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Accounts

Toward Direct Synthesis of Organonitrogen Compounds from Dinitrogen: The Chemistry of Diazoalkane Complexes Derived from Dinitrogen Complexes

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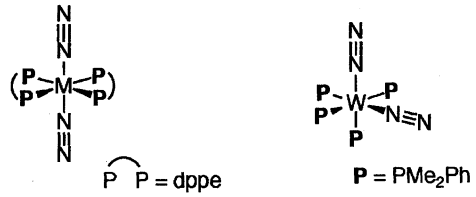
The hydrazido complexes *trans*-$[MX(NNH_2)(dppe)_2]^+$ (**3**) and *cis,mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ (**4**) (M = Mo, W; X = halogen; dppe = 1,2-bis(diphenylphosphino)ethane), which are readily derived from dinitrogen complexes *trans*-$[M(N_2)_2(dppe)_2]$ (**1**) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**2**) by protonation with acid, undergo condensation with aldehydes or ketones (RR′C=O) to give a series of diazoalkane complexes, *trans*-$[MX(NNCRR')(dppe)_2]^+$ and *cis,mer*-$[MX_2(NNCRR')(PMe_2Ph)_3]$. The diazoalkane ligand in those complexes has a singly-bent structure with the N–N–C bond angle of ca. 120° and the essentially linear N–N–M bond, and may be regarded as a four-electron-donating ligand. Owing to the conjugate structure including the metal center M≡N–N=CRR′, the diazoalkane complexes exhibit various reactivities including nucleophilic addition, deprotonation, conjugate addition, and reductive dimerization. Condensation of hydrazido complexes **3** and **4** with dialdehydes or their equivalents leads to complexes with nitrogen heterocyclic ligands incorporating the terminal nitrogen atom by way of the cyclization of intermediary diazoalkane complexes. By this method are prepared complexes containing phthalimidine, 1,3-dihydro-2*H*-pyrrol-2-one, 1,5-dihydro-2*H*-pyrrol-2-one, and pyrrole moieties. Interestingly, the (1-pyrrolyl)imido complexes with dppe ligands *trans*-$[MX(NNCH{=}CHCH{=}CH)(dppe)_2]^+$ (**26**; M = Mo, W) undergo unusual electrophilic substitution reactions at the β-position of the pyrrole ring. Various types of organonitrogen compounds such as acetone azine, pyrazoles, phthalimidines, pyrroles, and *N*-aminopyrrole are liberateded from the above complexes in good yields. As a typical reaction, pyrrole and *N*-aminopyrrole are formed by the $LiAlH_4$ reduction of complexes **26**. In this reduction, tetrahydrido complexes $[MH_4(dppe)_2]$ (M = Mo, W) are obtained as the metal products, which can be converted back to the starting dinitrogen complexes **1**. Thus, a synthetic cycle for the formation of pyrrole and *N*-aminopyrrole from dinitrogen has been accomplished by using dinitrogen complexes **1**.

Dinitrogen has been regarded as one of the most inert molecules, which hardly undergoes chemical transformation under usual conditions. Industrially, organonitrogen compounds fundamentally depend for their nitrogen source on ammonia produced by the Haber–Bosch process, where very harsh reaction conditions are required in order to activate dinitrogen to react. Therefore, it is a fascinating and challenging goal to develop chemical processes which enable direct transformation of dinitrogen into organonitrogen compounds under mild conditions.

It is now well-known that low valent metal centers with adequate ancillary ligands react with dinitrogen to form dinitrogen complexes. Recent advances in the chemistry of dinitrogen complexes can be followed in several excellent reviews.[1] Among a wide variety of dinitrogen complexes known to date, bis(dinitrogen) complexes of molybdenum and tungsten with tertiary phosphine ligands *trans*-$[M(N_2)_2(dppe)_2]$[2,3] (**1a**, M = Mo; **1b**, M = W; dppe = 1,2-bis(diphenylphosphino)ethane) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$[3,4] (**2a**, M = Mo; **2b**, M = W) are quite unique (Chart 1). Since the first discovery of **1a** in this laboratory in 1969, these dinitrogen complexes have attracted outstanding attention, because they can be readily prepared on a large scale, and more importantly, C–N bond formation occurs at the coordinated dinitrogen by reaction with organic compounds, which is essential for direct syntheses of organonitrogen compounds from dinitrogen.

Thus, the ligating dinitrogen in the diphosphine complexes **1** undergoes alkylation or acylation by reaction with alkyl or acyl halides to form alkyldiazenido (NNR) or acyldiazenido



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

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

Chart 1.

