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Recent Advances in the Chemistry of Dinitrogen Complexes

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Yasushi Mizobe was born in Yamaguchi, Japan, in 1953. He received the Dr. Eng. degree from the University of Tokyo in 1981 under the supervision of Professors Masanobu Hidai and Yasuzo Uchida. After two postdoctoral years with Professor R. H. Holm at Harvard University, he joined the University of Tokyo, where he is currently Associate Professor of Department of Chemistry and Biotechnology. His research interest is centered on the syntheses, structures, and reactivities of organometallic complexes which can be used for the activation of small molecules.

I. Introduction

Development of the chemical N_2-fixing system converting a quite inert N_2 molecule into nitrogenous compounds under mild conditions is a challenging topic in chemistry. Inductrial NH_3 production from N_2 and H_2 gases (Haber–Bosch process) has successfully been carried out for more than 80 years by the use of Fe-based heterogeneous catalysts, but it requires extremely drastic conditions. Although a Ru-on-graphite catalyst developed recently in the Kellogg advanced ammonia process allows some milder operating conditions (70–105 bar, 350–470 °C),[1] this apparently awaits further improvement.

In contrast, biological N_2-fixing system can reduce N_2 gas into NH_3 at ambient temperature and pressure (eq 1), and it has long been recognized that Mo

$$N_2 + 8H^+ + 8e^- + 16MgATP \longrightarrow 2NH_3 + H_2 + 16MgADP + 16P^i \quad (1)$$

is involved in the catalytic component as an element essential to display an activity. More recent studies

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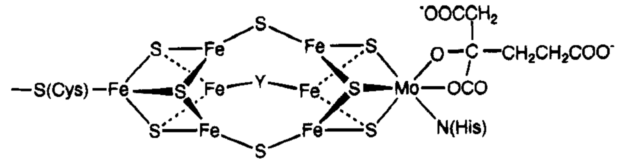
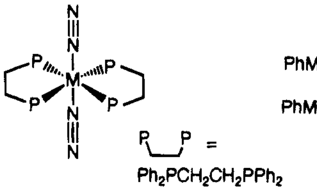


Figure 1. Structural model of the FeMo cofactor site of resting state in Mo-containing nitrogenases determined by X-ray crystallography. The third bridging ligand Y, which was unknown according to the initial reports,[2] is now considered to be a third sulfide.[4]

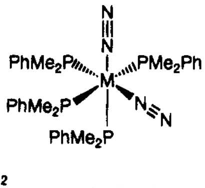
have clarified the presence of two associated proteins in the enzyme nitrogenase, *viz.* FeMo and Fe proteins, and it is believed that the substrate binding and reduction occur at the multimetallic site involved in the former, which consists of Mo and Fe atoms bridged by sulfide ligands. Quite attractive is the FeMo cofactor structure model deduced recently from single-crystal X-ray analysis for FeMo proteins of *Azotobacter vinelandii* [2] and *Clostridium pasteurianum*,[3] which contains the cuboidal Fe_4S_3 and Fe_3MoS_3 units bridged by three sulfides (Figure 1). EXAFS analysis also confirmed the presence of this core in both the isolated *A. vinelandii* FeMo protein and cofactor, with a slight relaxation of the cluster structure in the latter upon removal from the protein matrix.[4] How the N_2 molecule binds to this active site is still uncertain. At a glance, a trigonal prismatic cavity surrounded by six coordinatively unsaturated Fe atoms seems to be susceptible to N_2 insertion, giving the μ_6-N_2 ligand, although the cavity size demonstrated at least for this dithionite reduced form is considered to be too small to accommodate N_2.[2a] Alternatively, extended Hückel type calculations using a model $[HFe(\mu_3\text{-}S)_3Fe_3(\mu_2\text{-}S)_3Fe_3(\mu_3\text{-}S)_3MoH_3]^-$ suggested the coordination of N_2 rather to the edge or the face of the Fe_6 trigonal prism as a bridge between two cuboidal units.[5] On the other hand, coordination of CN^- to the isolated FeMo cofactor has been reported to take place at the Mo atom from the EXAFS criteria.[4]

Albeit this ambiguity of the binding and reduction mechanism of N_2 in the biological system, it is apparent that the transition metals play an important role in promoting this transformation under mild conditions. Studies of the syntheses and reactions of N_2 complexes are therefore of particular interest. The recent discovery of the nitrogenases containing either V in place of Mo or only Fe as a transition metal component[6] may imply that a wide range of transition metals possibly facilitate the intriguing reactions of N_2 in their coordination sphere.

Two pioneering findings associated with the chemical N_2-fixing system using transition metal compounds are the isolation of the first dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$ [7] and the formation of NH_3 by treatment of N_2 gas with a mixture of transition metal salt and organomagnesium, -lithium, or -aluminum followed by hydrolysis,[8] demonstrating that even N_2 can coordinate to the metal to give a stable N_2 complex and N_2 can be converted readily into nitrogenous compounds in the presence of transition metal species. Stimulated by these observations, syntheses of N_2 complexes have been attempted for a wide range of transition metals, and now unequivocally characterized N_2 complexes are known for almost all transition metals. However, despite the occurrence of numerous N_2 complexes, those which react in a well-defined manner to give nitrogen-containing ligands and/or compounds are relatively limited. It may be emphasized that Mo and W dinitrogen complexes containing tertiary phosphines as ancillary ligands are most intensively studied since the initial preparation of *trans*-$[Mo(N_2)_2(dppe)_2]$ (**1a**) in this laboratory[9] because of, at least in part, their possible relevance to the active site of FeMo nitrogenases. Interestingly, these Mo and W complexes, especially *trans*-$[M(N_2)_2(dppe)_2]$ (**1**) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**2**), have actually proved to undergo numerous transformations of their N_2 ligands, demonstrating the rich chemistry of N_2.



1a: M = Mo
1b: M = W



2a: M = Mo
2b: M = W

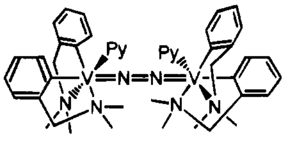
This review deals with the recent progress in the syntheses and reactions of N_2 complexes. Significant emphasis is also placed upon the organic chemistry of the hydrazido(2−) ($MNNH_2$) complexes readily derived from N_2 complexes of Mo and W and that of the nitrido (MN) complexes prepared from gaseous N_2. In relation to these reactions, some intriguing reactivities displayed at the M−N multiple bonds in certain imido complexes are also cited regardless of whether the origin of the nitrogen atom in the organonitrogen ligand comes from molecular nitrogen or not. As for the older works, readers can refer to several comprehensive reviews which appeared previously.[10−13] More reviews are also available, which cover some limited areas in this chemistry.[14−21]

II. Advances in Syntheses and Structures of Dinitrogen Complexes

Since syntheses and structures of N_2 complexes were extensively surveyed previously,[10] this chapter deals mainly with N_2 complexes reported more recently. Furthermore, herein are cited only the complexes which are considered to be of significant importance due to involvement of new metals or coligands, the novel coordination mode displayed by N_2 ligand, or the new synthetic route.

A. Metals

Dinitrogen complexes of V have been attracting considerable attention because of the presence of V-containing nitrogenases. However, it was in 1989 that the structurally characterized V dinitrogen complex was reported for the first time, although the N_2 fixing ability of V(II) species had been well demonstrated much earlier. The first dinitrogen complex $[\{(o\text{-}Me_2NCH_2C_6H_4)_2V(py)\}_2(\mu\text{-}N_2)]$ (**3**)[22] was prepared from $[V(TMEDA)_2Cl_2]$ with o-$Me_2NCH_2C_6H_4Li$, which contains a μ-η^1:η^1-N_2 ligand with essentially linear V−N−N−V linkage. Several V complexes have subsequently been isolated, which include mononuclear complexes with terminal end-on N_2 ligands, *e.g.* $[Na(THF)][V(N_2)_2(dppe)_2]$ (**4**)[23] and dinuclear complexes with a μ-η^1:η^1-N_2 ligand such as $[\{V(CH_2Bu^t)_3\}_2(\mu\text{-}N_2)]$ (**5**),[24] $[\{(Pr^i{}_2N)_3V\}_2(\mu\text{-}N_2)]$,[25] $[\{[(Me_3Si)NC(Ph)N(SiMe_3)]_2V\}_2(\mu\text{-}N_2)]$,[26] and $[Na(diglyme)][Na\{(2,4,6\text{-}Me_3C_6H_2)_3V\}_2(\mu\text{-}N_2)]$ (**6**).[27] In the latter complex, a μ-N_2 ligand further interacts with a Na^+ cation in a side-on manner.



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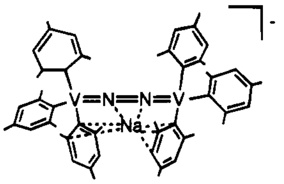

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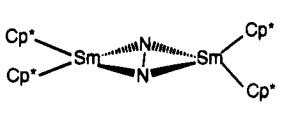
By the finding of these V complexes, only Pd and Pt are left as the metals involved in groups 4 to 10 for which no stable N_2 complexes have been isolated. With respect to f-block elements, two Sm complexes with a μ-η^2:η^2-N_2 ligand, $[(Cp^*Sm)_2(\mu\text{-}N_2)]$ (**7**)[28] and $[\{(THF)_2Li(OEPG)Sm\}_2(N_2)Li_4]$ (**8**),[29] are known. Another N_2 complex to be noted is a $[\{(THF)_3Li\}_2(\mu\text{-}N_2)]^{2+}$ cation (**9**).[30] Although interaction of Li^+ cation with N_2 ligand has been demonstrated already in certain transition metal complexes, the N_2 ligand bound only to non-transition metals had been unprecedented.



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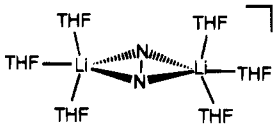

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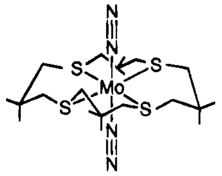
B. Ancillary Ligands

It is well known that the formation and structures of N_2 complexes are very sensitive to the nature of ligands such as phosphines. For example, the cis or trans geometry of Mo and W dinitrogen complexes of the type $[M(N_2)_2(\mathbf{P})_4]$, prepared from WCl_6, $MoCl_5$, or $MCl_4(\mathbf{P})_2$ by the reduction with Mg in the presence of an appropriate phosphine, is controlled by subtle factors. Thus the N_2–diphosphine complexes with $(\mathbf{P})_4$ = $(dppe)_2$, $(dppp)_2$, (dppe)(dppm), (dppe)(dppp), (dppe)(depe), etc.,[9,31,32] as well as the PPh_2Me complexes[33] are trans, while the N_2 complexes containing dppm[34] and PMe_3[35] are cis. Interestingly, $[Mo(N_2)_2(dppm)_2]$ obtained from $Mo(acac)_3/AlEt_3$ under N_2 proved to be trans.[9b] It is to be noted that for $Na[V(N_2)_2(dmpe)_2]$, which is isoelectronic with these Mo(0) and W(0) complexes, both the cis and trans isomers are formed from the reaction of $[VCl_3(THF)_3]$ with Na in the presence of dmpe under N_2. The cis and trans product ratio depends on the temperature, and the ratio of 12:1 at 195 K changes to 4:1 at 250 K and then to 3:1 at 290 K. The interconversion between two isomers with varying temperature is reversible.[23c]

The recent study of the syntheses of W(0) complexes containing PR_2Ph (R = Et, Pr^n) ligands disclosed the formation of three different types of N_2 complexes: $[\{W(N_2)_2(PR_2Ph)_3\}_2(\mu\text{-}N_2)]$, *trans*-$[W(N_2)_2(PR_2Ph)_4]$, and $[W(\eta^6\text{-}C_6H_5PR_2)(N_2)(PR_2Ph)_2]$.[36] This presents a sharp contrast to the fact that, for R = Me, only *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**2b**) and its less common trans isomer[37] are known to be formed by similar reactions. Interestingly, the Mo complex *trans*-$[Mo(N_2)_2(PPr^n{}_2Ph)_4]$ has proved to be converted into a novel mononuclear tris(dinitrogen) complex *mer*-$[Mo(N_2)_3(PPr^n{}_2Ph)_3]$ on being dissolved in THF.[38]

Typical ancillary ligands widely utilized for the syntheses of N_2 complexes may be organophosphines, amines, and cyclopentadienyl groups. However, recent studies have revealed that more diversified types of ligands can be used to isolate stable N_2 complexes. One important class of ligands is those containing sulfur atoms. The importance of sulfur coligands apparently arises from the structure of N_2 binding site proposed for nitrogenases, which consists of the metal centers surrounded by sulfur atoms. However, well-characterized N_2 complexes having sulfur donor ligands are still limited, and coordination of N_2 to the multimetallic core with sulfide ligand(s) has not yet been demonstrated. The complexes reported to date include the relatively low-valent complexes *trans*-$[Mo(N_2)_2(Me_8[16]aneS_4)]$ (**10**)[39] and $[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$[40] as well as the higher valent complexes $[Re(N_2)(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(PPh_3)]$,[41] $[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (**11a**),[42] $[\{Cp^*WMe_2(SR)\}_2(\mu\text{-}N_2)]$,[43] and $[\{Ta(SR)_3(THF)\}_2(\mu\text{-}N_2)]$.[44] Comparison of electrochemical, spectral, and structural data for **10** with those of **1a** suggests that the $\{Mo(Me_8[16]aneS_4)\}$ unit can exhibit the stronger π-basic character than the related phosphine moiety $\{Mo(dppe)_2\}$ and high reactivities observed for the N_2 ligand in **10** described later may, at least in part, be ascribed to the strong back-donation from the metal to the N_2 ligand. As for the reactivities of the other complexes shown above, few are reported to date except for the protonation of **11a** (vide infra).



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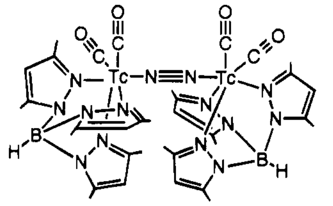

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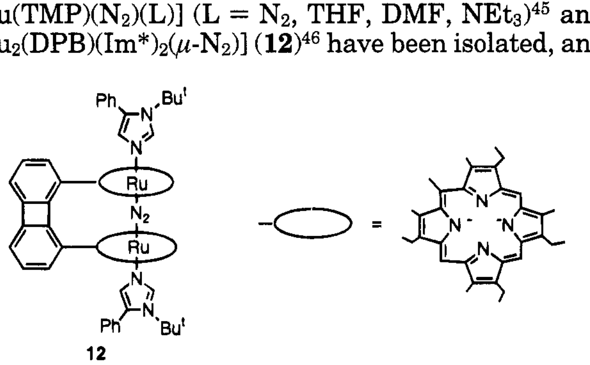
Other N_2 complexes containing biologically important ancillary ligands are those with porphyrins and pyrazolylborate. Mono- and dinuclear Ru complexes $[Ru(TMP)(N_2)(L)]$ (L = N_2, THF, DMF, NEt_3)[45] and $[Ru_2(DPB)(Im^*)_2(\mu\text{-}N_2)]$ (**12**)[46] have been isolated, and the structure of the former (L = THF) has been determined in detail by the X-ray analysis, while two



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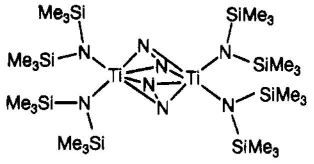
dinuclear complexes $[\{[HB(3,5\text{-}Me_2C_3N_2H)_3]Tc(CO)_2\}_2(\mu\text{-}N_2)]$ (**13**)[47] and $[\{[HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3]Co\}_2(\mu\text{-}N_2)]$[48] have appeared recently as the first examples of the N_2 complex with pyrazolylborate ligand. It is also to be noted that several N_2 complexes of early transition metals such as V (vide supra) and Ti $[\{[(Me_3Si)_2N]_2Ti\}_2(\mu\text{-}N_2)_2]^-$ (**14**)[49] are available by employment of sterically congested amido ligands, which demonstrate another new class of complexes containing N-donor ligands solely or predominantly. Novel mono- and dinuclear N_2 complexes of Mo with triamidoamine ligand $[C_6F_5\text{-}N_3N]$ have also been prepared recently, although the X-ray structure is available only for the silyldiazenido derivative $[[C_6F_5\text{-}N_3N]Mo(NNSiPr^i_3)]$ obtained from $[[C_6F_5\text{-}N_3N]\text{-}Mo(N_2)\{Na(ether)_x\}]$ and Pr^i_3SiCl.[50] Quite recently the dinuclear N_2 complex containing a triamidoamine ligand with Bu^tMe_2Si substituent $[\{[Bu^tMe_2Si\text{-}N_3N]Mo\}_2(\mu\text{-}N_2)]$ (**15**) was successfully isolated and characterized by X-ray crystallography.[51]



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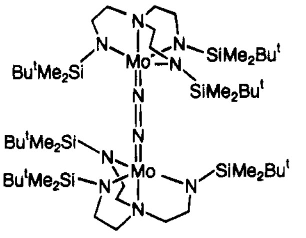

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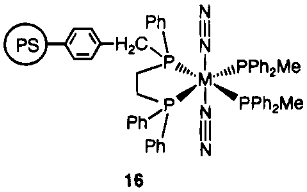
In addition to the thioether, porphyrin, and pyrazolylborate complexes shown above, a significant number of N_2 complexes having tridentate or quadridentate ligands have appeared recently. Most of these contain polyphosphines or modified polyphosphines in which one P atom is replaced by other heteroatoms such as N, O, or S. Among the complexes of this type, those exhibiting interesting properties or reactivities will be referred later.

