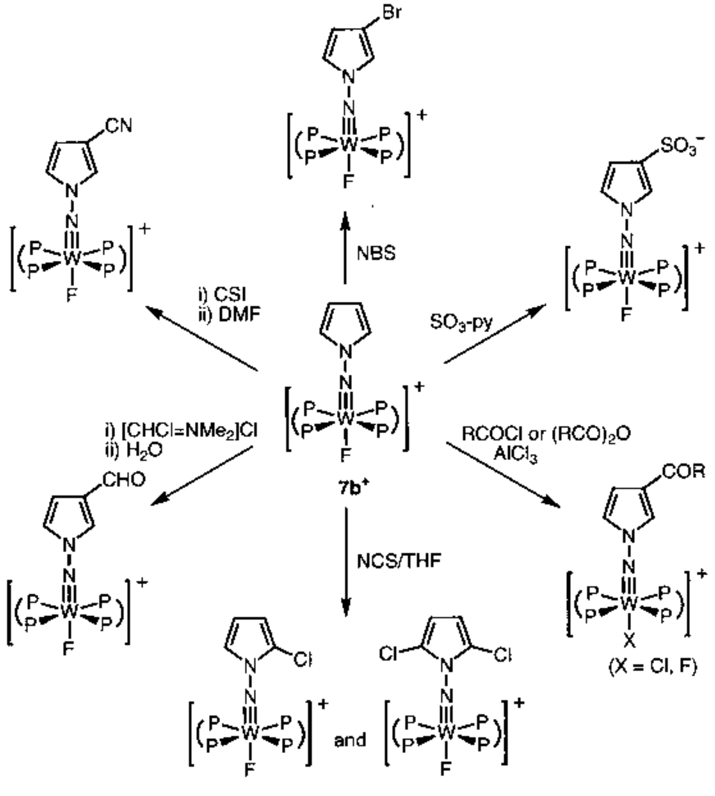


Fig. 1. (a) ORTEP drawing for the cationic part of *trans*-[WF(N$\overline{\text{NCH=CHCH=C}}$H)(dppe)$_2$]PF$_6$ ($\mathbf{7b}^+$PF$_6$). Hydrogen atoms are omitted for clarity. (b) Space filling view of $\mathbf{7b}^+$PF$_6$.

by hydrolysis, and acid chloride/$AlCl_3$, respectively. The only exception we observed is chlorination with *N*-chlorosuccinimide (NCS) giving a mixture of the α-monochloro and α,α′-dichloro complexes.

Reaction of the pyrrolylimido complexes **7**$^+$ with $LiAlH_4$ followed by work-up with MeOH gave rise to the formation of pyrrole, ammonia, and *N*-aminopyrrole, where the yield of ammonia was comparable with that of pyrrole. Pyrrole and ammonia were the major products from both molybdenum and tungsten complexes **7**$^+$, however, the tungsten complex **7b**$^+$ liberated pyrrole and ammonia much more selectively than the molybdenum analogue **7a**$^+$. From this reaction, the tetrahydride complexes $[MH_4(dppe)_2]$ (**9**) were recovered in moderate yields as the metal products, which are known to be transformed to the original dinitrogen complexes **1**. Thus, a synthetic cycle for the formation of pyrrole and *N*-aminopyrrole from dinitrogen has been accomplished starting from dinitrogen complexes **1** (Scheme 4). β-Substituted pyrroles can be liberated from the metal in an analogous way. Similar treatment of the pyrrolylimido complex containing PMe_2Ph ligands **8b** (X = Br) with $LiAlH_4$ also gave pyrrole and ammonia selectively, while reaction of **8b** (X = Br) with KOH in ethanol produced *N*-aminopyrrole predominantly via the fission of the W–N bond [12,13].

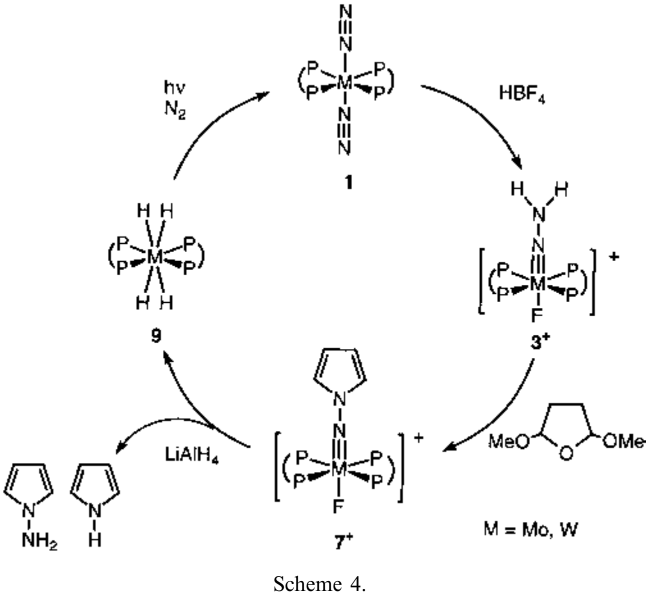


Scheme 3.