(NNCOR) ligands, respectively.[1] However, the monophosphine (PMe_2Ph) complexes **2** often liberate dinitrogen on treatment with organic halides and no C–N bond formation in **2** has been observed.[5] In contrast, silylation and germylation of coordinated dinitrogen smoothly proceed in both **1** and **2** by reaction with silyl and germyl halides, respectively.[6] Moreover, complex **2a** acts as an active catalyst for the formation of silylamines from dinitrogen, silyl chlorides and sodium.[7] Arylation of the coordinated dinitrogen in **1** has also been achieved through activation of aryl fluorides on chromium and ruthenium species.[8]

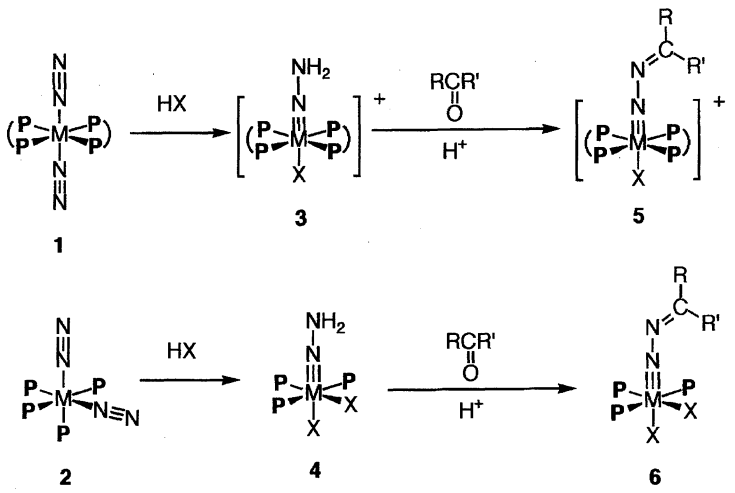
Another intriguing and more versatile reactions have been developed in this laboratory which lead to the C–N bond formation at the coordinated dinitrogen in both **1** and **2**. The reactions comprise two steps. The first step is protonation of the coordinated dinitrogen by acid (HX) to form hydrazido complexes *trans*-$[MX(NNH_2)(dppe)_2]^+$ (**3**) and *cis,mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ (**4**). The second step is the condensation reaction of hydrazido complexes **3** and **4** with aldehydes or ketones ($RR'C{=}O$) to give diazoalkane complexes *trans*-$[MX(NNCRR')(dppe)_2]^+$ (**5**) and *cis,mer*-$[MX_2(NNCRR')(PMe_2Ph)_3]$ (**6**) (Scheme 1).[9,10]

Diazoalkane complexes themselves have been a subject of intense interest in inorganic and organometallic chemistry,[11] not only because the coordination modes of diazoalkanes are quite diversified, but also because diazoalkane complexes are considered as a key intermediate in the metal complex-catalyzed cyclopropanation.[12] Usually diazoalkane complexes have been prepared by reaction of metal fragments with free diazoalkanes, and several special types of diazoalkane complexes have been obtained by using other nitrogenous compounds such as azine, hydrazone, and diazirine. In contrast, the diazoalkane ligand in Scheme 1 is prepared by combining a dinitrogen unit and an aldehyde or ketone unit on the metal center. It is of great interest that a variety of diazoalkanes, which easily lose dinitrogen if not stabilized by coordination, can be readily prepared starting from dinitrogen. In addition, the unique structure of diazoalkane complexes **5** and **6** with the conjugated M≡N–N=C system endows rich reactivities to the ligand. Here we wish to summarize our recent studies on the synthesis, structures, and reactivities of the diazoalkane complexes toward the direct synthesis of organonitrogen compounds from dinitrogen.

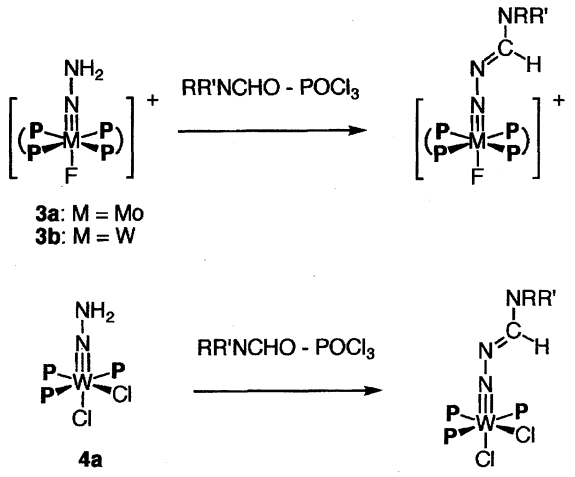
Synthesis and Structures of Diazoalkane Complexes Derived from Dinitrogen Complexes. Condensation of hydrazido complexes **3** and **4** with aldehydes or ketones yields a series of molybdenum or tungsten complexes with diazoalkane ligands (N_2CRR') in high yields (Scheme 1).[9,10] The reaction is much accelerated by the addition of a catalytic amount of acid, especially in the reactions with ketones, and this condensation can be applied to a wide variety of carbonyl compounds to introduce an organic group onto the coordinated dinitrogen.