Another N_2 complex to be noted with respect to the nature of coligand is the resin-supported N_2 complex *trans*-$[Mo(N_2)_2(PS\text{-}diphos)(PPh_2Me)_2]$ (**16**).[52] The N_2 ligand attached to Mo anchored to polystyrene–divinylbenzene (2%) resin through a $CH_2P(Ph)CH_2CH_2PPh_2$ moiety is susceptible to protonation, affording hydrazido(2−) ligand or hydrazine. Polymer-bound N_2 complexes of Mo,[53] Co,[54] and Mn[55] were also reported earlier, but the reactions of coordinated N_2 had not been uncovered in a well-defined manner.



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C. Coordination Modes

Among the various binding modes of N_2 to transition metals summarized in Figure 2, a terminal end-on type (**i**) is most ubiquitous. There exist many structurally characterized complexes of this type, and their N−N bond distances are essentially similar at around 1.12 Å irrespective of the nature of metals and coligands.[10,17] The other well-known coordination mode is an end-on bridging type with the almost linear M−N−N−M linkage (**ii**). For group 4 and 5 metal complexes, type **ii** is commonly observed and type **i** is rather rare. Most of these $\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2$ complexes are homometallic, having a symmetrical structure,[18] but some heterometallic complexes are also known. In the latter are included the Re/Mo,[56] W/Mo,[57] W/Ta,[58] and W/Zr[59] complexes analyzed by X-ray crystallography. The $\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2$ complexes may *formally* be classified into three types, *viz.* those containing the dinitrogen $(N_2)^0$, diazenido(2−) $(N_2)^{2-}$, or hydrazido(4−) $(N_2)^{4-}$ ligand, which may be represented by the form **ii-a**, **ii-b**, or **ii-c**, respectively. Although the choice of the formalism often becomes arbitrary, complexes formulated as **ii-a** show relatively short N−N distances (1.12−1.20 Å), while the N−N bonds in those represented by **ii-c** are much longer and fall in the range of 1.25−1.34 Å.[18] For $[WI(PMe_2Ph)_3(py)(\mu\text{-}N_2)ZrCp_2Cl]$ (**17**), the electron count around two metals as well as the bonding parameters associated with the M−N−N−M moiety might suggest that the N_2 binding mode in **17** can be described by **ii-b** as a predominant form.[59]

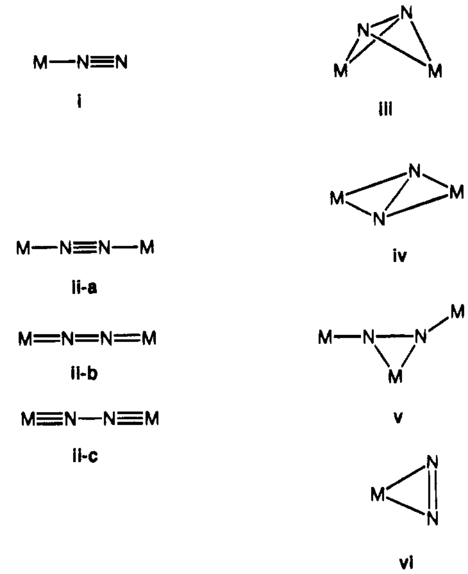
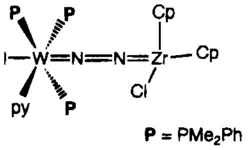


Figure 2. Binding modes of N_2 in mononuclear and multinuclear complexes.



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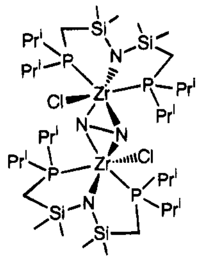
Complexes with a side-on bridging N_2 ligand are also known. Examples of this type initially reported were Ni complexes consisting of a folded M_2N_2 ring (**iii**).[60] More recently dititanium complex **14** has been isolated, whose X-ray study has revealed the presence of two $\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$ ligands of this type **iii**.[49] The N−N bond in this complex is significantly long at 1.38(2) Å. Several side-on bridging N_2 complexes with a planar M_2N_2 moiety (**iv**) have appeared recently. In the Sm complex **7**,[28] the N−N distance (1.09(1) Å) is comparable to those of free N_2 (1.10 Å) and the N_2 bound only to two Li^+ cations in **9** (1.06(1) Å).[30] In contrast, the Zr complex $[\{[(Pr^i_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}N_2)]$ (**18**) has a remarkably long N−N bond at 1.55(1) Å.[61] This and the Sm complex **8**[29] with the N−N bond at 1.525(4) Å, in which the planar Sm_2N_2 core is present but the $\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$ ligand is further bound to four Li^+ cations, are those containing the most elongated N−N units reported to date. The unusually long feature of these N−N bonds is apparent if compared with the N−N distance of 1.47 Å in N_2H_4.

For the $\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$ complex **18** and its Cp derivative containing the $\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2$ ligand $[\{[(Pr^i_2PCH_2SiMe_2)_2N]ZrCp\}_2(\mu\text{-}N_2)]$ (**19**), it has been shown that the resonance Raman spectroscopy can be used as a good measure to distinguish the two modes of N_2 coordination, *viz.* side-on bridging for the former and end-on bridging for the latter. Full assignment of the peaks associated with the N_2 moiety has been done by comparing the spectra of **18** and **19** with those of ^{15}N analogues. In contrast to the spectrum of **18** exhibiting a single intense peak at 1211 cm^{-1}, which can be ascribed to the symmetrical $\nu(NN)$, that of **19** is more complicated due to the presence of many isotope-sensitive peaks, among which the strong 731 cm^{-1} peak can be assigned to a totally symmetric mode composed primarily of $\nu(NN)$ character.[62] Apparent differences in the spectral features between these two types of N_2 ligands may indicate that the resonance Raman spectroscopy provides a convenient method for determining the N_2 bridging mode unambiguously.



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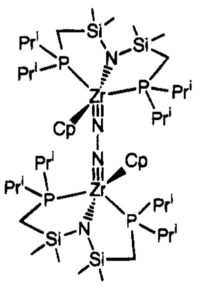

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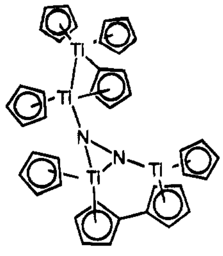
Ab initio quantum calculations performed on the M_2N_2 unit have demonstrated that the unusually long N−N distance observed in **18** can be interpreted in terms of the metal interaction with both the in-plane and the out-of-plane π^*-orbitals of N_2. It has also been concluded that such type of state is stable only for the metals on the very left of the periodic table and not the first-row metals, *i.e.* for Zr and Y.[63]

Another fully characterized coordination mode of N_2 was found in the Ti complex $[\{(C_{10}H_8)Cp_2Ti_2\}\{(C_5H_4)Cp_3Ti_2\}(\mu_3\text{-}N_2)]$ (**20**) reported much earlier, in which the N_2 unit with a N−N distance at 1.30(1) Å exists as a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ ligand (**v**).[64] Side-on coordination of N_2 to a single metal center (**vi**) has not yet been demonstrated, although such a species was proposed as the intermediate of the end-to-end rotation of coordinated $\eta^1\text{-}N_2$ ligand in $[Cp^*Re(CO)_2(N_2)]$.[65] The Zr complex $[Cp_2Zr(CH_2SiMe_3)(N_2)]$ was suggested to contain this $\eta^2\text{-}N_2$ ligand on the basis of EPR and IR data,[66] but details are still uncertain.



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D. Formation of Dinitrogen Ligands

Not only N_2 gas but numerous nitrogenous moieties can be used to synthesize N_2 complexes. In fact, the N_2 ligand in the first N_2 complex $[Ru(NH_3)_5(N_2)]^{2+}$ had its origin in hydrazine. Although N_2 complexes derivable from molecular N_2 seem more attractive in view of the development of effective chemical N_2-fixing systems, those prepared by indirect methods are also of importance in their own right since they also can provide much fundamental information associated with the N_2 chemistry.

Some terminal end-on N_2 ligands have been derived from certain organonitrogen ligands. Thus $[RhCl(N_2)(PPr^i_3)_2]$ has been prepared by thermal decomposition of the diazoalkane complex $[RhCl(N_2CPh_2)(PPr^i_3)_2]$,[67] while $[Cp^*Re(CO)(L)(N_2)]$ has been obtained by treatment of the aryldiazenido complex $[Cp^*Re(CO)(L)(NNC_6H_4OMe\text{-}p)][BF_4]$ with Bu^tLi (L = phosphines, phosphites).[68] Conversion of an organodiazenido ligand into coordinated N_2 had been manifested earlier for the syntheses of a series of Re complexes of the type $[ReCl(N_2)(L)_4]$ from $[ReCl_2(NNCOPh)(PPh_3)_2]$.[69]

For $\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2$ complexes, several new synthetic routes have been developed. These include firstly the coupling of two N_1 moieties; Os complexes $[(pic)_2Cl_3Os(\mu\text{-}N_2)OsCl(pic)_4]^+$ [70] and $[\{Os(NH_3)_4(MeCN)\}_2(\mu\text{-}N_2)]^{5+}$ [71] have been obtained by dissolving $[OsNCl_4]^-$ in neat pic for the former and upon photoirradiation of a mixture of $[Os(NH_3)_4N]^{3+}$ and hexamethylbenzene in MeCN for the latter, respectively, while the oxidative coupling of two ammine ligands in $[(NH_3)_2Ru_2(DPB)(Im^*)_2]$ has afforded a N_2 complex of a cofacial metallodiporphyrin (**12**).[46b]

On the other hand, hydrazine and azine are also used as the sources of the $\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2$ ligand, although formation of a terminal N_2 ligand from N_2H_4 has been well demonstrated, for example, for the Ru complex $[Ru(NH_3)_5(N_2)]^{2+}$ shown above and $[CpM(CO)_2(N_2)]$ (M = Mn,[72] Re[73]) obtained from $[CpM(CO)_2(N_2H_4)]/H_2O_2/Cu^{2+}$. Thus the reaction of N_2H_4 with alkoxide complex $[W(PhCCPh)(OBu^t)_4]$ gives a $\mu\text{-}N_2$ complex $[\{W(PhCCPh)(OBu^t)_2\}_2(\mu\text{-}N_2)]$ accompanied by the liberation of Bu^tOH.[74] Essentially the same method has been used for preparing $[(Cp^*MoMe_3)_2(\mu\text{-}N_2)]$ (**21a**) from $[Cp^*MoMe_3(OC_6H_3Pr^i_2\text{-}2,6)][PF_6]$ and N_2H_4,[57] which has further been extended to the reaction of this aryloxide complex with a hydrazido(2−) complex $[Cp'WMe_3(NNH_2)]$ to give a heterometallic complex $[(Cp^*MoMe_3)(\mu\text{-}N_2)(Cp'WMe_3)]$.[57] As closely related reactions, formation of $[(Cp^*WMe_3)_2$-

(μ-N_2)] (**21b**) or [(Cp^*WMe_3)(μ-N_2)(Cp^*TaMe_2)] from a diazenido complex [{$Cp^*WMe_3(NNH)$}$_2${μ-Mg(TMEDA)}] with [Cp^*WMe_4][PF_6] or [Cp^*TaMe_3Cl], respectively, has been reported,[58] in which the diazenido proton is eliminated as CH_4. Preparation of μ-N_2 complexes by the use of the azine as a N_2 source was reported earlier, as shown, for example, in eq 2.[75]

$$2[M(=CHBu^t)(THF)_2Cl_3] + PhCH{=}NN{=}CHPh \longrightarrow [\{M(THF)_2Cl_3\}_2(\mu\text{-}N_2)] + 2PhCH{=}CHBu^t \quad (M = Nb, Ta) \tag{2}$$

Employment of the electroreductive conditions for the synthesis of low-valent complexes is less common, compared with the use of chemical reduction. Most of the low-valent N_2 complexes are prepared from the higher valent precursors in the presence of reductants such as Na, Mg, and Zn under N_2. For complexes **1**, it has been shown that the controlled potential electrolysis of the solutions containing a range of precursors including oxide,[76] imide,[77] hydrazido(2−),[78] halide, and thiolate[79] complexes under N_2 affords the N_2 complexes in satisfactory yields.

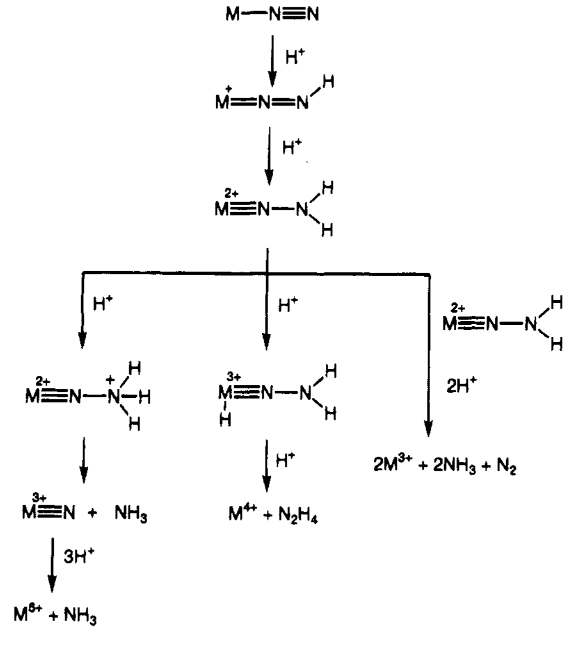
III. Protonation Reactions of Coordinated Dinitrogen

As expected, molecular nitrogen bound to the metal center(s) is activated more or less and in certain complexes it becomes susceptible to protonation under mild conditions. Such reactions have been extensively studied in relation to the biological N_2 fixation. A significant number of mono- and multinuclear N_2 complexes are now available which can facilitate the conversion of N_2 into NH_3 and in some cases into N_2H_4 upon protonation by acid or, less commonly, by water. Although biological N_2 reduction gives NH_3 exclusively as the nitrogen-containing product, it should be noted that the enzyme during turnover has proved to liberate N_2H_4 upon quench by acid or base.[80]

A. Protonation of N_2 Coordinated to a Single Transition Metal Center

Almost quantitative conversion of one N_2 ligand in **2b** into NH_3 by treatment with sulfuric acid in MeOH at room temperature was observed by Chatt and his co-workers in 1975,[81] and since then intensive studies have been made for clarifying the mechanism of N_2 reduction operating in this and related systems using complexes of the type [$M(N_2)_2(\mathbf{P})_4$] (M = W, Mo; **P** = tertiary phosphine). The M−N_2 interactions in end-on N_2 complexes are ascribed to the synergistic σ-bonding and π-back bonding, as is well recognized for CO ligand. Molecular orbital and charge distribution analyses using the model compounds [$M(N_2)_2(PH_3)_4$] have suggested stronger M−N_2 interactions for group 6 metals than the later transition metals with the order of W > Mo > Cr, along with the presence of significant negative charges on the N_2 ligand, especialy on the terminal N atom.[82] The latter feature is in good agreement with the fact that the protonation of these W and Mo complexes proceeds not at the metal center but at the terminal N atom in the N_2 ligand.

