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10. The $g_{\parallel}$ value for [Cu(II)BDB] is 2.231, whereas that for its square-planar analog (a cyclohexyl-1,2-diimine backbone) is smaller at 2.195 [E. I. Solomon, *Comm. Inorg. Chem.* **III**, 227 (1984)].
11. The stoichiometry has been determined by both EPR (77 K) and optical titrations (RT).
12. The Cu(II) complexes are oxidized either by tris(4-bromophenyl)aminium hexachloroantimonate, [$(TPA^+)(SbCl_6^-)$], or nitrosonium tetrafluoroborate [$(NO)^+(BF_4)^-$].
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16. Larger *g* values observed for the Br and S substituted ligands result from the larger spin-orbit couplings of heavier elements. The *g* values for the Zn analogs and their corresponding phenoxyl radicals are as follows: $[Zn(II)BSP]^{+\bullet}$, 2.0060; 2-thiomethyl-4-methylphenoxyl, 2.0059; $[Zn(II)BDB]^{+\bullet}$, 2.0045; 2,4-di-*t*-butylphenoxyl, 2.0045; $[Zn(II)BBr]^{+\bullet}$, 2.0057; 2,4-dibromophenoxyl, 2.0061. See Fig. 1 legend for nomenclature. Stable Zn phenoxyl-radical species have been reported [A. Sokolowski *et al.*, *J. Am. Chem. Soc.* **119**, 8889 (1997)].
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27. Two rapid, sequential, 1 e^- transfers through the intermediacy of a superoxide-Cu(II) species will be considered mechanistically indistinguishable from a concerted 2 e^- transfer.
28. The aqueous pK_a values for H_2O_2 and $PhCH_2OH$ are about 12 and 16, respectively. Although the pK_a values in $PhCH_2OH$ will certainly be much higher, the ratio of the values should remain effectively constant.
29. The reaction rate dramatically decreases as the reaction proceeds, probably because of H_2O_2 inhibition. Addition of a 100-fold excess of 1,4-diazabicyclo[2,2,2]octane H_2O_2 [P. G. Cookson, A. G. Davies, N. Fazal, *J. Organometallic Chem.* **99**, C31 (1975)] to the reaction mixture inhibits the catalysis.
30. In the later stages of the reaction, the O_2:benzaldehyde ratio slowly increases to ~2:1, consistent with disproportionation of H_2O_2 to water and O_2, a reaction known to be catalyzed by Cu(II) complexes. Positive qualitative tests for H_2O_2 with KI containing starch and an aqueous Ti(IV) reagent [W. C. Wolfe, *Anal. Chem.* **34**, 1328 (1962)] are also observed.
31. Excess O_2: 0.1 ml of a 1.0 mM CH_2Cl_2 solution of $[Cu(I)BSP]^-$ at RT was injected directly into 0.9 ml of CH_2Cl_2 that was presaturated with 1 atm of O_2 ($[O_2] = 3.8$ mM) [K. D. Karlin *et al.*, *J. Am. Chem. Soc.* **116**, 1324 (1994)].
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Bimetallic System for Nitrogen Fixation: Ruthenium-Assisted Protonation of Coordinated N_2 on Tungsten with H_2

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Treatment of the tungsten dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (Me = methyl, Ph = phenyl) with an equilibrium mixture of $[RuCl(dppp)_2]X$ and *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]X$ [X = BF_4, PF_6, or OSO_2CF_3; dppp = 1,3-bis(diphenylphosphino)propane] under 1 atmosphere of dihydrogen at 55 degrees Celsius for 24 hours gave NH_3 in moderate yield. The same reaction in the presence of acetone produced acetone azine in high yield. None of these reactions proceeded in the absence of dihydrogen.

Dinitrogen has been regarded as one of the most inert molecules under normal laboratory conditions. Industrially, organonitrogen compounds fundamentally depend for their nitrogen source on NH_3 produced by the energy-consuming Haber-Bosch process, where extremely drastic reaction conditions are required in order to activate N_2 (*1*). The development of chemical processes that enable direct transformation of N_2 into compounds such as NH_3 and organonitrogen compounds under mild conditions is an important goal.