The W(V) hydrazido complexes *mer,trans*-$[WX_3(NNH_2)(PMe_2Ph)_2]$ derived from **4** also react with carbonyl compounds to form the W(V) diazoalkane complexes *mer,trans*-$[WX_3(NNCRR')(PMe_2Ph)_2]$.[13] Carbonyl groups in esters and amides do not react directly with hydrazido complexes **3** and **4**. However, Vilsmeier reagents, which can be readily prepared from *N,N*-dialkylformamides and $POCl_3$, smoothly react with **3a** (M = Mo, X = F), **3b** (M = W, W = F), and **4a** (M = W, X = Cl) to give (dialkylamino)diazomethane complexes in good yields (Scheme 2).[14]

Similar diazoalkane complexes, *trans*-$[MBr(NNCRR')(dppe)_2]Br$ were previously obtained from the reactions of dinitrogen complexes **1** with *gem*-dibromides $RR'CBr_2$ under photoirradiation conditions.[15] However, this method is not applicable to the dinitrogen complexes **2** having PMe_2Ph li-



Scheme 1.

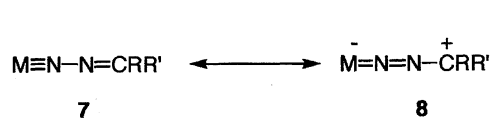


Scheme 2.

gands, and availability of *gem*-dibromides is limited. Therefore, the condensation method is much more practical for preparation of a variety of diazoalkane complexes.

Diazoalkane complexes **5** and **6** have been well-characterized by spectroscopic and X-ray diffraction studies. Pertinent bond lengths and angles of diazoalkane complexes are given in Table 1. The M–N–N linkage is essentially linear, whereas the N–N–C bond is bent with a bond angle of 116—125°. The N–N and N–C distances lie in the range of 1.27—1.35 Å and 1.29—1.32 Å, respectively, both being intermediate between a single and a double bond. Based on these structural features, the diazoalkane ligands in these molybdenum and tungsten complexes are considered to behave as a formal four-electron donor represented as M≡N–N=CRR′ (**7**), and receive some contribution of the resonance structure M^-=N=N–C^+RR′ (**8**), especially when R and R′ substituents are alkyl groups (Scheme 3). In aryl(diazo)methane complexes of tungsten, contribution of another resonance structure M^+=N=N–C^-RR′ has been proposed on the basis of their IR data.[20] The short M–N distances clearly reflect the M–N multiple bonding character. The IR spectra of these diazoalkane complexes exhibit a characteristic ν(C=N) absorption in the region between 1510 and 1590 cm^{-1}.

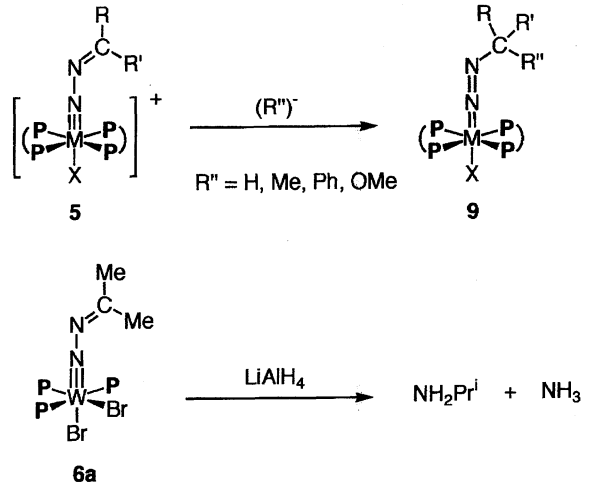
Similar singly-bent diazoalkane ligands are also found in molybdenum and tungsten complexes such as [M(NNCHR)(CO)($S_2CNR'_2$)$_2$], [21] [M(NNCHR)X_2($S_2CNR'_2$)$_2$] [21] (M = Mo, W; R = Ph, *p*-Tol; R'_2 = Me_2, Et_2, $(CH_2)_4$; X = Cl, Br), [Mo(NNCPh_2)(OBu^t)$_4$], [22] and [CpMo{C(*p*-Tol)$_2$}{NNC(*p*-Tol)$_2$}MoCp(CO)$_3$] [23] (Cp = η^5-C_5H_5), which are prepared directly from diazoalkanes.