Scheme 1



Although formation of NH_3 and/or N_2H_4 upon protonation by acid or water has been demonstrated for a considerable number of N_2 complexes, these Mo and W systems are unique in that several intermediate stages have been isolated and characterized unambiguously. Accumulated data for these systems indicate that the protonation of the N_2 ligand proceeds in a stepwise manner, accompanied by the transfer of required electrons from the central metal to the nitrogenous ligand (Scheme 1). Considerably high yields of nitrogen hydrides presumably arise from the strong reducing power of the W and Mo atoms. The hydrazido(2−) complexes isolated widely[31,83] demonstrate the most important intermediate stage involved in the reduction pathway, and structural details of the hydrazido(2−) ligand have already been clarified by X-ray analyses for more than ten complexes containing dppe,[83a−d] PMe_2Ph,[83e,f] or depe[83g,h] as coligands. All of these complexes contain essentially linear M−N−N linkages in which the N−N bond lengths are of the bond order between 1 and 2 and the M−N distances are suggestive of the multiple bonding nature. Diazenido complexes probably formed prior to the hydrazido(2−) complexes have not yet been isolated directly from the corresponding N_2 complexes but were derived from hydrazido(2−) complexes and weak base (eq 3).[84] Because of the lack of X-ray structure determination, a detailed structure of the diazenido ligand in these complexes is still unknown.

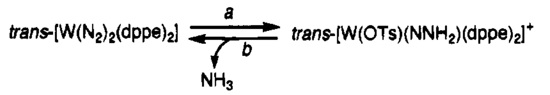
$$[MX(NNH_2)(dppe)_2]^+ \underset{H^+}{\overset{NEt_3\text{ or }K_2CO_3}{\rightleftharpoons}} [MX(NNH)(dppe)_2] \quad X = \text{halide} \tag{3}$$

After the formation of the hydrazido(2−) complexes, reduction is believed to follow the different reaction courses, depending upon the nature of the metal and coligand as well as the reaction conditions. Thus, as proposed for the reaction of **2b** with sulfuric acid in MeOH, further protonation at the terminal nitrogen atom gives a hydrazidium complex and then the following N−N bond scission affords a nitrido complex and NH_3. Additional NH_3 is produced by subsequent acidolysis of the nitrido complex with concurrent formation of M(VI) species.[81b] Recently the first hydrazidium complex *trans*-$[WCl(NNH_3)(PMe_3)_4]Cl_2$ was isolated from the reaction of either *cis*-$[W(N_2)_2(PMe_3)_4]$ or $[WCl(NNH_2)(PMe_3)_4]Cl$ with HCl gas and fully characterized, although the reaction of this hydrazidium complex with HCl in MeOH gives neither NH_3 nor N_2H_4.[85]

In the second reaction course, protonation of the hydrazido(2−) complex occurs at the central metal, generating a hydrido−hydrazido(2−) complex. Subsequent protonation finally results in the predominant formation of N_2H_4 and M(IV) species. Such a mechanism may operate, for example, in the reaction of **2** (M = W, Mo) with HCl gas,[86] and several hydrido−hydrazido(2−) complexes have been isolated and fully characterized.[86,87]

The third reaction course involves the disproportionation of two hydrazido(2−) ligands, forming NH_3 and N_2 together with M(III) product. In contrast to the first and second mechanisms above, this mechanism is essentially intermolecular, where one hydrazido(2−) complex acts as a reducing agent for the other. Reactions of Mo complexes, *e.g.* *trans*-$[Mo(N_2)_2(dpepp)(PPh_3)]$[88] and *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ (**22**), with HBr in THF and protonolysis of the hydrazido(2−) complexes derived from these[44] are considered to follow this pathway. This can be supported by the facts that the N_2 complex **16** as well as the hydrazido(2−) complex $[MoF(NNH_2)(PS\text{-}diphos)(PPh_2Me)_2][BF_4]$, in which the direct interaction between the N_2 ligands or the hydrazido(2−) ligands hardly takes place, give no NH_3 by the reaction with HBr in THF, whereas the addition of soluble Mo or W hydrazido(2−) complexes as the reductant results in the production of NH_3 from the polymer-bound hydrazido(2−) moiety.[52]

These findings have subsequently led to the observation that, in the reactions of both the polymer-bound and the soluble Mo dinitrogen complexes **16**, **22**, and *trans*-$[Mo(N_2)_2(dppee)(PPh_3)]$ with HBr, addition of two electron reducing agents such as Sn(II) and Ge(II) halides considerably increases the yields of NH_3, since all of the hydrazido(2−) ligand generated in this system can be used as the NH_3 source due to the presence of the added reductant.[83c,89] As a related reaction, the two-electron reduction of $[W(OTs)(NNH_2)(dppe)_2]^+$ under the conditions of controlled potential electrolysis have been shown to give NH_3. An interesting feature of the present system is the recovery of the parent N_2 complex *trans*-$[W(N_2)_2(dppe)_2]$ (**1b**) in high yield, which in principle allows for repetition of the cycle involving (*a*) the protonation of the N_2 complex to the hydrazido(2−) complex and (*b*) electroreduction of the hydrazido(2−) complex forming NH_3 accompanied by regeneration of the N_2 complex (eq 4). However, the total amount of NH_3 produced after three cycles in one vessel has been reported to be 0.72 mol/W atom.[78] Further, it should be noted that the evolution of a large amount of H_2 takes place during the electrochemistry when acid is present, *e.g.* in the cycle.



(4)

a) TsOH/THF; *b*) N_2/electrolysis/THF.

The V(−1) complexes **4** and its dmpe analogue, which are isoelectronic with Mo(0) and W(0) complexes shown above, have been reported to give 1 mol of NH_3 per mole of V by treatment with HBr gas.[23b] Concomitant oxidation of the V(-1) center to the V(II) state has been suggested.

Recent elucidation of the nitrogenase active site structure cited above has evoked renewed interest in the chemistry of Fe dinitrogen complexes. Mono- and dinuclear complexes of Fe containing a terminal end-on or bridging N_2 ligand have been known since the early 1970s, but reactivities of coordinated N_2 in these complexes have not been demonstrated except for the replacement by certain π-acceptor ligands. Only the poorly defined complex $[\{FeEt(N_2)(PPh_3)_2\}_2Mg(THF)_4]$ was previously shown to give N_2H_4 (0.11 mol/Fe atom) and NH_3 (0.11 mol/Fe atom).[90] Recent investigation has clarified that the Fe(0) complex $[Fe(N_2)(dmpe)_2]$ generated in situ from $[FeH(N_2)(dmpe)_2]$ and $KOBu^t$ produces NH_3 (0.06−0.12 mol/Fe atom) upon protonation by H_2SO_4 or HCl.[91] The resultant major Fe species was assigned as $[FeCl_2(dmpe)_2]$ for the latter system. Formation of comparable amounts of NH_3 was also observed for $[Fe(N_2)(depe)_2]$ analogously obtained in situ from $[FeH(N_2)(depe)_2]$. Very recently, isolation and full characterization of $[Fe(N_2)(depe)_2]$ have been carried out by a different group, and somehow the isolated complex gave no NH_3 but only N_2 and H_2 gases by acidolysis.[92]

B. Protonation of N_2 Coordinated to More Than Two Transition Metals

Since the complete reduction of coordinated N_2 into NH_3 or N_2H_4 by protonolysis requires the concomitant transfer of six or four electrons, formation of these nitrogen hydrides in high yields from mononuclear N_2 complexes may be expected only for N_2 bound to a strongly reducing metal, which can supply the multielectrons to the coordinated N_2. This presumably accounts, at least in part, for the highly effective NH_3 and N_2H_4 production observed for zero-valent W and Mo complexes described above. On the other hand, multimetallic activation of N_2 may require less electrons per one metal for the formation of nitrogen hydrides, and therefore more diversified metals are possibly used for this transformation.

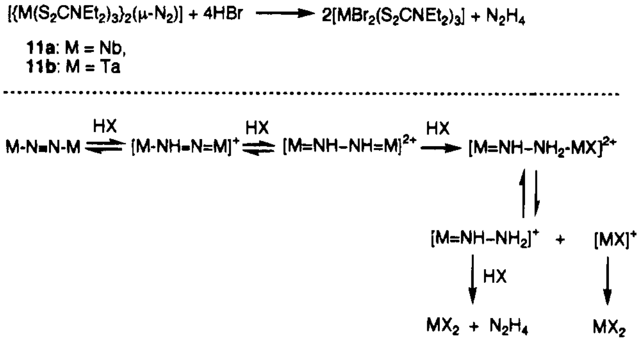
Actually a considerable number of multinuclear N_2 complexes have been proven to afford NH_3 or N_2H_4 by protonolysis under mild conditions. Thus the previous reports described the formation of NH_3 from a binuclear Ni complex dimer $[\{(LiPh)_3(Et_2O)_{1-1.5}Ni\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]_2$[93] and a tetranuclear μ_3-N_2 Ti complex **20**[64] as well as the formation of N_2H_4 from a binuclear Zr complex $[\{Cp^*{}_2Zr(N_2)\}_2(\mu\text{-}N_2)]$[94] and a series of binuclear Ta complexes, *e.g.* $[\{TaCl_3(THF)_2\}_2(\mu\text{-}N_2)]$.[75] In addition, recent studies have demonstrated the formation of NH_3 from **21** (M = Mo,

Table 1. Protonation of Bridging Dinitrogen Ligands Forming Ammonia and/or Hydrazine

complex	acid/solvent	product (%)[a]
$[\{(C_{10}H_8)Cp_2Ti_2\}\{(C_5H_4)Cp_3Ti_2\}(\mu_3\text{-}N_2)]$ (**20**)	H_2O	N_2H_4 (major) + NH_3 (total 90)
$[\{Cp^*Zr(N_2)\}_2(\mu\text{-}N_2)]$	HCl/toluene	N_2H_4 (33)[b]
$[\{(o\text{-}Me_2NCH_2C_6H_4)_2V(py)\}_2(\mu\text{-}N_2)]$ (**3**)	HCl	NH_3 (33)
$[Na\{(2,4,6\text{-}Me_3C_6H_2)_3V\}_2(\mu\text{-}N_2)]^-$ (**6**)	HCl/H_2O	N_2H_4 (36) + NH_3 (11)
$[\{Nb(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (**11b**)	HCl/solvent[c]	N_2H_4 (>90)
$[\{TaCl_3(THF)_2\}_2(\mu\text{-}N_2)]$	HCl/ether	N_2H_4 (80)
$[\{Ta(CH_2Bu^t)_3(THF)\}_2(\mu\text{-}N_2)]$	HCl/ether	N_2H_4 (86)
$[(Cp^*MoMe_3)_2(\mu\text{-}N_2)]$ (**21a**)	HCl/THF	NH_3 (16)
$[(Cp^*WMe_3)_2(\mu\text{-}N_2)]$ (**21b**)	HCl/THF	NH_3 (17)
$[\{(LiPh)_3(Et_2O)_{1-1.5}Ni\}_2(\mu\text{-}N_2)]_2$	H_2O	NH_3 (33)
$[WCl(PMe_2Ph)_4(\mu\text{-}N_2)TiCp_2Cl]$	H_2SO_4/MeOH	N_2H_4 (8) + NH_3 (43)
$[WI(PMe_2Ph)_4(\mu\text{-}N_2)ZrCp_2Cl]$	H_2SO_4/MeOH	N_2H_4 (16) + NH_3 (17)

[a] Based on total nitrogen in the N_2 complex. [b] A half of N_2H_4 results from the initial μ-N_2 ligand. [c] THF, CH_2Cl_2, or MeCN.

Scheme 2



W)[43,57] and V complex **3**,[95] the formation of N_2H_4 from $[\{M(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (M = Nb, **11a**; M = Ta, **11b**)[96] and Zr complexes **18** and **19**,[61b] and the formation of both N_2H_4 and NH_3 from V complex **6**[27] and heterobimetallic complexes $[WX(PMe_2Ph)_4(\mu\text{-}N_2)MCp_2Cl]$ (M = Ti, X = Cl; M = Zr, X = I).[59] These results are summarized in Table 1.

Interestingly, by reaction with HCl, the V alkyl complex **5** liberates the whole coordinated N_2 as a N_2 gas with concurrent formation of neopentane,[24] indicating the attack by proton occurs on the α-carbon atom, while related Ta complex $[\{Ta(CH_2Bu^t)_3(THF)\}_2(\mu\text{-}N_2)]$ is treated similarly to afford N_2H_4 in moderate yield.[75] It should also be noted that the multinuclear Ni and Ti dinitrogen complexes give NH_3 by treatment with such a weak acid as water (Table 1), and in the case of **20** the reaction with HCl instead of water surprisingly results in the evolution of N_2 gas exclusively.[64]

Despite the appearance of many multinuclear N_2 complexes giving nitrogen hydrides, none of these have given any isolable intermediate stages, and the mechanism of the protonation operating on the multimetallic center is still uncertain. It may be quite important to clarify until which stage the multinuclearity of the complex is retained. However, even such a fundamental feature has been specified for only a few of the systems reported to date. For only the Nb and Ta complexes **11** has it been suggested by spectroscopic data that the protonation of N_2 proceeds in a stepwise manner with retention of a dinuclear core until the μ-$NHNH_2$ stage (Scheme 2).[18,96] Another important finding associated with this system is that the proton transfer to the bridging N_2 in **11** is much slower than that of the terminal N_2 in mononuclear $[M(N_2)_2(\mathbf{P})_4]$.[97] This significant difference in the reactivity has been accounted for by attack by a proton at the electrons delocalizing over the M–N–N–M moiety in the former, which is in contrast to the proton attack at the lone-pair electrons localized on the terminal N atom in the latter.

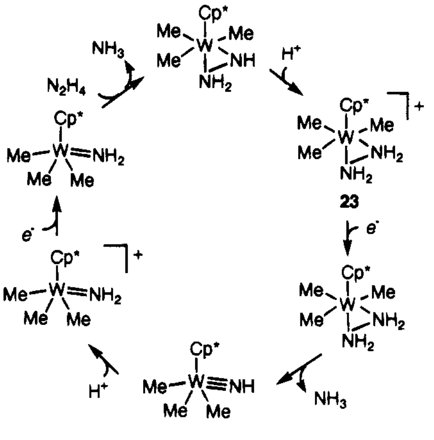
IV. Reactions of Hydrazines Relevant to Nitrogen Fixation

Nitrogenase is a catalyst capable of reducing numerous substrates, and it has been shown that free N_2H_4 is also reduced to NH_3, *i.e.* $N_2H_4 + 2H^+ + 2e^- \rightarrow 2NH_3$.[98] Reactivities of N_2H_4 toward transition metal complexes are therefore of much interest.