Studies of the reactivities of coordinated N_2 in complexes of the type $M(N_2)_2(L)_4$ (M = Mo or W; L = phosphine) (*2*)—the first of which is *trans*-$[Mo(N_2)_2(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane], prepared by our group in 1969 (*3*)—have shown that the ligating N_2 can be transformed into NH_3 or hydrazine by treatment with inorganic acids such as H_2SO_4 and HCl (*4*). A detailed mechanism for the formation of nitrogen hydrides has been proposed on the basis of the reactivities of isolable intermediate complexes such as hydrazido(2-) complexes (*4*). However, H_2 could not be used for the synthesis of nitrogen hydrides because H_2 replaced the ligating N_2 in the complexes to form $MH_4(L)_4$ without formation of the N–H bond (*5*). Previously, metal carbonyl hydrides such as $HCo(CO)_4$ were used for the N–H bond formation of the coordinated N_2 (*6*). Recently, Morris *et al.* tried to use an acidic H_2 complex $[CpRu(dtfpe)H_2]BF_4$ {Cp = η^5-C_5H_5; dtfpe = 1,2-bis[bis(*p*-trifluoromethylphenyl)phosphino]ethane} with pK_a = 4.3 (K_a is the acid

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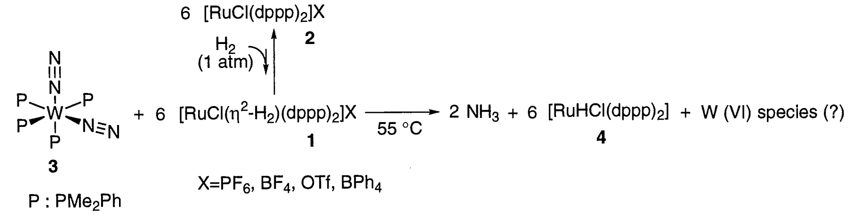
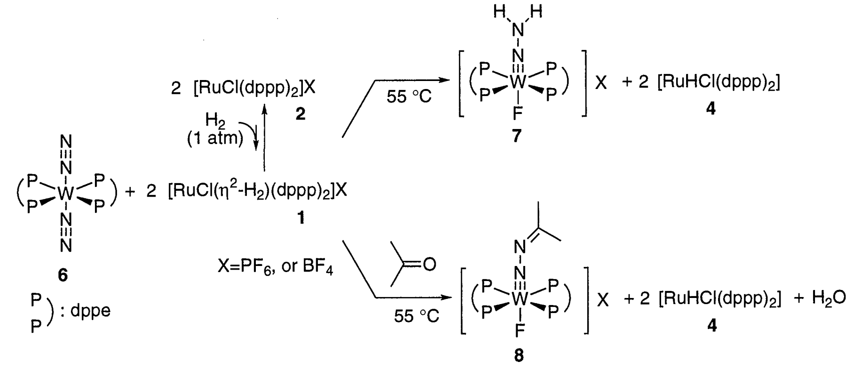
Table 1. Reaction of **3** with an equilibrium mixture of **1** and **2** derived from 10 equiv of **2** under 1 atm of H_2 in dichloroethane-benzene at 55°C for 24 hours unless otherwise indicated. Yield is based on the W atom. Free yield was before base distillation of the reaction mixture, and basic yield was after, to fully liberate NH_3.

X^- of **2**	Yield of NH_3 (%)		
	Free	Basic	Total
PF_6	10	45	55*
PF_6†	3	23	26
PF_6‡	1	1	2
PF_6§	8	26	34
BF_4	16	38	54*
OTf	9	36	45*
BPh_4	6	2	8

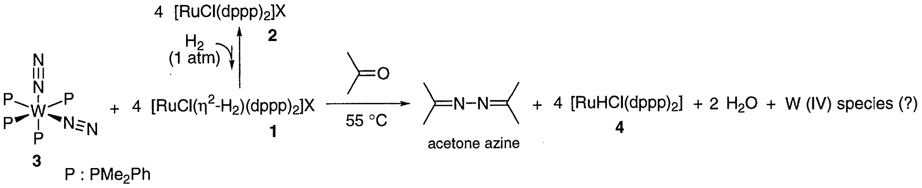
*Variation ±3% between experiments. †In THF. ‡At room temperature. §*mer*-$WBr_2(NNH_2)(PMe_2Ph)_3$ (**5**) was used instead of **3**.



Scheme 1.



Scheme 2.



Scheme 3.

constant) to protonate the ligating dinitrogen in *trans*-$[W(N_2)_2(dppe)_2]$ (7). The H_2 complex reacted with the N_2 complex to form a hydrazido(2-) complex, although the H_2 complex was not available directly from H_2 but from an inorganic acid. Recently, Fryzuk *et al.* reported N–H bond formation when a dinuclear zirconium dinitrogen complex was treated with H_2 (8); however, no NH_3 was formed. This reaction seems quite different from Morris's protonation of the coordinated N_2 with the acidic H_2 complex.