Scheme 3.

Reactivities of Diazoalkane Ligands Derived from Dinitrogen. The diazoalkane complexes **5** and **6** may be regarded as metallohydrazone and have some contribution of the resonance structure **8**. Thus, they are susceptible to nucleophilic attack at the diazo carbon atom. Diazoalkane complexes **5** undergo nucleophilic attack by $LiAlH_4$, alkyllithium or NaOMe to form the corresponding diazenido complexes **9**.[15] Further, the complex **6a** (M = W, R, R′ = Me, X = Br) reacts with $LiAlH_4$ to yield isopropylamine and ammonia after hydrolysis (Scheme 4).[10]

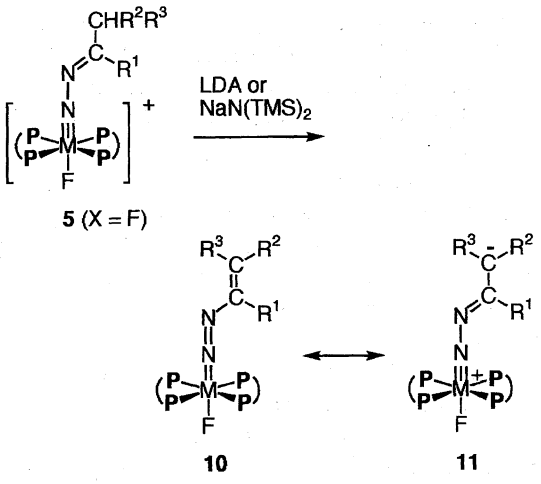
Treatment of diazoalkane complexes **5** and **6** with base gives the corresponding Mo(II) or W(II) alkenyldiazenido complexes such as **10** (Scheme 5). When the diazoalkane ligand bears an electron-withdrawing group at the β-position of the diazo group, such deprotonation becomes facile and the corresponding alkenyldiazenido complexes are isolated as stable products.[24] In contrast, deprotonation of diazoalkane complexes without electron-withdrawing functional groups proceeds by using strong bases such as lithium diisopropylamide (LDA) or $NaN(SiMe_3)_2$, and only sterically bulky alkenyldiazenido complexes can be isolated in pure form.[25]



Scheme 4.

Table 1. Structural Parameters Found in Diazoalkane Complexes Derived from Dinitrogen Complexes

Complex	M–N/Å	N–N/Å	N–C/Å	M–N–N/°	N–N–C/°
trans-[WF(NNCMeCH_2COMe)(dppe)$_2$][BF_4] [9a]	1.77(2)	1.32(2)	1.30(3)	174(2)	125(2)
trans-[WBr(NNCMe_2)(dppe)$_2$]Br [16]	1.724(12)	1.355(18)	1.290(17)	171.3(7)	123.9(11)
trans-[WBr(NNCH$(CH_2)_3$OH)(dppe)$_2$][PF_6] [16]	1.772(13)	1.32(2)	1.30(3)	172.6(12)	116.2(15)
trans-[WF(NNCMeCH(CONHPh)$_2$(dppe)$_2$][BF_4] [17]	1.77(1)	1.33(2)	1.30(3)	170.4(12)	122.2(16)
mer,trans-[WBr_3(NNCMePh)(PMe_2Ph)$_2$] [13]	1.810(9)	1.27(1)	1.30(2)	167.5(10)	120.0(12)
cis,trans-[WCl_2(NNCMePh)(=CMeNHBu^t)(PMe_2Ph)$_2$] [18]	1.770(17)	1.31(2)	1.32(3)	170.6(13)	118.1(13)
cis,trans-[WCl_2(C_2H_4)(NNCMe_2)(PMe_2Ph)$_2$] [19]	1.750(6)	1.34(1)	1.29(1)	167.3(6)	116.7(7)



Scheme 5.