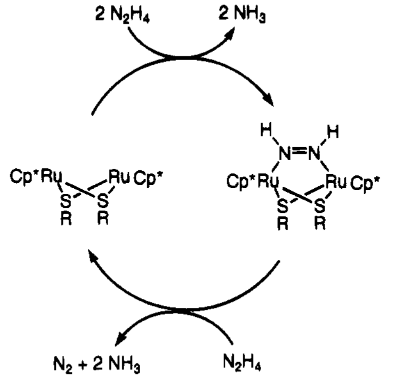
The high-valent mononuclear hydrazine complex $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)][OTf]$ (**23**) prepared from $[Cp^*WMe_3(OTf)]$ and N_2H_4 undergoes reduction by Na/Hg to give NH_3 and $[Cp^*WMe_3(NH)]$. Almost stoichiometric formation of NH_3 has been observed when **23** is reduced by Zn/Hg or Cp_2Co in the presence of lutidine hydrochloride as a proton source. This system has successfully been extended to the catalytic reaction converting N_2H_4 into NH_3. Thus, when **23** is reduced in the presence of 10 equiv of N_2H_4, the yield of NH_3 reaches ca. 16 mol/W atom (Scheme 3).[99] Essentially the same result has been obtained also for the Mo analogue.[100]

In certain systems without external reduction, coordinated N_2H_4 can be converted into NH_3 by the disproportionation reaction, *i.e.* $3N_2H_4 \rightarrow 4NH_3 + N_2$. Recently we have shown that the coordinatively unsaturated diruthenium complex $[Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*]$ catalyzes this reaction effectively.[101] Spec-

Scheme 3



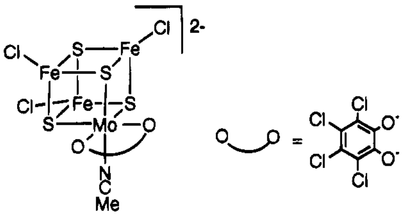
Scheme 4



troscopic data of the reaction mixture suggest the involvement of the μ-diazene complex [Cp*Ru(μ-SPr^i)$_2$(μ-NHNH)RuCp*] as an intermediate. The catalytic cycles proposed for this Ru system are shown in Scheme 4.

The reaction of silylated 2-pyridinethiol 2-HSC$_5$H$_3$N-3-SiMe$_3$ with MoCl$_5$ or [MoCl$_4$(MeCN)$_2$] has been shown to give mononuclear 1*H*-pyridine-2-thione complex [MoCl$_4$(2-SC$_5$H$_3$NH-3-SiMe$_3$)$_2$] or a dinuclear complex with bridging disulfide and the thione ligands, [Mo$_2$Cl$_4$(μ-S$_2$)(μ-2-SC$_5$H$_3$NH-3-SiMe$_3$)(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$], respectively. These two complexes catalyze not only the disproportionation of hydrazine in the absence of an external reductant and a proton source but also the reduction of hydrazine in the presence of Zn/Hg and lutidine hydrochloride. Experimental evidence suggests that for the catalytic NH$_3$ production both systems using the mono- and dinuclear complexes as the catalyst precursor involve the same intermediate [Mo$_2$Cl$_3$(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$].[102]

A more sophisticated model system which relates to the reduction of N$_2$H$_4$ in nitrogenase is found in reactions using MoFe$_3$S$_4$ single cubane clusters [(Cl$_4$-cat)MoFe$_3$S$_4$Cl$_3$(MeCN)]$^{2-}$ (**24**) and [(citr)MoFe$_3$S$_4$Cl$_3$]$^{3-}$ (**25**).[103] In the absence of a reducing agent and a proton source, the disproportionation of N$_2$H$_4$ is slowly catalyzed by the former but not by the latter. On the other hand, by addition of Cp$_2$Co and 2,6-lutidine hydrochloride, both clusters catalyze the reduction of N$_2$H$_4$ into NH$_3$ with good turnovers. The EPR study confirms the retention of the cluster core during the whole turnovers. From the reaction of **24** containing an easily displaceable MeCN ligand with PhNHNH$_2$, [(Cl$_4$-cat)MoFe$_3$S$_4$Cl$_3$(NH$_2$NHPh)]$^{2-}$ has been isolated[103,104] and the stoichiometric and catalytic reduction of the terminally bound PhNHNH$_2$ in this adduct has afforded PhNH$_2$ and NH$_3$, while the N$_2$H$_4$-bridged double cubane [{(Cl$_4$-cat)MoFe$_3$S$_4$Cl$_3$}$_2$(μ-NH$_2$NH$_2$)]$^{4-}$ [105] available from **24** and N$_2$H$_4$ exhibits only a low catalytic activity. In addition, [Fe$_4$S$_4$Cl$_4$]$^{2-}$ shows no catalytic activity. These results suggest that the Mo atom in the MoFe$_3$S$_4$ single cubanes is directly involved as the reaction site in this catalysis. Furthermore, the finding that the activity observed for **25** containing the Mo atom coordinated by tridentate citrate ligand is similar to that of **24** implies that in the structurally resembling FeMo cofactor (Figure 1) the coordinatively saturated Mo atom by bidentate homocitrate as well as one N and three S atoms may also serve as the site of substrate binding and reduction. The hapticity change of the citrate ligand upon protonation, for example, might provide the coordination site for substrate reduction. It has been clarified subsequently that the double cubane cluster [MoFe$_3$S$_4$Cl$_3${SCH(CH$_3$)COO}]$_2$$^{4-}$, which contains the Mo atom coordinated by carboxylate, also exhibits a high catalytic activity. The active species in this system has also been characterized to be a single cubane cluster.[106]



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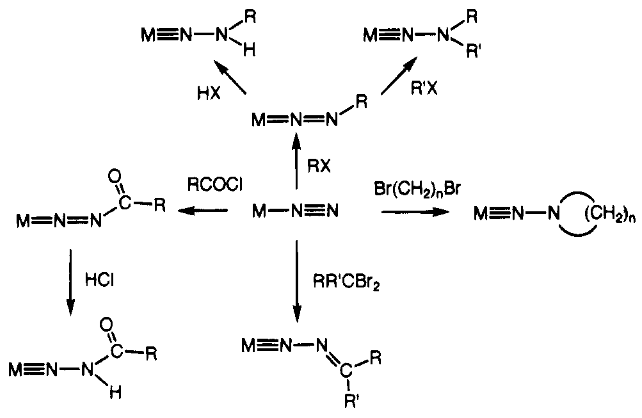
V. Conversion of Coordinated Dinitrogen into Organonitrogen Ligands and Compounds

One-pot synthesis of nitrogen-containing organic compounds from molecular nitrogen may open a new field in organic syntheses. Initial study associated with this area appeared in 1966, which showed the formation of PhNH$_2$ along with NH$_3$ by treatment of Cp$_2$TiCl$_2$ or Cp$_2$TiPh$_2$ with excess PhLi in ether at room temperature and under an atmospheric pressure of N$_2$ followed by hydrolysis. An increase in the N$_2$ pressure up to 80–100 bar considerably raised the yield of PhNH$_2$ (0.10–0.15 mol/Ti atom).[107] However, the details of this reaction are unknown due to the lack of any information about the intermediate species. Several C–N bond-forming reactions that proceed in well-defined N$_2$ complexes have subsequently been clarified, and most of these have been observed for the Mo and W complexes.

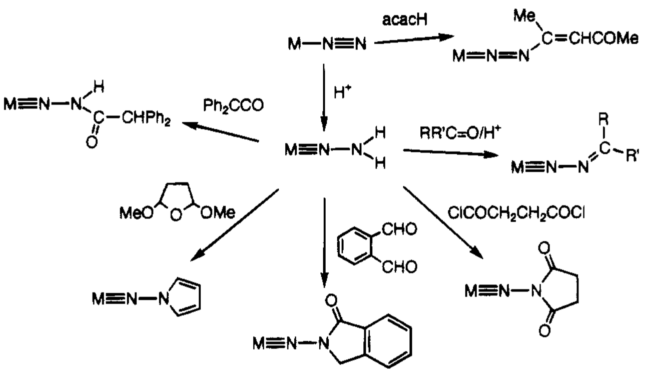
A. C–N Bond Formation at Coordinated N$_2$ by Reaction with Organic Halides

Formation of a C–N bond at the N$_2$ ligand was initially observed in the reactions of Mo and W complexes **1** with RCOCl.[108] The products were characterized to be acyl- and aroyldiazenido complexes *trans*-[MCl(NNCOR)(dppe)$_2$], and the X-ray structure is available for *trans*-[MoCl(NNCOPh)(dppe)$_2$].[109] A similar reaction also proceeds for *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$].[108a] Another C–N bond-forming reaction defined in detail is the formation of alkyldiazenido complexes *trans*-[MX(NNR)(dppe)$_2$] from **1** and alkyl halides under irradiation of a W lamp.[108a,110] The mechanism of this alkylation involves attack of the alkyl radical on the N$_2$ ligand, which is generated by homolysis of RX occurring within the coordination sphere.[111] In contrast, the former acylation is now believed to proceed via nucleophilic attack of the terminal N atom on the acyl carbon.[17] The terminal N atoms in these diazenido ligands are significantly nucleophilic, and a series of acyl-, aroyl-, and alkylhydrazido(2−) complexes *trans*-[MCl(NNHCOR)(dppe)$_2$]$^+$ and *trans*-[MX(NNHR)(dppe)$_2$]$^+$ are readily derived upon protonation by acid. Analogously, dialkylhydrazido(2−) complexes *trans*-[MBr(NNMeEt)-

Scheme 5



Scheme 6



$(R_2PCH_2CH_2PR_2)_2]^+$ (M = Mo, W) have been prepared for R = Et and various aryl groups from the reaction of *trans*-$[MBr(NNEt)(R_2PCH_2CH_2PR_2)_2]$ and MeI that proceeds via an S_N2 mechanism.[112] One-pot dialkylation observed upon treatment of **1b** with MeBr to give *trans*-$[WBr(NNMe_2)(dppe)_2]Br$ is also believed to follow these two steps. A series of dialkylhydrazido(2−) complexes of the type *trans*-$[MBr\{\overline{NN(CH_2)_nCH_2}\}(dppe)_2]Br$ (M = Mo, W; $n = 2-4$) are similarly available by the use of α,ω-dibromides,[113] while extention of this reaction to that with *gem*-dibromide has led to the isolation of diazoalkane complexes *trans*-$[WBr(NNCRR')(dppe)_2]Br$ (R, R′ = H, Me).[114] It should be noted that the C−N bond formation at coordinated N_2 by reaction with alkyl halides is only observed for diphosphine complexes such as **1** but not for monophosphine complexes such as **2**.

The much higher reactivity of the Mo tetrathioether N_2 complex **10** toward organic halides compared with the phosphine complex **1a** is noteworthy. Thus **10** reacts not only with MeI but also with $PhCH_2Br$ to give dialkylhydrazido(2−) complexes *trans*-$[MoX(NNR_2)(Me_8[16]aneS_4)]X$. Furthermore, even aryl halides (ArX) such as PhBr, PhI, and *p*-$MeOCOC_6H_4I$ react readily with **10** to afford novel aryldiazenido complexes *trans*-$[MoX(NNAr)(Me_8[16]aneS_4)]$.[115] Neither benzylation nor arylation of the coordinated N_2 in Mo and W phosphine complexes has been successful except for the arylation using a unique bimetallic system (vide infra).

The C−N bond-forming reactions described in this section are summarized in Scheme 5.

B. C–N Bond Formation at Coordinated N_2 via Hydrazido(2–) or Diazenido Complexes

The Mo and W hydrazido(2−) complexes such as *trans*-$[MF(NNH_2)(dppe)_2][BF_4]$ (**26**) and *cis,mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ (**27**; X = Cl, Br, I), easily derived from the reactions of **1** with aqueous HBF_4 in THF or those of **2** with aqueous HX in MeOH, are not only the important intermediate stages for the reduction of coordinated N_2 but serve as the versatile precursors to prepare organodinitrogen ligands. Owing to the significant nucleophilicity of the terminal N atom, the hydrazido(2−) ligands in **26** and **27** react with various substrates containing a >C=O group, giving a series of organodinitrogen ligands (Scheme 6).

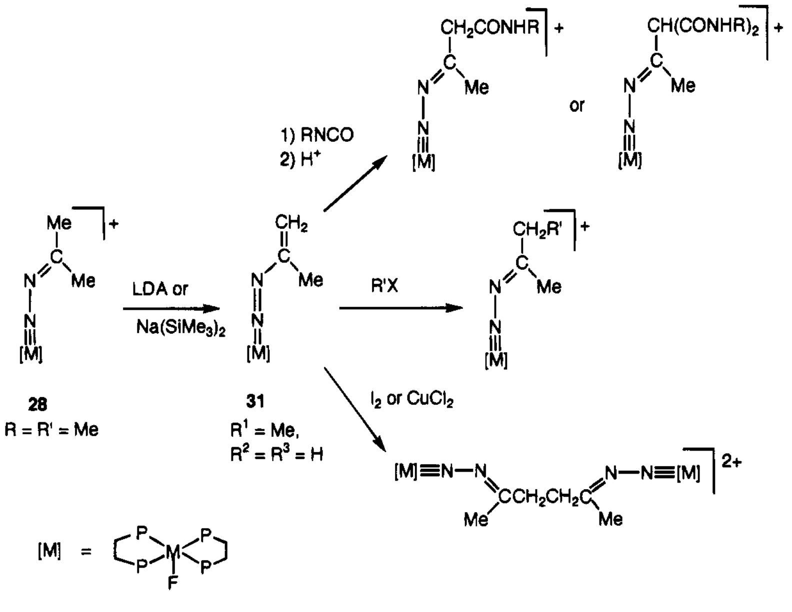
The reaction of **26b** (M = W) with succinyl chloride results in the formation of cyclic diacylhydrazido(2−) complex *trans*-$[WF(\overline{NNCOCH_2CH_2CO})(dppe)_2][BF_4]$ (nucleophilic substitution),[116] while the reaction of **27** (X = Cl) with diphenylketene gives the monoacylhydrazido(2−) complexes $[MCl_2(NNHCOCHPh_2)(PMe_2Ph)_3]$ (nucleophilic addition).[117] Similar reaction of $[MBr(NNH_2)(dppe)_2]Br$ (M = Mo, W) with phenyl isocyanate seems to occur, but the products containing the NNHCONHPh ligand were only poorly characterized.[116]

More intriguing reactions of the hydrazido(2−) ligand are the condensation with ketones and aldehydes to give a numerous body of diazoalkane complexes such as *trans*-$[MF(NN{=}CRR')(dppe)_2][BF_4]$ (**28**) and *cis,mer*-$[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ (**29**).[118] The reactions are markedly enhanced by the addition of catalytic amounts of acid, HBF_4 or HX. Related diazoalkane complexes *trans*-$[WBr(NN{=}CRR')(dppe)_2]Br$ are accessible from the reactions of **1b** with *gem*-dibromides as described already.[114] However, this condensation method may provide a more convenient route to derive diazoalkane ligands since the carbonyl compounds with various substituents are more easily available than *gem*-dibromides. Furthermore, the present method is applicable to both dppe and PMe_2Ph complexes **1** and **2**, whereas the reactions of **2** with organic halides giving diazoalkane complexes are unknown.

Formation of an alkenyldiazenido ligand from a N_2 ligand has been demonstrated for the reaction of **2b** with acetylacetone in MeOH. The product has been spectroscopically characterized to be *mer*-$[W(acac)(NNCMe{=}CHCOMe)(PMe_2Ph)_3]$ (**30**), which has been supported by the X-ray structure determination of its HBr adduct *mer*-$[W(acac)(NNHCMe{=}CHCOMe)(PMe_2Ph)_3]Br$.[119] Formation of the alkenyldiazenido ligand in **30** may proceed via initial protonation presumably by acetylacetone forming hydrazido(2−) ligand and its successive condensation with acetylacetone followed by deprotonation.

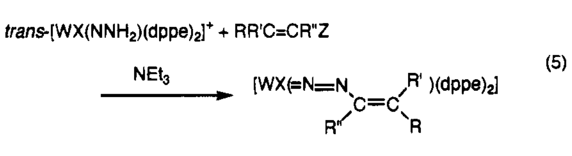
Free diazoalkanes are highly reactive species, but their instability sets the limitation in utilizing these potential reagents for organic synthesis. Reactivities of coordinated diazoalkanes in **28** and **29** derived from a variety of aldehydes and ketones are therefore of particular interest,[120] the study of which may lead

Scheme 7



to the development of new synthetic pathways toward organonitrogen compounds from molecular N_2. The reactions of **28** and **29** demonstrated recently in this context are as follows.