As an extension of our bimetallic approach for N_2 fixation (6, 9), we used the Ru-H_2 complexes *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]X$ with $pK_a = 4.4$, which are directly derived from H_2 (10). Ruthenium-assisted protonation of coordinated N_2 with H_2 produced NH_3 and acetone azine $[(CH_3)_2CNNC(CH_3)_2]$. This may be a first step to realize the synthesis of NH_3 from N_2 and H_2 under mild conditions, in sharp contrast to the Haber-Bosch process.

The H_2 complex *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]X$ [X = PF_6 (**1a**)] is slowly formed in situ from $[RuCl(dppp)_2]X$ [X = PF_6 (**2a**)] under 1 atm of H_2 (10). Thus, an equilibrium mixture of **2a** and **1a** in a ratio of about 9 to 1 was obtained when a solution of **2a** in a dichloroethane-benzene mixture was stirred under 1 atm of H_2 at ambient temperature for 12 hours. Addition of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**3**) to the equilibrium solution containing 10 equivalents (equiv) of the Ru atom based on the W atom and the subsequent reaction under 1 atm of H_2 at 55°C for 24 hours afforded NH_3 in 55% total yield based on the W atom. Free NH_3 in 10% yield was observed in the reaction mixture, and further NH_3 in 45% yield was released after base distillation. Direct treatment of **3** with 10 equiv of **2a** under 1 atm of H_2 at 55°C for 24 hours afforded NH_3 in 22% total yield. This result indicates that pretreatment of **2** under 1 atm of H_2 is necessary to increase the yield of NH_3. The ^{31}P nuclear magnetic resonance (NMR) spectrum of the reaction mixture showed the formation of $[RuHCl(dppp)_2]$ (**4**) and free PMe_2Ph. Complex **4** has been isolated and characterized by spectroscopy. Because hydrazido(2-) intermediate complexes (vide infra) were not observed in the NMR spectrum of the reaction mixture, we are inclined to believe that the coordinated N_2 converted into NH_3 and NH_4^+. Thus, base distillation of the reaction mixture was carried out to fully liberate NH_3. The yield of NH_3 was lower when tetrahydrofuran (THF) was used as solvent.

Interestingly, the reaction was critically dependent on the nature of the counteranion of **2**. In the case of $[RuCl(dppp)_2]X$ [X = BF_4 (**2b**)] and $[RuCl(dppp)_2]X$ [X = OTf, OTf = OSO_2CF_3 (**2c**)], NH_3 was obtained in 54 and 45% total yield, respectively. In contrast, in the case of $[RuCl(dppp)_2]X$ [X = BPh_4 (**2d**)], NH_3 was obtained in only 8% total yield. The ideal stoichiometry for the formation of NH_3 is shown in Scheme 1. The typical results are shown in Table 1. Both Ru complexes **2** and H_2 are essential to this reaction. In fact, in the absence of **2** or H_2, no NH_3 was obtained. In all cases, only a trace amount of NH_2NH_2 was observed. Independently, we confirmed that the reaction of anhydrous NH_2NH_2 with the equilibrium mixture derived from **2a** under 1 atm of H_2 in a mixture of dichloroethane and benzene at 55°C for 24 hours gave NH_3 in quantitative yield (11). This result means that NH_2NH_2 is converted into NH_3 quantitatively in this reaction system, even if NH_2NH_2 is formed.

The tungsten hydrazido(2-) complex *mer*-$WBr_2(NNH_2)(PMe_2Ph)_3$ (**5**), which is available by protonation of **3** with HBr, reacted with the same Ru mixture under 1 atm of H_2 to afford NH_3 in 34% total yield. Thus, the Ru-assisted protonation of **3** with H_2 seems to proceed by way of tungsten hydrazido(2-) complexes similar to **5** as an intermediate complex. This proposed mechanism is further supported by the finding that the reaction of *trans*-$[W(N_2)_2(dppe)_2]$ (**6**) with an equilibrium mixture derived from 2 equiv of **2a** or **2b** under 1 atm of H_2 in a dichloroethane-benzene mixture gives the hydrazido(2-) complexes *trans*-$[WF(NNH_2)(dppe)_2]X$ [X = PF_6 (**7a**); X = BF_4 (**7b**)] in 40 to 60% yield together with **4** (Scheme 2). The same hydrazido(2-) complexes are also prepared from **6** by protonation with HBF_4 or HPF_6 (12). These results are direct evidence for protonation of the coordinated N_2 with H_2 in the presence of **2**. Although the detailed reaction mechanism for the formation of NH_3 is not yet clear, the first step must be the direct reaction of the N_2 complex **3** with the H_2 complexes **1** to form hydradizo(2-) complexes. In this reaction, the heterolytic cleavage of H_2 occurs at the Ru center, where one H atom is used for protonation of the coordinated N_2 on the W atom and the other H atom remains at the Ru atom as a hydride. Further protonation of the hydrazido(2-) complexes with the H_2 complexes **1** results in the formation of NH_3. Because **3** is synthesized under 1 atm of N_2 at ambient temperature, the present reaction allows the formation of NH_3 directly from N_2 and H_2 under mild conditions.