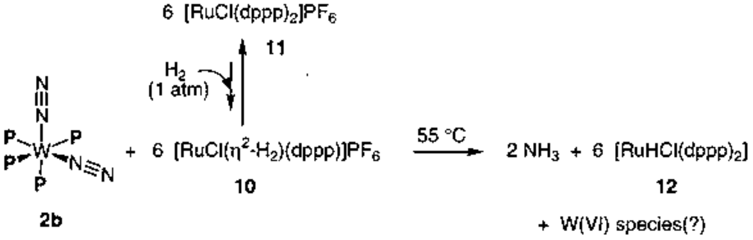
Interestingly, the tungsten hydrazido(2 −) complexes [$WCl_2(NNH_2)(L)(PMe_2Ph)_2$] (L = CO, C_2H_4), which were readily obtained by the selective replacement of the phosphine ligand *trans* to the chloride anion in the hydrazido(2 −) complex **4b** (X = Cl) with CO or ethylene, reacted with 2,4,6-trimethylpyrylium tetrafluoroborate to give the (1-pyridinio)imido complexes [$WCl_2(NNC_5H_2Me_3)(L)(PMe_2Ph)_2$]$BF_4$ containing a pyridine ring. The N–N bond in these complexes was cleaved upon treatment with KOH in MeOH to give 2,4,6-trimethylpyridine and ammonia in good yields. These reactions are in sharp contrast to the reaction of **8b** with KOH in ethanol giving 1-aminopyrrole via the selective W–N bond cleavage (vide supra) [14].

3. A bimetallic system for nitrogen fixation: ruthenium-assisted protonation of co-ordinated N_2 on tungsten with H_2

The co-ordinated dinitrogen in complexes **2** can be transformed into NH_3 or hydrazine by treatment with inorganic acids such as H_2SO_4 [1,4,15]. A detailed mechanism for the formation of nitrogen hydrides has been proposed that includes hydrazido(2 −) complexes **4** as key intermediates. However, H_2 could not be used for the formation of nitrogen hydrides because the ligating N_2 was readily replaced by H_2 without the N–H bond formation [16,17]. Previously, metal carbonyl hydrides such as [$HCo(CO)_4$] were employed for the protonation of the ligating N_2 [18,19]. Later, Morris et al. observed the formation of the hydrazido(2 −) complex **3b**$^+$ (M = W, X = F) by treatment of complex **1b** (M = W) with an acidic H_2



Scheme 4.

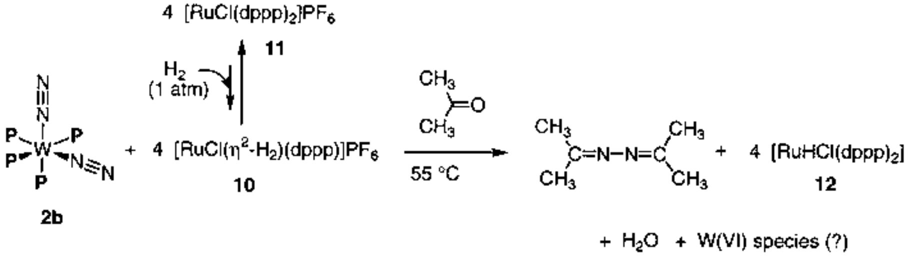


Scheme 5.

complex $[(\eta^5\text{-}C_5H_5)Ru(dtfpe)H_2]BF_4$ (dtfpe = 1,2-bis[bis(*p*-trifluoromethylphenyl)-phosphino]ethane), although the H_2 complex was not available directly from H_2, but from an inorganic acid [20]. Recently, Fryzuk et al. have reported the N–H bond formation at the bridging N_2 in a dinuclear zirconium complex under H_2, but no NH_3 was formed [21].

As an extension of our bimetallic approach for nitrogen fixation, we have very recently used the Ru–H_2 complex *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]PF_6$ (**10**; dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) with $pK_a = 4.4$, which is directly derived from H_2 and $[RuCl(dppp)_2]PF_6$ (**11**) [22]. Thus, the W dinitrogen complex **2b** was added to an in situ generated equilibrium mixture of **11** and **10** in a ratio of about 9:1 containing ten equivalents of the Ru atom based on the W atom. When the mixture was stirred at 55°C for 24 h under 1 atm of H_2, NH_3 was obtained in 55% total yield based on the W atom, where free NH_3 in 10% yield was observed in the reaction mixture and further NH_3 in 45% yield was released after base distillation. No NH_3 was formed in the absence of H_2. The ^{31}P-NMR spectrum of the reaction mixture showed the concurrent formation of $[RuHCl(dppp)_2]$ (**12**). The ideal stoichiometry for the formation of NH_3 is shown in Scheme 5. The ruthenium-assisted protonation of complex **2b** with H_2 seems to proceed via tungsten hydrazido(2 −) complexes similar to **4**. This is strongly supported by the finding that analogous treatment of dinitrogen complex **1b** with an equilibrium mixture of **11** and **10** under 1 atm of H_2 gives the hydrazido(2 −) complex $\mathbf{3b}^+PF_6$ (M = W; X = F) in moderate yield concurrent with **12**. Although the detailed mechanism for the formation of NH_3 has not yet been elucidated, the first step must be the formation of a hydrazido(2 −) complex via the direct reaction between N_2 complex **2b** and H_2 complex **10**. In this reaction, the heterolytic cleavage of H_2 occurs at the Ru center and one H atom is used for the protonation of the ligating N_2 on the W atom, while the other H atom remains at the Ru atom as a hydride. Further protonation of the hydrazido(2 −) intermediate with **10** finally gives rise to the formation of NH_3. Although the present reaction is stoichiometric, this provides an unprecedented route to the formation of NH_3 directly from N_2 and H_2 under mild conditions [23].