Reactions of diazoalkane complexes **28** formulated as *trans*-$[MF(NN{=}CR^1CHR^2R^3)(dppe)_2][BF_4]$ with LDA or $NaN(SiMe_3)_2$ afford alkenyldiazenido complexes *trans*-$[MF(N{=}NCR^1{=}CR^2R^3)(dppe)_2]$ (**31**) quantitatively.[121] This presents a potential route to a series of alkenyldiazenido complexes. Reactions giving alkenyldiazenido complexes reported earlier had been the formation of **30** from **1b** (vide supra) and the synthesis of *trans*-$[MF(N{=}NCMe{=}CHCOMe)(dppe)_2]$ from **28** (R = Me, R′ = CH_2COMe) and NaOMe.[119] The complexes containing the alkenyldiazenido ligand highly substituted with electron-withdrawing groups were also obtained from the *N*-vinylation reaction of *trans*-$[WX(NNH_2)(dppe)_2]^+$ (X = F, Br) with equimolar amounts of the corresponding alkenes in the presence of NEt_3 (eq 5).[122] The probable nucleophile in this system is not the hydrazido(2−) complex but the diazenido complex $[WX(NNH)(dppe)_2]$ produced in situ from the hydrazido(2−) complex and the base. More recently, another route toward alkenyldiazenido complexes has been clarified, which involves the β-alkylation of α,β-unsaturated diazoalkane complexes by $LiCuR_2$ (eq 6).[123]



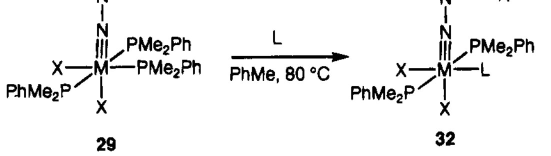
$$\textit{trans}\text{-}[WX(NNH_2)(dppe)_2]^+ + RR'C{=}CR''Z \xrightarrow{NEt_3} [WX(\equiv N{-}N{-}CR''{=}CR'R)(dppe)_2] \quad (5)$$

R = R' = CN, R" = H or Cl, Z = Cl or OEt
R = CN, R' = COOEt, R" = H, Z = Cl

$$[MF(\equiv N{-}N{=}CH{-}CR{=}CHR^1)(dppe)_2]^+ \xrightarrow{LiCuR^2_2} [MF(=N{=}N{-}CH{=}CR{-}CHR^1R^2)(dppe)_2] \quad (6)$$

Complexes **31** are susceptible to electrophilic attack at the terminal alkenyl carbon by RX, PhNCO, RCHO, etc., yielding new diazoalkane complexes containing ligands such as $NN{=}CR^1CR^2R^3R$, $NN{=}CMeCH_2CONHPh$, $NN{=}CMeCH(CONHPh)_2$, and $NN{=}CHCH{=}CHR$. On the other hand, oxidation of **31** ($R^1 = R^2 = H$, $R^3 = Me$; $R^1 = Me$, $R^2 = R^3 = H$) by I_2 or $CuCl_2$ gave dinuclear bis(diazo)alkane complexes $[\{$*trans*-$MF(dppe)_2\}_2(\mu\text{-}NN{=}CR^1CR^2R^3CR^2R^3\text{-}CR^1{=}NN)]$.[121a] Transformations starting from **28** described herein are summarized in Scheme 7 for the case of *trans*-$[MF(NN{=}CMe_2)(dppe)_2]^+$.

In **29**, the PMe_2Ph ligand trans to the halide can be replaced by a range of π-acceptor molecules L at elevated temperatures, and the resultant complexes containing these molecules cis to the diazoalkane ligand *cis,trans*-$[MX_2(NN{=}CRR')(PMe_2Ph)_2(L)]$ (**32**) have been isolated (L = CO, alkene, aldehyde, Bu^tNC) (eq 7).[124] From complexes **32** (L = Bu^tNC) were derived the carbene−diazoalkane complexes *cis,trans*-$[MX_2(NN{=}CMePh)(PMe_2Ph)_2({=}CMeNHBu^t)]$ upon treatment with $AlMe_3$ followed by hydrolysis.[125] In contrast to the formation of **32** from the thermal reaction with CO, **29** (M = W, X = Cl) gives cationic diazoalkane complex *mer*-$[WCl(NN{=}CMe_2)(PMe_2Ph)_3(CO)]^+$ (**33**) when reacted with CO in the presence of $ZnCl_2$(dioxane).[126]

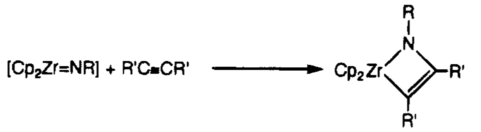


29 **32**

L = CO, alkene, aldehyde, Bu^tNC

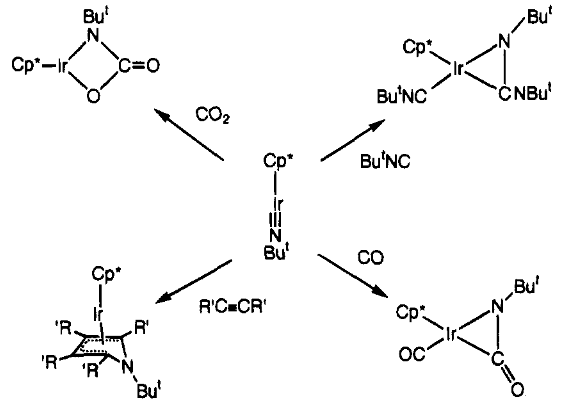
The reactivities of the coordinated L in **32** and CO in **33** toward the adjacent diazoalkane ligand is of particular interest, since this might open the alternative novel routes for preparing a variety of organonitrogenous ligands and compounds. Recently, the highly reactive nature of the metal−imido bonds has been clarified in coordinatively unsaturated Zr and

Ir complexes such as [$Cp_2Zr{=}NR$] generated from either [$Cp_2Zr({=}NR)(THF)$] or [$Cp_2Zr(NHR)_2$] and [$Cp^*Ir{\equiv}NBu^t$]. Thus reactions of the former Zr species with alkynes afforded azametallacyclobutene complexes (eq 8),[127] while treatment of the latter Ir complex with *e.g.* Bu^tNC, CO, CO_2, and alkynes also resulted in the addition of these molecules to the Ir–N multiple bond as depicted in Scheme 8.[128]



(8)

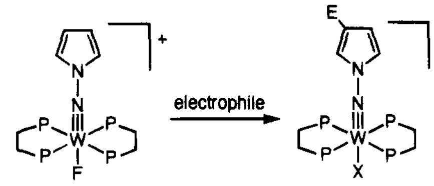
Scheme 8



However, in spite of intensive investigation of the reactivities of the M≡N bond in **32**, its carbene–diazoalkane derivatives, and **33**, any reactions have not yet been found in which the diazoalkane ligand interacts with the substrate species in cis position. It might be noteworthy that reduction of the cationic complex **33** by Mg under CO resulted in the isolation of the dinuclear bis(diazenido) complex [{*trans,trans*-$WCl(CO)_2(PMe_2Ph)_2\}_2(\mu\text{-}N{=}NCMe_2CMe_2N{=}N)$].[126]

Complexes **29** (M = W) also react with excess CH_2X_2 in hot toluene, resulting in the formation of paramagnetic diazoalkane comlexes *mer,trans*-[$WX_3(NN{=}CRR')(PMe_2Ph)_2$] (X = Br, I).[129] The bonding parameters associated with the diazoalkane ligand in this W(V) complex (X = Br, R = Me, R′ = Ph) are quite similar to those in the W(IV) complexes.

Recent extention of the condensation reaction of hydrazido(2−) complexes with monocarbonyl compounds to that with dialdehydes has led to the formation of nitrogen heterocyclic ligands. Thus the reaction of **26** with 2,5-dimethoxytetrahydrofuran, a succinaldehyde equivalent, yields 1-pyrrolylimido complexes *trans*-[$MF(NNCH{=}CHCH{=}CH)(dppe)_2$][$BF_4$] (**34**).[130] Interestingly, the pyrrole ring in **34b** (M = W) undergoes β-regioselective electrophilic substitution reactions; treatment of **34b** with NBS gives only the β-bromo derivative. Exclusive β-cyanation and β-benzoylation also occur, when reacted with chlorosulfonyl isocyanate and $PhCOCl/AlCl_3$, respectively (eq 9). This presents a sharp contrast to the electrophilic substitutions of free pyrrole, which are known to proceed preferentially at the α-position. This remarkable difference in the reactivity between the pyrrole ring in **34b** and free pyrrole is presumably ascribed to the steric effect of the dppe ligands, protecting the α-position of the pyrrole ring.



(9)

34b

electrophile	E	X
NBS	Br	F
$ClSO_2NCO$	CN	F
$PhCOCl/AlCl_3$	COPh	Cl

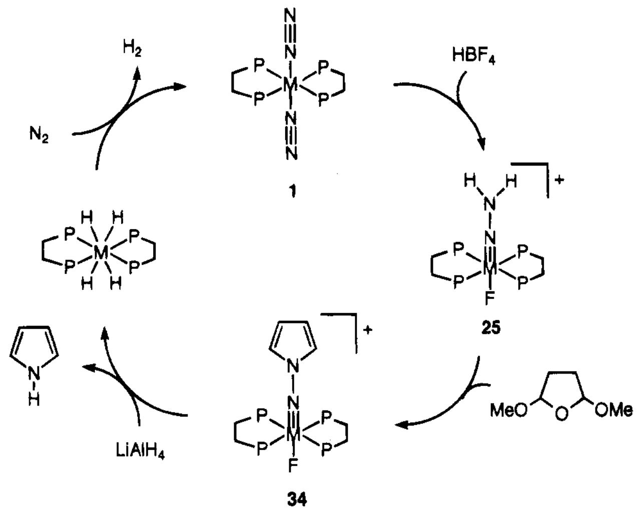
The reaction of **27b** (X = Cl) with phthalaldehyde results in the formation of a phthalimidine ring. For the dppe complex **26b**, only the condensation of the hydrazido(2−) ligand with one aldehyde group proceeds to give the diazoalkane complex *trans*-[$WF(NN{=}CHC_6H_4CHO\text{-}o)(dppe)_2$]$^+$ in high yield. However, this diazoalkane ligand can also be converted into the phthalimidine ring by subsequent reaction with $AlCl_3$ in THF at reflux (Scheme 6).

C. Synthesis of Nitrogen-Containing Organic Compounds from Coordinated N_2

As shown in the previous sections, considerably diversified routes are now available to obtain the organodinitrogen ligands from coordinated N_2, although most of these are still limited to the Mo and W complexes with tertiary phosphine ligands. The products characterized in a well-defined manner include organodiazenido, organohydrazido(2−), or diazoalkane ligands. Much effort has been given to liberating these ligands as the nitrogen-containing organic compounds, since such reactions may provide important information in designing the chemical N_2-fixing system capable of producing organonitrogen compounds catalytically from gaseous N_2. It is now apparent that some organodinitrogen complexes referred above can produce nitrogenous compounds under certain conditions. In this section, the reactions which appeared in fairly old references have also been cited to cover the whole reactivities of organonitrogen ligands.

Initial observation concerning the liberation of organonitrogen compounds was the reductive destruction of the Mo and W dialkylhydrazido(2−) complexes *trans*-[$MBr\{NN(CH_2)_3CH_2\}(dppe)_2$]Br by $LiAlH_4$ at 80 °C for 65 h. Pyrrolidine was obtained in moderate yields after workup of the reaction mixtures with MeOH and then HBr. Analogous treatment of *trans*-[$WBr(NNMe_2)(dppe)_2$]Br afforded Me_2NH in high yield. Direct base distillation of these complexes also resulted in the formation of the amines, although the yields were lower, while treatment of the latter complex with H_2SO_4 afforded $MeNH_2$ and Me_2NH in low yields.[131] In the reaction of **34** with $LiAlH_4$ followed by treatment with MeOH, pyrrole was obtained in high yield along with a small amount of *N*-aminopyrrole.[130] The reaction of **34** proceeds readily at room temperature and completes

Scheme 9



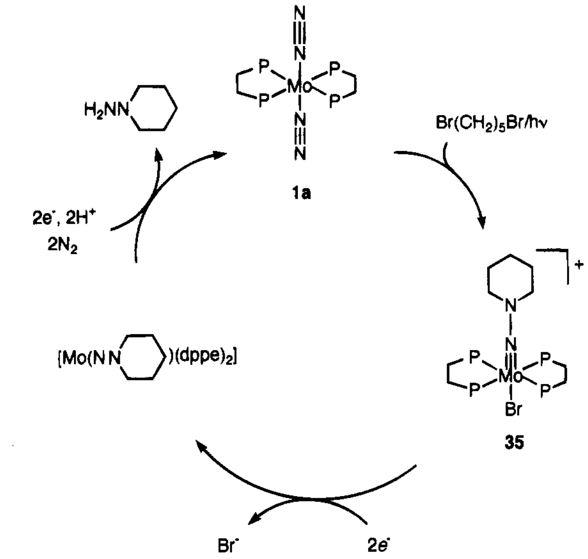
in only 2 h. More importantly, $[MH_4(dppe)_2]$ can be isolated in moderate yields from the resultant reaction mixtures. Since the conversion of these hydrido complexes to the parent N_2 complexes **1** has been reported previously, the present pyrrole synthesis can be represented as the cyclic system shown in Scheme 9.