Interestingly, when **3** was treated in the presence of acetone with an equilibrium mixture derived from 10 equiv of **2a**, **2b**, or **2c** under 1 atm of H_2 at 55°C for 24 hours, acetone azine was formed in 65, 80, or 100% yield based on the W atom, respectively (Scheme 3). The yield of acetone azine depended on the nature of the counteranion of **2**. The formation of acetone azine was not observed without H_2. However, when complex **6** was used instead of complex **3**, the diazoalkane complexes *trans*-$[WF(NNCMe_2)(dppe)_2]X$ [$X = PF_6$ (**8a**); $X = BF_4$ (**8b**)] were formed in high yields. Complex **8b** has been isolated and characterized by spectroscopy. The same complexes are well known to be derived from the condensation of *trans*-$[WF(NNH_2)(dppe)_2]X$ with acetone (*13*). The formation of acetone azine has previously been observed upon treatment of **3** with a methanol-acetone mixture at 50°C (*14*). We believe that the mechanism of the present reaction is essentially similar to the previous one, which includes a diazoalkane complex as an intermediate. However, it is noteworthy that H_2 can be used in place of methanol.

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Isolation of an Intrinsic Precursor to Molecular Chemisorption

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Over the past 70 years, numerous gas-surface adsorption studies have indicated the existence of a weakly bound, mobile intermediate that is a precursor to chemical bond formation. The direct observation and characterization of such a species are presented. Precursor and chemisorbed benzene on a silicon surface were clearly distinguished with the use of a tunable-temperature scanning tunneling microscope. Precursor decay to chemisorption was observed, allowing the salient features of the potential energy surface to be determined.

The microscopic details of gas-surface adsorption dynamics have been actively studied for the better part of a century. Much of the conceptual framework in use today builds upon the pioneering work of Langmuir (*1*) and Lennard-Jones (*2*), who studied the nature of forces acting when atomic or molecular species come into contact with a surface. Although knowledge of physical interactions between adsorbates and surfaces (physisorption) and of relatively strong chemical interactions (chemisorption) has advanced steadily over the years, important issues remain to be addressed. One such issue, central to a discussion of adsorption phenomena and a recurring theme throughout the history of surface science, involves an adsorption intermediate known as a precursor. Although no direct observation or characterization has been achieved, numerous observations consistent with precursor-mediated adsorption have led to widespread use of the concept (*3*). Here, we describe the direct observation of this evasive but likely common entity.

In Langmuir's early work, a simple scenario was considered in which an impinging species either was chemisorbed when striking an adsorbate-free surface site or was scattered back into the gas phase upon encountering an occupied site, leading to a linear dependence of the sticking coefficient (that is, the probability of adsorbing) on surface coverage. Exceptions to this behavior—systems exhibiting near-unity sticking probability at high coverage—were noted early on, for example, Cs (*4*) and N_2 (*5*) adsorption on tungsten. To account for these observations, more sophisticated models by Morrison and Roberts (*6*) and Kisliuk (*7*) invoked a weakly bound, mobile intermediate state that allowed incoming adsorbates to search for a free site. Later adsorption studies, usually measurements of sticking coefficients (*8–10*), pointed to such a precursor-mediated adsorption mechanism (*3*). Numerous theoretical papers have modeled the role of precursor states in adsorption and desorption (*11*, *12*). A notable advance came with the work of Doren and Tully, who pointed out that rather the free energy of interaction, not only the enthalpy, should be considered in understanding precursors (*11*).

Two very different types of precursor have been described. The extrinsic precursor is associated with incoming molecules blocked from direct chemisorption by preexisting adsorbed molecules. It is weakly bound to an adsorbate-covered portion of the surface through van der Waals interactions but is free to diffuse laterally, increasing the opportunity to find a free site for chemisorption. Our focus is on the intrinsic precursor, a physisorbed intermediate state that does not arise from simple blocking of adsorption sites. Rather, it exists spatially at virtually the same point where chemisorption can occur, but is inhibited from forming a stronger bond by a barrier related to the structural distortion or realignment of the molecule, the surface, or both. The intrinsic precursor is thought to be physisorbed and laterally free-moving, like the extrinsic precursor. Although they are fundamentally different entities, both precursor types are described by the schematic po-

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