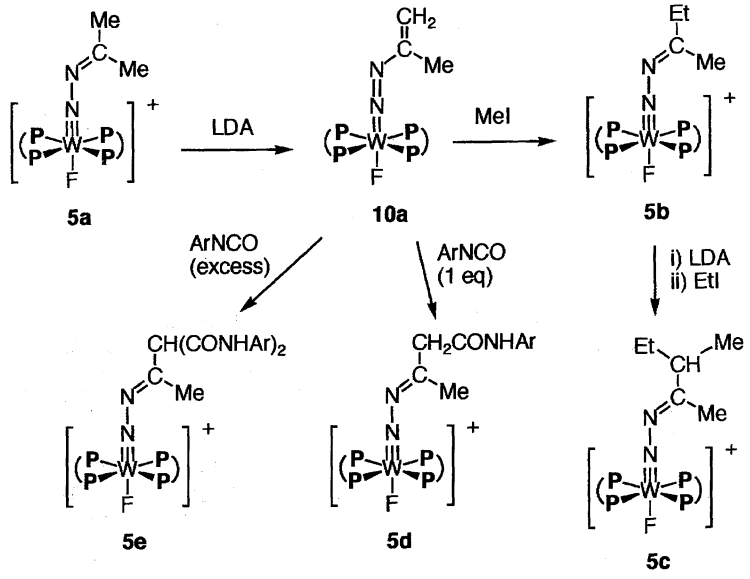
The X-ray analysis of the molecular structure of an alkenyldiazenido complex *trans*-[WF(N=NCH=CMe$_2$)(dppe)$_2$] [25a] shows that the N=N bond length (1.29(3) Å) is relatively long, while the N–C bond length (1.26(3) Å) is short. These structural features are in full agreement with the IR spectra, which exhibit the ν(N=N) absorption at 1376—1448 cm^{-1} and the ν(C=C) band at 1567—1610 cm^{-1}. These findings strongly support the existence of a considerable contribution of the resonance structure **11** (Scheme 5), in which the terminal carbon of the C=C bond is negatively charged. Evidently the metal center accommodates the positive charge to stabilize the charge-separated resonance structure.

Another interesting point of this deprotonation is the regio- and stereoselectivity with regard to the C=C double bond formed. Thus, the 2-diazopropane complex *trans*-[WF(NNCMe$_2$)(dppe)$_2$]$^+$ (**5a**) undergoes the deprotonation regioselectively at the *exo*-Me group to give *trans*-[WF(N=NCMe=CH$_2$)(dppe)$_2$] (**10a**) (Scheme 6). This regioselectivity is particularly advantageous for the selective modification of diazoalkane ligands (vide infra). On the other hand, deprotonation of the 1-diazopropane complex *trans*-[WF(NNCHEt)(dppe)$_2$]$^+$ with NaN(SiMe$_3$)$_2$ shows interesting *Z*-selectivity and a 12 : 1 mixture of *Z* and *E* isomers of *trans*-[WF(N=NCH=CHMe)(dppe)$_2$] (**10b**) is obtained at 0 °C.

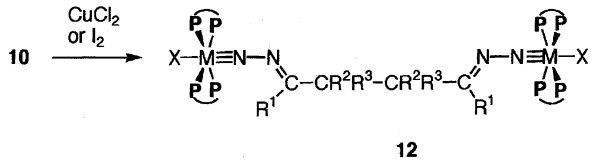
Contribution of the resonance structure **11** strongly indicates that the terminal carbon of the alkenyldiazenido ligand shows nucleophilic reactivities.[17,25] In fact, treatment of **10** with excess amounts of alkyl halide (RX) results in formation of the corresponding C-alkylated diazoalkane complexes *trans*-[WF(NNCR^{1}CR^{2}R^{3}R)(dppe)$_2$]$^+$. This provides a convenient route to the modification of diazoalkane ligands. Interestingly, the high regioselectivity in the deprotonation mentioned above makes it possible to achieve the selective α,α-dialkylation of complex **5a** by repeated deprotonation–alkylation reactions. A few examples are shown in Scheme 6. Thus, sequential methylation and ethylation of **5a** give *trans*-[WF(NNCMeCHMeEt)(dppe)$_2$]$^+$ (**5c**) in a good yield. Further, reactions with electrophilic heterocumulenes such as phenyl isocyanate, phenyl isothiocyanate, and diphenylketene afford C-acylated diazoalkane complexes after aqueous workup. In the reaction of **10a** with aryl isocyanates, the use of 1 equivalent of the reagent leads to the formation of the α-monocarbamoyl complexes **5d**, while the use of excess amounts of the aryl isocyanate produced the α,α-dicarbamoyl complexes **5e**. Aldol-type condensation also occurs in the reaction of **10** with aldehydes having no α-hydrogen such as benzaldehyde and pivalaldehyde.

On the other hand, the electron-rich conjugated system of alkenyldiazenido complexes including the Mo(II) or W(II) center is susceptible to one-electron oxidation. Thus, complexes **10** undergo oxidative coupling by treatment with I_2 or $CuCl_2$ to form dinuclear μ-bis(diazo)alkane complexes **12** (Scheme 7).[25a]

This coupling reaction exhibits moderate to good stereo-



Scheme 6.