On the other hand, the reaction with acid also proceeds cleanly, when the hydrazido(2−) complex reduced by two electrons is used. Thus [Mo{$\overline{\mathrm{NN(CH_2)_4}}\mathrm{CH_2}$}(dppe)$_2$], prepared from *trans*-[MoBr{$\overline{\mathrm{NN(CH_2)_4}}\mathrm{CH_2}$}(dppe)$_2$]Br (**35**) by either electroreduction or reaction with LiBu^t, reacted with excess HBr in THF to give piperidine and *trans*-[MoBr(NH)(dppe)$_2$]Br in 74 and 67% yields, respectively.[132]

As for organodiazenido complexes, the reaction of *trans*-[MoBr(NNBu^n)(dppe)$_2$] with $NaBH_4$ or NaOMe in benzene/MeOH at elevated temperature was carried out, which gave NH_3 together with butylamines (Bu^{n}NH$_2$ and Bu^{n}NMeH).[110]

Treatment of the diazoalkane complexes **29** (X = Br, R = R′ = Me) with HX results in the formation of a mixture of N_2H_4 and acetone azine, while that with $LiAlH_4$ gives Pr^{i}NH$_2$ together with NH_3.[118b] Both reactions proceed at room temperature. In relevance to the former system, formation of acetone azine has been observed by treatment of **2b** or *trans*-[W(N$_2$)$_2$(PPh$_2$Me)$_4$] with a MeOH/acetone mixture at 50 °C.[133] Details of this reaction course are uncertain, but the mechanism involving the formation of a hydrazido(2−) complex and the subsequent condensation of this species with acetone forming a diazoalkane complex has been suggested. The Mo complex **2a** gives no azine, but the Mo tetrathioether complex **10** does afford the azine under similar conditions.[115] It is to be noted that conversion of coordinated N_2 into acetone azine was also observed for the reactions of dinuclear Ta complexes such as [{TaCl$_3$(PR$_3$)$_2$}$_2$(μ-N$_2$)] and [{TaL$_3$(THF)}$_2$(μ-N$_2$)] (L = CH$_2$Bu^t, OBu^t) with acetone. In these reactions, formation of acetone azine presumably results from the double bond metathesis between the Ta=N and >C=O units, which may support the diimide structure proposed for these ditantalum complexes.[75]

Scheme 10

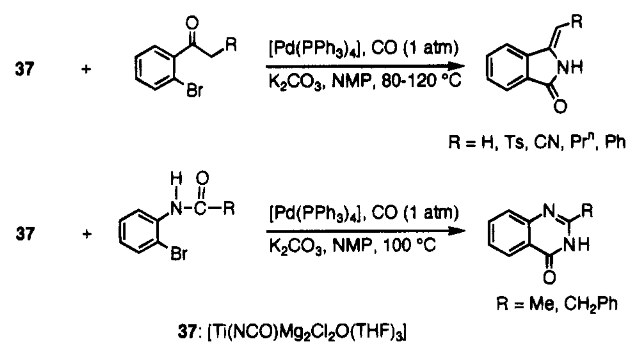


Reactions of organodinitrogen complexes under electroreductive conditions were also investigated previously. An important feature of these systems is that the elimination of the nitrogenous compound may be accompanied by the recovery of the parent N_2 complex in the case of the organodinitrogen complexes containing appropriate coligands. Thus controlled potential electrolysis of **35** (M = Mo) in THF under N_2 gave *N*-aminopyrrolidine and the N_2 complex **1a** in 60−70 and 45% yields, respectively (Scheme 10).[134] As a related reaction, formation of 5-amino-4-cyanopyrazole in ca. 40% yield from dicyanovinylhydrazido(2−) complex *trans*-[WF{NNHCH=C(CN)$_2$}(dppe)$_2$][BF$_4$] under electroreductive conditions has been reported.[135] Dicyanovinylhydrazine may be liberated by electrolysis prior to the cyclization to give the pyrazole. The W species present in the reaction mixture under N_2 was characterized to be the hydrazido(2−) complex **26b**. In these reactions using organohydrazido(2−) complexes, the M−N bond cleavage occurs favorably rather than the N−N bond fission, which presents a sharp contrast to the almost exclusive NH_3 formation from *trans*-[W(OTs)(NNH$_2$)(dppe)$_2$]$^+$ by electrolysis (vide supra).[78]

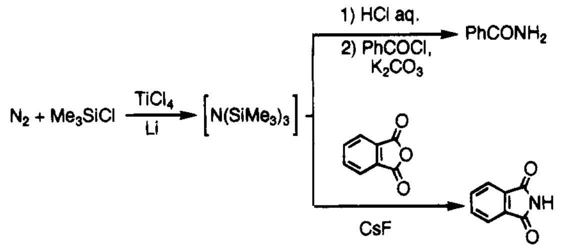
D. Organic Synthesis Using Nitrido Complexes Derived from Molecular N$_2$ as Key Intermediate

In certain systems, molecular nitrogen is incorporated into organometallic compounds with concurrent N−N bond scission, although in most cases the resultant nitrido species are poorly defined. The complex obtained from the reaction of N_2 with a TiCl$_3$/Mg/THF system is believed to be a nitrido species having a composition of [TiNMg$_2$Cl$_2$(THF)] (**36**),[136] which further reacts with PhCOCl or CO_2 to give the Ti compounds formulated as [TiNCl(PhCO)$_{1.5}$][136] or [Ti(NCO)Mg$_2$Cl$_2$O(THF)$_3$] (**37**),[137] respectively. Recently synthesis of a variety of organonitrogen compounds using in situ generated **36** and **37** has been reported.

Scheme 11



Scheme 12



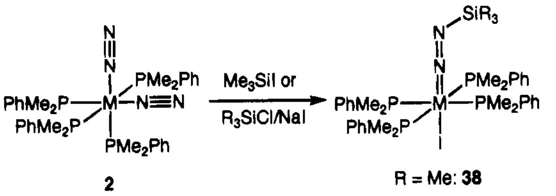
Treatment of **36**, prepared from $TiCl_3$ or $TiCl_4$, with excess aroyl chloride in THF at room temperature or at reflux followed by hydrolysis gives a mixture of $RCONH_2$ and $(RCO)_2NH$. From the reaction of **37** with phthaloyl dichloride or phthalic anhydride in py, phthalimide is obtained. Alternatively, when this reaction using **37** is combined with the carbonylation reaction of aryl halide using $[Pd(PPh_3)_4]$ catalyst, the imides are produced directly from the corresponding aryl halides, *e.g.* $(PhCO)_2NH$ from PhBr and phthalimide from *o*-BrC_6H_4COOH.[138] This combination of carbonylation and nitrogenation has further been extended to the one-step synthesis of isoindolinones from *o*-halophenyl alkyl ketones and that of quinazolinones from *o*-haloanilides (Scheme 11).[139] The related reactions forming indole and quinoline derivatives have also been reported.[140]

More recently, catalytic synthesis of $PhCONH_2$ from PhCOCl has been demonstrated by the use of a mixture of $TiCl_4$/Li/Me_3SiCl under N_2 (2.43 mol/Ti atom). Phthalic anhydride was also converted into phthalimide catalytically in the presence of CsF along with $TiCl_4$/Li/Me_3SiCl under N_2 (2.04 mol/Ti atom).[141] The mechanism proposed for these reactions involves the catalytic formation of $N(SiMe_3)_3$ on the reduced Ti species, which subsequently reacts with HCl(aq) or CsF, respectively, and is finally trapped as the amide or imide (Scheme 12). Catalytic formation of $N(SiMe_3)_3$ was observed earlier by treatment of Me_3SiCl and Li in the presence of several transition metal salts such as $CrCl_3$ under N_2.[142] This catalytic nitrogenation reaction using $TiCl_4$/Li/Me_3SiCl/CsF has also applied to the synthesis of a variety of heterocyclic compounds including indole and pyrrole derivatives using numerous diketo compounds.[143]

Stepwise transformation of nitrido ligand in *trans*-$[MoCl(N)(dppe)_2]$ toward glycine and alanine methyl esters has been demonstrated in a well-defined manner.[144] The nitrido complex may be prepared from **1a** by dialkylation of a coordinated N_2 and subsequent N−N bond cleavage upon acidolysis.[132b] The pathway converting the nitrido ligand into amino acid methyl esters involves initial N−C bond formation by treatment with ICH_2COOMe, giving imido complex *trans*-$[MoCl(NCH_2COOMe)(dppe)_2]I$. Removal of one proton attached to the α-carbon atom gives *trans*-$[MoCl(N{=}CHCOOMe)(dppe)_2]$, which is further treated with MeI to give another imido complex, *trans*-$[MoCl\{NCH(Me)COOMe\}(dppe)_2]I$. The Mo−N bond cleavage in these imido complexes takes place under electroreductive conditions, resulting in the liberation of glycine and alanine methyl esters in 70 and 80% yields, respectively.

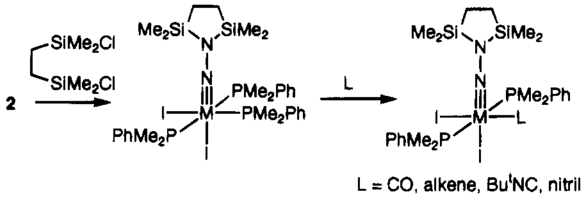
E. Silylation and Germylation of Coordinated N_2 and Catalytic Conversion of Molecular N_2 into Silylamines

The Mo and W complexes **1** and **2** react with Me_3SiI at 50 °C in benzene under rigorouly dry conditions to give the silyldiazenido complexes $[MI(NNSiMe_3)(dppe)_2]$ and *trans*-$[MI(NNSiMe_3)(PMe_2Ph)_4]$ (**38**) (eq 10). In the presence of adventitious moisture, the



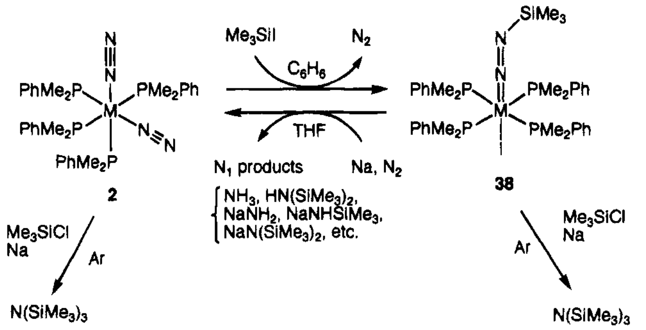
(10)

silylhydrazido(2−) complexes $[MI(NNHSiMe_3)(dppe)_2]I$ and *cis,mer*-$[MI_2(NNHSiMe_3)(PMe_2Ph)_3]$ are also formed.[145] Silylation of the terminal nitrogen in **1b** and **2b** also proceeds by the use of Me_3SiOTf, yielding the corresponding OTf complexes.[146] Although Me_3SiCl does not react with **1** and **2** under similar conditions, treatment of **2b** with Me_3SiCl in the presence of excess NaI results in the formation of **38b** (M = W) in moderate yield. Following this procedure, a variety of silyldiazenido complexes are readily derived from **2b** by the use of numerous R_3SiCl (eq 10).[147] It is to be noted that the further silylation of the silyldiazenido ligands did not proceed in any reactions using excess amounts of monosilyl halides. However, treatment of **2** with a mixture of $ClSiMe_2CH_2CH_2SiMe_2Cl$/NaI afforded disilylhydrazido(2−) complexes *cis,mer*-$[MI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$, and a subsequent replacement of one PMe_2Ph ligand by a series of π-acceptor molecules L gave numerous *cis,trans*-$[MI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2(L)]$ (eq 11).[148] Moreover, the germyldiazenido complexes *trans*-$[WI(NNGeR_3)(PMe_2Ph)_4]$ (R = Me, Ph) were also obtained from the reactions using R_3GeCl in place of R_3SiCl.[147,148a] Silylation of coordinated N_2 by silyl halide has also been observed in the reaction of Mo complex $[[C_6F_5\text{-}N_3N]Mo(N_2)$-



(11)

Scheme 13



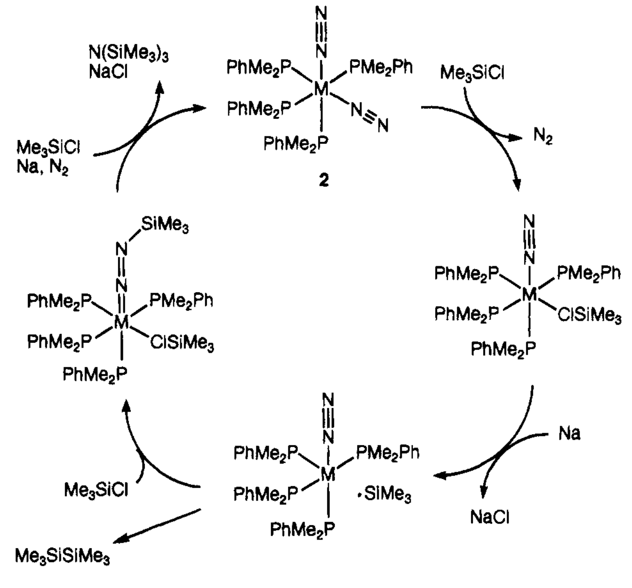
$\{Na(ether)_x\}]$ and Pr^i_3SiCl (vide supra).[50] Further study of the silylation of the N_2 ligand in **1** and **2** has led to the finding that the silylcobalt complex $[Ph_2MeSiCo(CO)_4]$ can also serve as the silylating reagent and the silyldiazenido complexes of the type *trans*-$[\{M(NNSiPh_2Me)(\mathbf{P})_4\}(\mu\text{-}OC)Co(CO)_3]$ have been isolated.[149] Upon protonation by water, MeOH, or HBr, the diazenido complex (M = W, **P** = $^1/_2$ dppe) is converted into a cationic silylhydrazido(2−) complexes *trans*-$[WX(NNHSiPh_2Me)(dppe)_2][Co(CO)_4]$ (X = OH, OMe, Br).

Interestingly the reduction of the silyldiazenido complexes **38** with Na in THF under Ar gives a mixture of N_1 products such as NH_3, $HN(SiMe_3)_2$, $NaNH_2$, $NaNHSiMe_3$, and $NaN(SiMe_3)_2$, along with some N_2 gas. Furthermore, the parent N_2 complexes **2** can be isolated from the reaction mixtures in moderate yields when the reduction is carried out under N_2. In the presence of excess Me_3SiCl under Ar, complexes **38** give $N(SiMe_3)_3$ as a principal nitrogenous product. On the other hand, treatment of **2** with Na in the presence of Me_3SiCl under Ar gives $N(SiMe_3)_3$ in good yield.[146,150] These findings shown in Scheme 13 have led to the attempts in converting N_2 gas directly into $N(SiMe_3)_3$ by using the Me_3SiCl/Na system containing complexes **2** as the catalyst (eq 12). In consequence, the Mo complex **2a** has been found to remarkably facilitate the expected transformation.[150] In an optimum run using the equimolar mixture of Me_3SiCl and Na in the presence of 0.5 mol % of **2a**, $N(SiMe_3)_3$ was obtained in 37% yield (ca. 24 mol/Mo atom) at 30 °C after 15 h. The major byproduct was $Me_3SiSiMe_3$, the formation of which was also accelerated by **2a**. Among the complexes studied, the catalytic activity decreases in the order **2a** ≫ **1a** ≫ **1b**, **2b**.

$$N_2 + Me_3SiCl + Na \xrightarrow[\text{THF}]{\textbf{1}\text{ or }\textbf{2}} N(SiMe_3)_3 + HN(SiMe_3)_2 + Me_3SiSiMe_3 \quad (12)$$

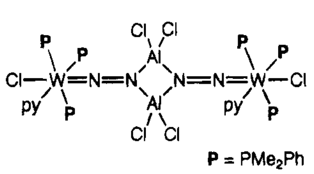
One possible mechanism for the formation of $N(SiMe_3)_3$ along with $Me_3SiSiMe_3$ is depicted in Scheme 14. As in the alkylation of coordinated N_2 (vide supra), the silyl radical $Me_3Si^\bullet$ may be generated by homolytic cleavage of Me_3SiCl within the coordination sphere and then attack on the remaining N_2 ligand to form a silyldiazenido ligand. If the radical couples to each other, $Me_3SiSiMe_3$ may be formed. However, we must await further investigation to elucidate the detailed mechanism for this catalytic N_2 fixation. Other chlorosilanes can also be used for the transformation of N_2 gas into the corresponding silylamines by the catalysis of **2a**, although the turnover was lower.[147]

Scheme 14



VI. Reactions of Coordinated N_2 with Lewis Acids or Organometallic Reagents

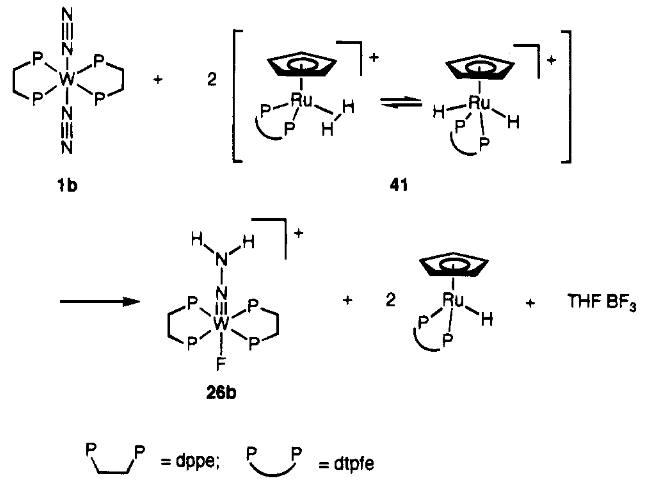
Besides the reactivities toward a variety of protic acids and organic electrophiles described above, reactions of coordinated N_2 with metal species have also been investigated. As expected from the nucleophilicity or basicity of the terminal N atom in an end-on N_2 ligand, the reactions with various Lewis acidic metal compounds result in the formation of the corresponding Lewis acid−base adducts. Thus the adducts with a main group acceptor, *e.g.* $[M(NNAlMe_3)(N_2)(dppe)_2]$ and *trans*-$[ReCl(NNAlMe_3)(\mathbf{P})_4]$ (**P** = PMe_2Ph, $^1/_2$ dppe), as well as those with a transition metal π-acceptor, *e.g.* $[ReCl(PMe_2Ph)_4(NNMCl_5)]$ (M = Nb, Ta) and $[\{ReCl(PMe_2Ph)_4(NN)\}_2MCl_4]$ (M = Ti, Zr), are known.[151] It may be noteworthy that the reactions of **2b** with AlX_3 (X = Cl, Br) in the presence of py afford not the simple adducts but the ditungsten complexes with a bridging $NN(AlX_2)_2NN$ unit, $[\{WX(PMe_2Ph)_3(py)\}_2\{\mu\text{-}NN(AlX_2)_2NN\}]$ (**39**).[152] A structurally similar dicobalt complex, $[\{(Me_3P)_3Co\}_2(\mu\text{-}NN(AlMe_2)_2NN\}]$, was also prepared upon treatment of $[(Me_3P)_3CoNNK]$ with Me_2AlCl.[153] The transition metal heteronuclear complexes $[\{WX(PMe_2Ph)_4\}(\mu\text{-}NN)MCp_2Cl]$ (M = Ti, X = Cl; M = Zr, Hf, X = I)[59] described already are also available in the related reactions of **2b** with Cp_2TiCl_2 or Cp_2MCl_2/NaI (M = Zr, Hf).