Interestingly, when complex **2b** was treated in the presence of acetone with an equilibrium mixture of **11** and **10** under 1 atm of H_2 in a similar way, acetone azine was produced in good yield. The ideal stoichiometry for the formation of acetone azine is shown in Scheme 6. Use of complex **1b** in place of **2b** in this reaction results



Scheme 6.

in the formation of the diazoalkane complex **5b**$^+$PF$_6$ (M = W; X = F; R = R′ = Me). The formation of acetone azine is believed to proceed through a similar diazoalkane complex. Acetone hyrazone is initially liberated from the metal, which is then converted to the final product by condensation with acetone. The present mechanism is essentially the same as that previously proposed for the reaction of **2b** with a methanol/acetone mixture [24].

4. Conclusion

We have developed a synthetic method to prepare nitrogen heterocycles such as pyrroles and phthalimidines from molecular nitrogen by using molybdenum and tungsten complexes. Further, utilization of a bimetallic system that activates N_2 on W and H_2 on Ru, respectively, has realized the formation of NH_3 from N_2 and H_2 at 55°C and 1 atm. Although those reactions are at present stoichiometric, we believe a new generation of nitrogen fixation chemistry will be opened in the near future where a variety of nitrogenous compounds are synthesized catalytically under mild conditions.

References

[1] M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115.
[2] T.A. Bazhenova, A.E. Shilov, Coord. Chem. Rev. 95 (1995) 1115.
[3] S. Gambarrota, J. Organomet. Chem. 500 (1995) 117.
[4] J.R. Dilworth, R.L. Richards, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, UK, 1982, p. 1073.
[5] M. Hidai, K. Tominari, Y. Uchida, A. Misono, Chem. Commun. (1969) 1392.
[6] J. Chatt, G.A. Heath, R.L. Richards, J. Chem. Soc. Chem. Commun. (1972) 1010.
[7] M. Hidai, Y. Mizobe, M. Sato, T. Kodama, Y. Uchida, J. Am. Chem. Soc. 100 (1978) 5740.
[8] P.C. Bevan, J. Chatt, M. Hidai, G.J. Leigh, J. Organomet. Chem. 160 (1978) 165.
[9] Y. Mizobe, Y. Uchida, M. Hidai, Bull. Chem. Soc. Jpn. 53 (1980) 1781.
[10] N. Clauson-Kaas, Z. Tyle, Acta Chem. Scand. 6 (1952) 667.
[11] H. Seino, Y. Ishii, M. Hidai, Inorg. Chem. 36 (1997) 161.
[12] H. Seino, Y. Ishii, T. Sasagawa, M. Hidai, J. Am. Chem. Soc. 117 (1995) 12181.
[13] M. Hidai, Y. Ishii, Bull. Chem. Soc. Jpn. 69 (1996) 819.

[14] Y. Ishii, S. Tokunaga, H. Seino, M. Hidai, Inorg. Chem. 35 (1996) 5118.
[15] J. Chatt, A.J. Pearman, R.L. Richards, Nature (Lond.) 253 (1975) 39.
[16] M. Hidai, K. Tominari, Y. Uchida, J. Am. Chem. Soc. 94 (1972) 110.
[17] T.A. George, R.C. Tisdale, Inorg. Chem. 27 (1988) 2909.
[18] M. Hidai, T. Takahashi, I. Yokotake, Y. Uchida, Chem. Lett. (1980) 645.
[19] H. Nishihara, T. Mori, Y. Tsurita, K. Nakano, T. Saito, Y. Sasaki, J. Am. Chem. Soc. 104 (1982) 4367.
[20] G. Jia, R.H. Morris, C.T. Schweitzer, Inorg. Chem. 30 (1991) 594.
[21] M.D. Fryzuk, J.B. Love, S.J. Rettig, V.G. Young, Science 275 (1997) 1445.
[22] E. Rocchini, A. Mezzetti, H. Rüegger, U. Burckhardt, V. Gramlich, A.D. Zotto, P. Martinuzzi, P. Rigo, Inorg. Chem. 36 (1997) 711.
[23] Y. Nishibayashi, S. Iwai, M. Hidai, Science 279 (1998) 540.
[24] A. Watakabe, T. Takahashi, D.M. Jin, I. Yokotake, Y. Uchida, M. Hidai, J. Organomet. Chem. 254 (1983) 75.