Scheme 7.

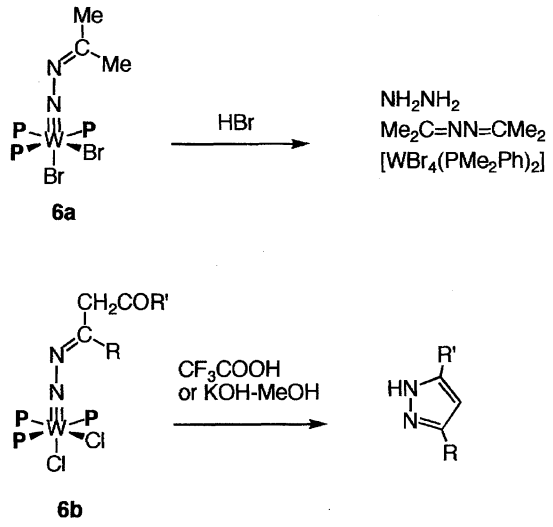
selectivity. For example, oxidation of complex **10b** gives *trans,trans*-[(dppe)$_2$WF(NNCHCHMeCHMeCHNN)FW(dppe)$_2$]$^{2+}$ as a mixture of two stereoisomers in a ratio of 8.3 : 1, where the *threo* isomer is predominant. Obviously the oxidative coupling of **10** proceeds via one-electron oxidation forming a 17-electron cationic Mo(III) or W(III) species [MF(N=NCR^1=CR^{2}R^3)(dppe)$_2$]$^+$ (**13**), in which the terminal carbon atom of the C=C bond is considered to have radical character owing to the conjugated double bond system including the metal atom. The radical coupling of the two molecules of **13** results in the formation of the μ-bis(diazo)alkane complex **12**.

Cationic diazoalkane complexes prepared from **3** and α,β-unsaturated aldehydes *trans*-[MF(NNCHCH=CHR)(dppe)$_2$]$^+$ (M = Mo, W) react with lithium cuprates LiCuR′$_2$ to give alkenyldiazenido complexes *trans*-[MF(N=NCH=CHCHRR′)(dppe)$_2$] (**14**) as conjugate addition products.[26] This reaction provides an alternative synthetic route to alkenyldiazenido complexes. The diazoalkane ligand in *trans*-[WF(NNCHC≡CR)(dppe)$_2$]$^+$ undergoes similar conjugate addition by LiCuR′$_2$ to yield reactive allenyldiazenido complexes *trans*-[MF(N=NCH=C=CRR′)(dppe)$_2$] (**15**). Further reactions of these alkenyl- and allenyldiazenido complexes **14** and **15** with electrophiles such as H$^+$, alkyl halides, phenyl isocyanate, I$_2$ or *N*-halosuccinimides lead to the formation of various functionalized diazoalkane ligands.

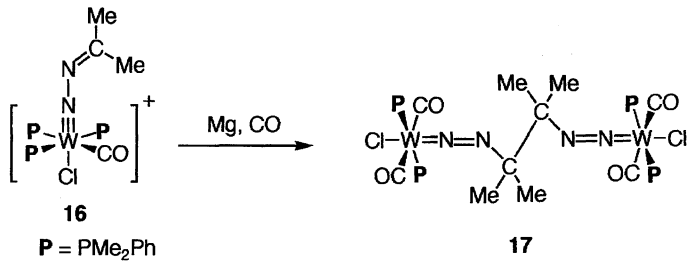
Electrochemical measurements of diazoalkane complexes **5** show that both oxidation and reduction processes exist.[20] In fact, electoreduction of a cationic diazomethane complex *trans*-[WF(NNCH$_2$)(dppe)$_2$][BF$_4$] (**5f**) affords an insoluble complex, which was formulated as a bridging diazenido complex [(dppe)$_2$WF(N=NCH$_2$CH$_2$N=N)FW(dppe)$_2$].[27] A proposed reaction mechanism includes one-electron reduction of complex **5f** leading to a W(III) diazomethane complex [WF(NNCH$_2$)(dppe)$_2$], in which the diazo carbon is supposed to have radical character, and its dimerization gives the bridging diazenido complex. More recently, we have prepared a carbonyl diazoalkane complex *mer*-[WCl(NNCMe$_2$)(CO)(PMe$_2$Ph)$_3$][ZnCl$_3$(THF)] (**16**) from the reaction of *cis,mer*-[WCl$_2$(NNCMe$_2$)(PMe$_2$Ph)$_3$] and CO in the presence of ZnCl$_2$, and found that its reduction with Mg under CO actually affords the fully characterized bridging diazenido complex [WCl(CO)$_2$(PMe$_2$Ph)$_2$(N=NCMe$_2$CMe$_2$N=N)WCl(CO)$_2$(PMe$_2$Ph)$_2$] (**17**) by the reductive coupling of the diazoalkane ligand (Scheme 8).[28]