39

The N_2 ligand in $[CpMn(CO)_2(N_2)]$ (**40**) can exhibit quite interesting reactivity. Thus **40** reacts with MeLi and then with $[Me_3O][BF_4]$ to give methyldiazene complex $[CpMn(CO)_2(MeN{=}NMe)]$. The initial

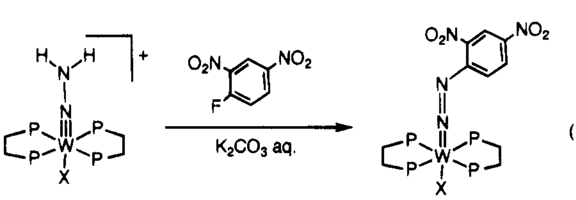
Scheme 15



product obtained from the reaction with MeLi has been formulated as $[CpMn(CO)_2(MeN{=}N^-Li^+)]$, which may be formed by the nucleophilic attack of the Me carbanion on the inner N atom.[154] This reaction was reported as early as 1978, but it is still unique in that the coordinated N_2 undergoes nucleophilic attack, forming the satisfactorily characterizable metal species. When treated with pressurized N_2, the methyldiazene complex is converted into **40** with concurrent liberation of the diazene.

Although **40** does not react with the metal hydrides such as MH (M = Li, Na, K), $LiAlH_4$, and $LiBEt_3H$,[154] **2b** reacts with $NaAlH_2(OCH_2CH_2OMe)_2$ and the base distillation of the evaporated reaction mixture residue gives NH_3 in moderate yield.[155] Reactions of **2** with a range of transition metal hydrides have also been investigated. As expected from the facile NH_3 formation from the reactions with sulfuric acid, **2b** reacts with acidic transition metal carbonyl hydrides such as $[HCo(CO)_4]$, $[H_2Fe(CO)_4]$, and $[HFeCo_3(CO)_{12}]$ to give NH_3 in substantial yields after base distillation of the reaction mixture.[83c,155,156] Besides these acidic hydrides, the hydridic transition metal compound $[Cp_2ZrHCl]$ also reacts with **2** to give NH_3 under the similar conditions.[155] Although any intermediate stages are unknown for the whole reactions of **2** with metal hydrides, a series of hydrazido(2−) complexes, *trans*-$[W(OR)(NNH_2)(dppe)_2][A]$ (A = $Co(CO)_4$, $FeCo_3(CO)_{12}$), were isolated from the reactions of **1b** with $[HCo(CO)_4]$ or $[HFeCo_3(CO)_{12}]$ in various ROH.[83c] Related silylation reaction of **1** and **2b** with $[Ph_2MeSiCo(CO)_4]$ giving the silyldiazenido complexes has been cited already.[149] More recently, formation of **26b** from the reaction of **1b** with 2 equiv of acidic Ru complex $[CpRu(dtfpe)H_2][BF_4]$ (**41**) has been reported (Scheme 15).[157] Complex **41** exists in solution as a slowly interconverting mixture of the dihydrogen and dihydride species $[CpRu(dtfpe)(\eta^2\text{-}H_2)]^+$ and $[CpRu(dtfpe)(H)_2]^+$, the pK_a values of which are estimated to be 4.3 and 4.4, respectively. In this reaction the heterolytic cleavage of the dihydrogen ligand within **41** into HBF_4 and [CpRu(dtfpe)H] is taking place. Formation of **26b** may be important toward development of the N_2-reducing system by H_2, including two different metal sites suitable for activating N_2 and H_2, although at present **41** is not available from gaseous H_2.

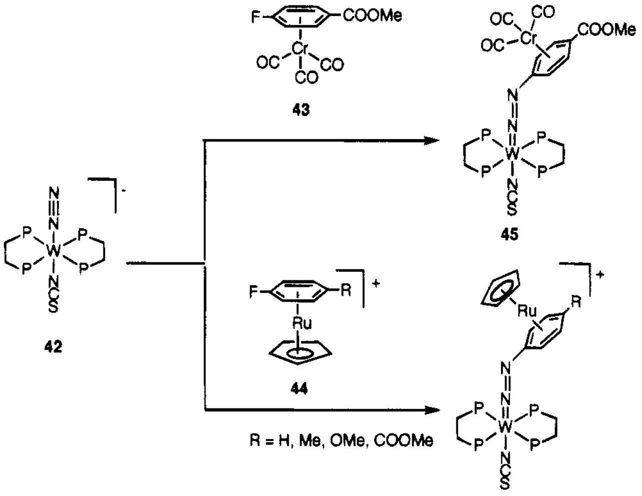
Arylation of coordinated N_2 is of significant interest due to its possible relevance to the synthesis of aromatic amines. Although alkylation of coordinated N_2 proceeds smoothly by reaction with alkyl halides, arylation of coordinated N_2 is hardly accessible, except for the reaction of aryl halides with the Mo tetrathioether complex **10** (vide supra)[115] and the reaction of $2,4\text{-}(O_2N)C_6H_3F$ with in situ generated $[WX(NNH)(dppe)_2]$ (X = F, Br, CF_3COO) (eq 13).[158]



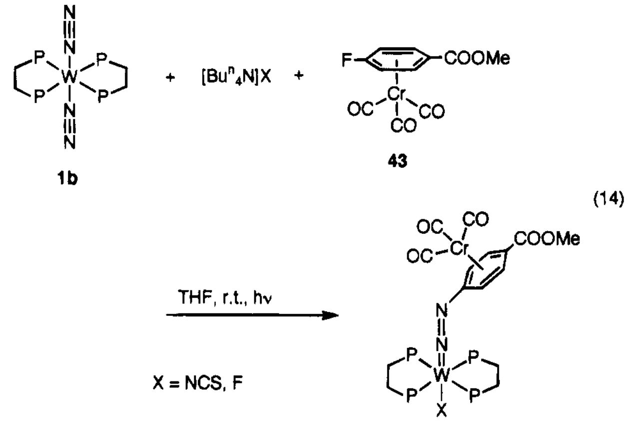
(13)

Recently it has been demonstrated that the anionic N_2 complex *trans*-$[Bu^n_4N][W(N_2)(NCS)(dppe)_2]$ (**42**) reacts with fluoroarene complexes such as $[(\eta^6\text{-}p\text{-}FC_6H_4COOMe)Cr(CO)_3]$ (**43**) and $[CpRu(\eta^6\text{-}FC_6H_4R)][PF_6]$ (**44**, R = H, Me, OMe, COOMe) under ambient conditions to give a series of novel dinuclear μ-aryldiazenido complexes *trans*-$[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dppe)_2]$ (**45**) and *trans*-$[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4R)RuCp]\}(dppe)_2][PF_6]$ (**46**) (Scheme 16).[159] Activation of both the N_2 ligand and the fluoroarene is required here; neither the reaction of the parent neutral complex **1b** with **43** or **44a** (R = H) nor that of the anionic complex **42** with free $p\text{-}FC_6H_4COOMe$ proceeds. It is also to be noted that, in contrast to the smooth reaction of **44a** with **42** to give **46**, the reaction of C_6H_5F bound to the $Cr(CO)_3$ moiety with **42** did not yield the *N*-arylated product, indicating that the $CpRu^+$ is a more efficient activating group for fluoroarenes than $Cr(CO)_3$. On the other hand, the reaction of $[CpFe(\eta^6\text{-}C_6H_5F)][PF_6]$ with **42** presumably results in the redox reaction between these two complexes, since one electron oxidized product $[W(N_2)(NCS)(dppe)_2]$ has been isolated from the reaction mixture.

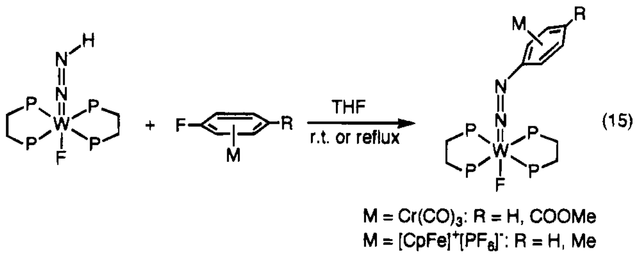
Scheme 16



Instead of starting from isolated **42**, when **1** was treated with **43** in the presence of $[Bu^n_4N]X$ (X = NCS, F) under irradiation by a W filament, the NCS complex **45** and its F analogue are obtained, by way of the in situ generation of $[WX(N_2)(dppe)_2]^-$ (eq 14).



In related reactions, formations of *trans*-$[WF\{N{=}N\text{-}[\eta^6\text{-}p\text{-}C_6H_4R]M\}(dppe)_2]$ (M = $Cr(CO)_3$, R = H; M = $CpFe^+PF_6^-$, R = H, Me) were observed from the reactions of the diazenido complex $[WF(NNH)(dppe)_2]$ with $[(\eta^6\text{-}p\text{-}FC_6H_4R)M]$ (eq 15).[159]



VII. Conclusions

It is now apparent that molecular nitrogen is activated sufficiently through coordination to one or more transition metals to form N–H, N–C, and N–Si bonds under mild conditions. Extensive studies on the synthesis and reactivities of N_2 complexes have disclosed that the reduction of N_2 can be promoted not only by the metals relevant to biological N_2-fixing system such as Fe, Mo, and V but also by the more diversified transition metals. Results of these studies may provide some basis for understanding reduction mechanism operating in the biological N_2-fixing system.

Other important advances in the chemistry of N_2 complexes are found in the discovery of numerous transformations of coordinated N_2 into organonitrogen compounds through the C–N bond formation at coordinated N_2 by reactions with organic compounds. Although the reaction systems demonstrated to date give the organonitrogen compounds mostly in less than stoichiometric amounts, further studies will lead to the development of the effective systems for the production of valuable nitrogen-containing organic compounds directly from molecular nitrogen as a nitrogen source.

VIII. Abbreviations

acac	acetylacetonate
$[Bu^tMe_2Si\text{-}N_3N]^{3-}$	$(Bu^tMe_2SiNCH_2CH_2)_3N$ trianion
$[C_6F_5\text{-}N_3N]^{3-}$	$(C_6F_5NCH_2CH_2)_3N$ trianion
citr	citrate trianion
Cl_4-cat	tetrachlorocatecholate dianion
Cp	η^5-C_5H_5
Cp*	η^5-C_5Me_5
Cp′	η^5-C_5Me_4Et
depe	$Et_2PCH_2CH_2PEt_2$
diglyme	$MeOCH_2CH_2OCH_2CH_2OMe$
dmpe	$Me_2PCH_2CH_2PMe_2$
DPB	diporphyrinatobiphenylene tetraanion
dpepp	$PhP(CH_2CH_2PPh_2)_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
dppee	$O(CH_2CH_2PPh_2)_2$
dppm	$Ph_2PCH_2PPh_2$
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
dtfpe	$(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2$
EXAFS	extended X-ray absorption fine structure
Im*	1-*tert*-butyl-5-phenylimidazole
LDA	$LiNPr^i_2$
$Me_8[16]aneS_4$	3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane
NBS	*N*-bromosuccinimide
NMP	*N*-methylpyrrolidone
OEPG	octaethylporphyrinogen tetraanion
pic	4-picoline
py	pyridine
TMEDA	$Me_2NCH_2CH_2NMe_2$
TMP	tetramesitylporphyrin dianion
Ts	*p*-toluenesulfonyl

IX. References

(1) *Chem. Eng. NY* **1993**, March, 19.

(2) (a) Rees, D. C.; Chan, M. K.; Kim, J. *Adv. Inorg. Chem.* **1994**, *40*, 89. (b) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677. (c) Kim, J.; Rees, D. C. *Nature (London)* **1992**, *360*, 553. (d) Chan, M. K.; Kim, J.; Rees, D. C. *Science* **1993**, *260*, 792. (e) Kim, J.; Woo, D.; Rees, D. C. *Biochemistry* **1993**, *32*, 7104. (f) Kim, J.; Rees, D. C. *Ibid.* **1994**, *33*, 389.

(3) (a) Bolin, J. T.; Campobasso, N.; Muchmore, S. W.; Morgan, T. V.; Mortenson, L. E. In *Molybdenum Enzymes, Cofactors, and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; American Chemical Society: Washington, DC, 1993; p 186. (b) Chen, J.; Christiansen, J.; Campobasso, N.; Bolin, J. T.; Tittsworth, R. C.; Hales, B. J.; Rehr, J. J.; Cramer, S. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1592.

(4) Liu, H. I.; Filipponi, A.; Gavini, N.; Burgess, B. K.; Hedman, B.; Cicco, A. D.; Natoli, C. R.; Hodgson, K. O. *J. Am. Chem. Soc.* **1994**, *116*, 2418.

(5) Deng, H.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1062.

(6) For example: (a) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377. (b) Eady, R. R. *Adv. Inorg. Chem.* **1991**, *36*, 77. (c) Eady, R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2739. See also references therein.

(7) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621.

(8) (a) Vol'pin, M. E.; Shur, V. B. *Dokl. Akad. Nauk. SSSR* **1964**, *156*, 1102. (b) Vol'pin, M. E. *Pure Appl. Chem.* **1972**, *30*, 607.

(9) (a) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. *J. Chem. Soc., Chem. Commun.* **1969**, 1392. (b) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110. (c) Uchida, T.; Uchida, Y.; Hidai, M.; Kodama, T. *Acta Crystallogr.* **1975**, *B31*, 1197.

(10) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(11) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. A. G., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982, Vol. 8; p 1073.

(12) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Radiochem.* **1983**, *27*, 197.

(13) Hidai, M. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Metal Ions in Biology Vol. 7; Wiley-Interscience: New York, 1985; p 285.

(14) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1989; Vol. 2, p 53.

(15) Hidai, M.; Mizobe, Y., in ref 3a, p 346.

(16) George, T. A.; DeBord, J. R. D., in ref 3a, p 363.

(17) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177.

(18) Henderson, R. A. *Transition Met. Chem.* **1990**, *15*, 330.

(19) Leigh, G. J. *J. Mol. Catal.* **1988**, *47*, 363.

(20) Colquhoun, H. M. *Acc. Chem. Res.* **1984**, *17*, 23.

(21) George, T. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; p 405.

(22) Edema, J. J. H.; Meetsma, A.; Gambarotta, S. *J. Am. Chem. Soc.* **1989**, *111*, 6878.

(23) (a) Woitha, C.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1438. (b) Rehder, D.; Woitha, C.; Priebsch, W.; Gailus, H. *J. Chem. Soc., Chem. Commun.* **1992**, 364. (c) Gailus, H.; Woitha, C.; Rehder, D. *J. Chem. Soc., Dalton Trans.* **1994**, 3471.

(24) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004.

(25) Song, J.-I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927.

(26) Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417.

(27) Ferguson, R.; Solani, E.; Floriani, C.; Shiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 396.

(28) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.

(29) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.

(30) Ho, J.; Drake, R. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1993**, *115*, 3792.

(31) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074. (b) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *Ibid.* **1984**, 469.

(32) Mizobe, Y.; Ishida, T.; Egawa, Y.; Ochi, K.; Tanase, T.; Hidai, M. *J. Coord. Chem.* **1991**, *23*, 57.

(33) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139.

(34) Dadkhah, H.; Dilworth, J. R.; Faiman, K.; Kan, C. T.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1523.

(35) (a) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014. (b) Carmona, E.; Galindo, A.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1985**, *24*, 4033.

(36) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1986**, 245.

(37) George, T. A.; DeBord, J. R. D.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295.

(38) Anderson, S. N.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1986**, 1591.

(39) Yoshida, T.; Adachi, T.; Kaminaka, M.; Ueda, T. *J. Am. Chem. Soc.* **1988**, *110*, 4872.

(40) Cruz-Garrits, D.; Gelover, S.; Torrens, H.; Leal, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2393.

(41) Dilworth, J. R.; Hu, J.; Thompson, R. M.; Hughes, D. L. *J. Chem. Soc., Chem. Commun.* **1992**, 551.

(42) Dilworth, J. R.; Henderson, R. A.; Hills, A.; Hughes, D. L.; Macdonald, C.; Stephens, A. N.; Walton, D. R. *J. Chem. Soc., Dalton Trans.* **1990**, 1077.

(43) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331.

(44) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050.

(45) (a) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137. (b) Camenzind, M. J.; James, B. R.; Dolphin, D.; Sparapany, J. W.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 3054.

(46) (a) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1992**, *114*, 8066. (b) Collman, J. P.; Hutchison, J. E.; Ennis, M. S.; Lopez, M. A.; Guilard, R. *Ibid.* **1992**, *114*, 8074.

(47) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Meyer, D.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1993**, *445*, 137.

(48) Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 6979.

(49) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986.

(50) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

(51) Shih, K. Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

(52) (a) Kaul, B. B.; Hayes, R. K.; George, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 2002. (b) George, T. A.; Kaul, B. B. *Inorg. Chem.* **1990**, *29*, 4969.

(53) DuBois, D. L. *Inorg. Chem.* **1984**, *23*, 2047.

(54) Koide, M.; Kato, M.; Tsuchida, E.; Kurimura, Y. *Makromol. Chem.* **1981**, *182*, 283.

(55) Kurimura, Y.; Ohta, F.; Gohda, J.; Nishide, H.; Tsuchida, E. *Makromol. Chem.* **1982**, *183*, 2889.

(56) (a) Mercer, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1637. (b) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 351.

(57) Schrock, R. R.; Kolodzidj, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

(58) Glassman, T. E.; Liu, A. H.; Schrock, R. R. *Inorg. Chem.* **1991**, *30*, 4723.

(59) Mizobe, Y.; Yokobayashi, Y.; Oshita, H.; Takahashi, T.; Hidai, M. *Organometallics* **1994**, *13*, 3764.

(60) (a) Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998. (b) Jonas, K.; Brauer, D. J.; Kruger, C.; Roberts, P. J.; Tsay, Y.-H. *J. Am. Chem. Soc.* **1976**, *98*, 74.

(61) (a) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 8185. (b) Fryzuk, M. D.; Haddad, T. S.; Mylvaganam, M.; McConville, D. H.; Rettig, S. J. *Ibid.* **1993**, *115*, 2782.

(62) Cohen, J. D.; Mylvaganam, M.; Fryzuk, M. D.; Loehr, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 9529.

(63) Blomberg, M. R.; Siegbahn, P. E. *J. Am. Chem. Soc.* **1993**, *115*, 6908.

(64) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482.

(65) Cusanelli, A,; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1719.

(66) Jeffery, J.; Lappart, M. F.; Riley, P. I. *J. Organomet. Chem.* **1979**, *181*, 25.

(67) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480.

(68) Klahn, A. H.; Sutton, D. *Organometallics* **1989**, *8*, 198.

(69) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 612.

(70) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605.

(71) Che, C.-M.; Lam, H.-W.; Tong, W.-F.; Lai, T.-F.; Lau, T.-C. *J. Chem. Soc., Chem. Commun.* **1989**, 1883.

(72) Sellmann, D. *Angew. Chem.* **1971**, *83*, 1017.

(73) Sellmann, D. *J. Organomet. Chem.* **1972**, *36*, C27.

(74) Churchill, M. R.; Li, Y.-J.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 4472.

(75) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.

(76) Hughes, D. L.; Mohammed, M. Y.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1481.

(77) Mohammed, M. Y.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1119.

(78) (a) Pickett, C. J.; Talarmin, J. *Nature (London)* **1985**, *317*, 652. (b) Pickett, C. J.; Ryder, K. S.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1453.

(79) Al-Salih, T. I.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1255.

(80) Thorneley, R. N. F.; Eady, R. R.; Lowe, D. J. *Nature (London)* **1978**, *272*, 557.

(81) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature (London)* **1975**, *253*, 39; (b) *J. Chem. Soc., Dalton Trans.* **1977**, 1852.

(82) Deeth, R. J.; Field, C. N. *J. Chem. Soc., Dalton Trans.* **1994**, 1943 and references therein.

(83) (a) Heath, G. A.; Mason, R.; Thomas, K. M. *J. Am. Chem. Soc.* **1974**, *96*, 259. (b) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694. (c) Nishihara, H.; Mori, T.; Tsurita, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367. (d) George, T. A.; Kaul, B. B.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 1706. (e) Hanson, I. R.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 390. (f) Chatt, J.; Pearman, A. J.; Richards, R. L. *Ibid.* **1978**, 1766. (g) Abu Bakar, M.; Hughes, D. L.; Hussain, W.; Leigh, G. J.; Macdonald, C. J.; Mohd-Ali, H. *Ibid.* **1988**, 2545. (h) Barclay, J. E.; Hills, A.; Hughes, D. L.; Leigh, G. J.; Macdonald, C. J.; Abu Bakar, M.; Mohd-Ali, H. *Ibid.* **1990**, 2503.

(84) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1520.

(85) Galindo, A.; Hills, A.; Hughes, D. L.; Richards, R. L.; Hughes, M.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1990**, 283.

(86) (a) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461; (b) **1979**, *101*, 3405.

(87) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luong-Thi, N. T. *J. Chem. Soc., Dalton Trans.* **1982**, 345.

(88) Baumann, J. A.; Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K.; Noddings, C. M. *Inorg. Chem.* **1985**, *24*, 3568.

(89) George, T. A.; Kaul, B. B. *Inorg. Chem.* **1991**, *30*, 883.

(90) Yamamoto, A,; Miura, Y.; Ito, T.; Chen, H.-L.; Iri, K.; Ozawa, F.; Miki, K.; Sei, T.; Tanaka, N.; Kasai, N. *Organometallics* **1983**, *2*, 1429.

(91) (a) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3041. (b) Leigh, G. J.; Jimenez-Tenorio, M. *J. Am. Chem. Soc.* **1991**, *113*, 5862.

(92) Komiya, S.; Akita, M.; Yoza, A.; Kasuga, N.; Fukuoka, A.; Kai, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 787.

(93) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520.

(94) (a) Sanner, R. D.; Manriquez, R. E.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351. (b) Manriquez, R. E.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *Ibid.* **1976**, *98*, 3042.

(95) Leigh, G. J.; Prieto-Alcon, R.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 921.

(96) (a) Henderson, R. A.; Morgan, S. H.; Stephens, A. N. *J. Chem. Soc., Dalton Trans.* **1990**, 1101. (b) Henderson, R. A.; Morgan, S. H. *Ibid.* **1990**, 1107.

(97) Lane, J. D.; Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1987**, 197.

(98) See, for example: Burgess, B. K. in ref 13, p 161.

(99) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760.

(100) Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 2767.

(101) Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1994**, *33*, 3619.

(102) Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 758.

(103) Coucouvanis, D.; Mosier, P. E.; Demadis, K. D.; Patton, S.; Malinak, S. M.; Kim, C. G.; Tyson, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 12193.

(104) Palermo, R. E.; Singh, R. E.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2600.

(105) Mosier, P. E.; Kim, C. G.; Coucouvanis, D. *Inorg. Chem.* **1993**, *32*, 2620.

(106) Demadis, K.; Coucouvanis, D. *Inorg. Chem.* **1994**, *33*, 4195.

(107) Vol'pin, M. E. *J. Organomet. Chem.* **1980**, *200*, 319 and references therein.

(108) (a) Chatt, J.; Diamantis, A. A.; Heath, G. A.; Hooper, N. E.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 688. (b) Chatt, J.; Heath, G. A.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1972**, 444.

(109) Sato, M.; Kodama, T.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1978**, *152*, 239.

(110) Bossard, G. E.; Busby, D. C.; Chang, M.; George, T. A.; Iske, S. D. A., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 1001.

(111) Chatt, J.; Head, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1638.

(112) Hussain, W.; Leigh, G. J.; Mohd-Ali, H.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1473.

(113) (a) Abu Bakar, M.; Hughes, D. L.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1988**, 2525. (b) Chatt, J.; Hussain, W.; Leigh, G. J.; Terreros, F. P. *J. Chem. Soc., Dalton Trans.* **1980**, 1408.

(114) Ben-Shoshan, R.; Chatt, J.; Leigh, G. J.; Hussain, W. *J. Chem. Soc., Dalton Trans.* **1980**, 771,

(115) Yoshida, T.; Adachi, T.; Ueda, T.; Kaminaka, M.; Sasaki, N.; Higuchi, T.; Aoshima, T.; Mega, I.; Mizobe, Y.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1040.

(116) Iwanami, K.; Mizobe, Y.; Takahashi, T.; Kodama, T.; Uchida, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1773.

(117) Aoshima, T.; Mizobe, Y.; Hidai, M.; Tsuchiya, J. *J. Organomet. Chem.* **1992**, *423*, 39.

(118) (a) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T. Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740. (b) Bevan, P. C.; Chatt, J.; Hidai, M.; Leigh, G. J. *J. Organomet. Chem.* **1978**, *160*, 165. (d) Mizobe, Y.; Uchida, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1781. (e) Mizobe, Y.; Ono, R.; Uchida, Y.; Hidai, M.; Tezuka, M.; Moue, S.; Tsuchiya, A. *J. Organomet. Chem.* **1981**, *204*, 377. (f) Hidai, M.; Mizobe, Y.; Uchida, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7824.

(119) Hidai, M.; Aramaki, S.; Yoshida, K.; Kodama, T.; Takahashi, T.; Uchida, Y.; Mizobe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 1562.

(120) Recent review on the reactions of coordinated diazoalkanes: Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281.

(121) (a) Ishii, Y.; Miyagi, H.; Jitsukuni, S.; Seino, H.; Harkness, B. S.; Hidai, M. *J. Am. Chem. Soc.* **1992**, *114*, 9890. (b) Ishii, Y.; Miyagi, H.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1569. (c) Miyagi, H.; Ishii, Y.; Aoshima, T.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1991**, 611.

(122) Colquhoun, H. M.; Crease, A. E.; Taylor, S. A.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1988**, 2781.

(123) Seino, H.; Ishii, Y.; Hidai, M. *Organometallics* **1994**, *13*, 364.

(124) Aoshima, T.; Tamura, T.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1992**, *435*, 85.

(125) Harada, Y.; Aoshima, T.; Mizobe, Y.; Oshita, H.; Hidai, M. *Chem. Lett.* **1994**, 797.

(126) Aoshima, T.; Tanase, T.; Mizobe, Y.; Yamamoto, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1992**, 586.

(127) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708.

(128) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

(129) Oshita, H.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1993**, *461*, 43.

(130) Seino, H.; Ishii, Y.; Hidai, M. *J. Am. Chem. Soc.* **1994**, *116*, 7433.

(131) Bevan, P. C.; Chatt, J.; Leigh, G. J.; Leelamani, E. G. *J. Organomet. Chem.* **1977**, *139*, C59.

(132) (a) Hussain, W.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1982**, 747. (b) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1989**, 425.

(133) (a) Watakabe, A.; Takahashi, T.; Jin, D.-M.; Yokotake, I.; Uchida, Y.; Hidai, M. *J. Organomet. Chem.* **1983**, *254*, 75. (b) Hidai, M.; Kurano, M.; Mizobe, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2719.

(134) Pickett, C. J.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1033.

(135) Colquhoun, H. M.; Crease, A. E.; Taylor, S. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1158.

(136) Yamamoto, A.; Go, S.; Ookawa, M.; Takahashi, M.; Ikeda, S.; Keii, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3110.

(137) Sobota, P.; Jezowska-Trzebiatowska, B.; Janas, Z. *J. Organomet. Chem.* **1976**, *118*, 253.

(138) Mori, M.; Uozumi, Y.; Shibasaki, M. *J. Organomet. Chem.* **1990**, *395*, 225.

(139) (a) Uozumi, Y.; Kawasaki, N.; Mori, E.; Mori, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1989**, *111*, 3725. (b) Uozumi, Y.; Mori, E.; Mori, M.; Shibasaki, M. *J. Organomet. Chem.* **1990**, *399*, 93.

(140) (a) Uozumi, Y.; Mori, M.; Shibasaki, M. *J. Chem. Soc., Chem. Commun.* **1991**, 81. (b) Mori, M.; Uozumi, Y.; Shibasaki, M. *Heterocycles* **1992**, *33*, 819.

(141) (a) Kawaguchi, M.; Hamaoka, S.; Mori, M. *Tetrahedron Lett.* **1993**, *34*, 6907. (b) Mori, M.; Kawaguchi, M.; Hori, M.; Hamaoka, S. *Heterocycles* **1994**, *39*, 729.

(142) Shiina, K. *J. Am. Chem. Soc.* **1972**, *94*, 9266.

(143) Hori, M.; Mori, M. *J. Org. Chem.* **1995**, *60*, 1480.

(144) Hughes, D. L.; Ibrahim, S. K.; Macdonald, C. J.; Mohd. Ali, H.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1762.

(145) (a) Hidai, M.; Komori, K.; Kodama, T.; Jin, D.-M.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. *J. Organomet. Chem.* **1984**, *272*, 155. (b) Komori, K.; Kodama, T.; Jon, D.-M.; Takahashi, T.; Uchida, Y.; Hidai, M. *Chem. Lett.* **1983**, 465.

(146) Komori, K.; Sugiura, S.; Mizobe, Y.; Yamada, M.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2953.

(147) Oshita, H.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 213.

(148) (a) Oshita, H.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1990**, 1303; (b) *Organometallics* **1992**, *11*, 4116.

(149) Street, A. C.; Mizobe, Y.; Gotoh, F.; Mega, I.; Oshita, H.; Hidai, M. *Chem. Lett.* **1991**, 383.

(150) Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. *J. Am. Chem. Soc.* **1989**, *111*, 1939.

(151) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2429; see also references therein.

(152) Takahashi, T.; Kodama, T.; Watakabe, A.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1983**, *105*, 1680.

(153) Klein, H.-F.; König, H.; Koppert, S.; Ellrich, K.; Riede, J. *Organometallics* **1987**, *6*, 1341.

(154) Sellmann, D.; Weiss, W. *J. Organomet. Chem.* **1978**, *160*, 183.

(155) Hidai, M.; Takahashi, T.; Yokotake, I.; Uchida, Y. *Chem. Lett.* **1980**, 645.

(156) Nishihara, H.; Mori, T.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1980**, 667.

(157) Jia, G.; Morris, R. H.; Schweitzer, C. T. *Inorg. Chem.* **1991**, *30*, 593.

(158) Colquhoun, H. M. *J. Chem. Res., (Synop.)* **1979**, 325.

(159) (a) Ishii, Y.; Kawaguchi, M.; Ishino, Y.; Aoki, T.; Hidai, M. *Organometallics* **1994**, *13*, 5062. (b) Ishii, Y.; Ishino, Y.; Aoki, T.; Hidai, M. *J. Am. Chem. Soc.* **1992**, *114*, 5429.

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