Interestingly, treatment of the phenyldiazomethane complex *trans*-[WF(NNCHPh)(dppe)$_2$][BF$_4$] with Na results in the formation of stilbene in a moderate yield. The reductive coupling of the diazoalkane ligand is also considered to occur in this reaction, but the bridging diazenido complex would be liberated by further reduction by Na.[29]

Liberation of diazoalkane ligands from the metal center is important from a standpoint of the synthesis of organonitrogen compounds. For this purpose, the reactivity of diazoalkane complexes **6** has been examined under various conditions. As is already mentioned, the LiAlH$_4$ reduction of **6a** cleaves the N–N bond of the diazoalkane ligand to give isopropyl amine.[10] In contrast, treatment of **6a** with HBr gives rise to the metal–N bond fission to give hydrazine, acetone azine and [WBr$_4$(PMe$_2$Ph)$_2$] (Scheme 9).[10] The primary organic product may be NH$_2$N=CMe$_2$, which disproportionates to produce hydrazine and acetone azine. When diazoalkane complexes prepared from β-diketones (**6b**) are treated with CF$_3$COOH or KOH–MeOH, a similar metal–N bond fission followed by cyclization affords pyrazoles in good yields. It is interesting to note that the N–N bond of dinitrogen is to-



Scheme 9.



Scheme 8.

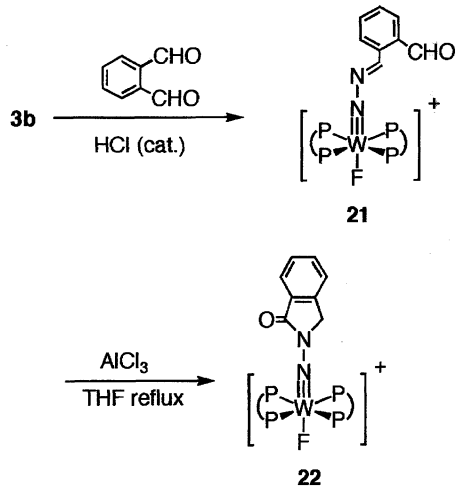
tally retained during the conversion into acetone azine or pyrazoles. This is in sharp contrast to the chemistry of metal nitrides prepared from metal or metal species and dinitrogen.[30]

Synthesis and Reactivities of Lactam-Type Ligands via Diazoalkane Complexes. Since nitrogen heterocycles such as pyrroles and lactams are widely found in natural and biologically active compounds, direct synthesis of nitrogen-heterocycles from dinitrogen is of special interest. Prior to our study, there was a study on preparation of simple cyclic amines such as piperidine by the hydride or electrochemical reduction of hydrazido complexes $[MBr\{NN(CH_2)_nCH_2\}(dppe)_2]^+$ (M = Mo, W; n = 3, 4), which in turn were prepared from **1** with 1,4-dibromobutane or 1,5-dibromopentane.[31] Aiming at extending the synthesis of organonitrogen compounds from dinitrogen, we have embarked on the synthesis of nitrogen heterocycles such as lactams and nitrogen heteroaromatics, which are particularly desirable targets from a standpoint of organic synthetic chemistry. For this purpose, the condensation reaction of hydrazido complexes **3** and **4** with carbonyl compounds developed in this laboratory is promising, because of its wide applicability and abundant reactivities of the resulting diazoalkane ligands (vide supra). We have actually found that reactions of hydrazido complexes **3** and **4** with dialdehydes or their equivalents provide an excellent route to heterocyclic ligands from dinitrogen.

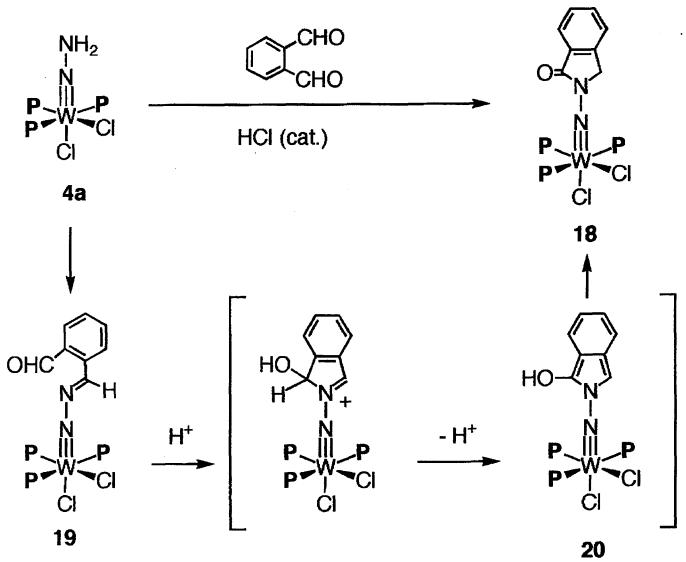
Reaction of hydrazido complex **4a** with phthalaldehyde in the presence of catalytic amounts of aqueous HCl smoothly proceeds at room temperature to give a (phthalimidin-2-yl)imido complex *cis,mer*-$[WCl_2(NNCOC_6H_4CH_2)(PMe_2Ph)_3]$ (**18**), which has a heterocycle involving the terminal nitrogen atom of the original coordinated dinitrogen (Scheme 10).[32] In the absence of the acid, the reaction stops at the stage of the diazoalkane complex *cis,mer*-$[WCl_2(NNCHC_6H_4CHO)(PMe_2Ph)_3]$ (**19**), which is quickly converted into complex **18** by addition of a small amount of aqueous HCl. Obviously complex **19** is the key intermediate of the cyclization. Partial incorporation of deuterium at the methylene group of the lactam ring was observed in a reaction promoted by DCl/D_2O. These findings supports a reaction mechanism which includes the intramolecular nucleophilic attack of the diazo nitrogen atom on the formyl group in complex **19** leading to an intermediate complex with the 1-hydroxyisoindole structure **20** and the subsequent proton migration giving the final product **18**.

Hydrazido complex **3b** also reacts with phthalaldehyde, but the reaction catalyzed by aqueous HCl stops at the stage of diazoalkane complex **21**. For further conversion to the (phthalimidin-2-yl)imido complex **22**, gentle heating and use of $AlCl_3$ as a promoter are required (Scheme 11). Because of the cationic nature of complex **21**, nucleophilicity of the diazo nitrogen in **21** would be weaker than that of **19**.

It should be mentioned here that the reaction of phthalal-



Scheme 11.



Scheme 10.

dehyde with hydrazine affords phthalazine with a six-membered ring. Therefore, hydrazido complexes **3** and **4** may be regarded as a protected form of hydrazine, a metallohydrazine, suitable for the construction of ring structures containing only the terminal nitrogen atom.

The W≡N bond in (phthalimidin-2-yl)imido complex **18** is cleaved by reaction of the complex with HBr to form *N*-aminophthalimidine in a good yield.[32] On the other hand, the N–N bond fission occurs on treatment with $NaAlH_2(OCH_2CH_2OMe)_2$ to give phthalimidine (Scheme 12). These reactions clearly show that both *N*-aminophthalimidine and phthalimidine can be selectively derived from dinitrogen under very mild conditions with or without retention of the original N–N bond, respectively.

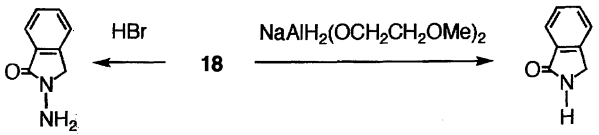
Complex **3b** also reacts with 2,5-dimethoxy-2,5-dihydrofuran, a synthetic equivalent of maleinaldehyde, to give two isomeric complexes with a γ-lactam skeleton.[32] Careful investigation of the products has revealed that the complex having a 1,3-dihydro-2*H*-pyrrol-2-one moiety **23** is first formed as the kinetic product. A prolonged reaction gradually converts complex **23** to the other isomer having the 1,5-dihydro-2*H*-pyrrol-2-one structure **24**, which is the thermodynamic product (Scheme 13). Both complexes have been fully characterized by X-ray diffraction study.

Investigation into the ^{1}H NMR behavior of complex **23** in the presence of DCl/D_2O has revealed that the isomerization of **23** to **24** proceeds through fast interconversion between complex **23** and the (2-hydroxy-1-pyrrolyl)imido complex **25** followed by slow proton migration leading to the final, thermodynamically stable product **24**. Therefore, it can be concluded that the reaction of **3b** with 2,5-dimethoxy-2,5-dihydrofuran gives the (2-hydroxy-1-pyrrolyl)imido complex **25** as the primary product by a process similar to that shown in Scheme 10, and complex **25** quickly isomerizes to the kinetic product **23** at an early stage of the reaction.

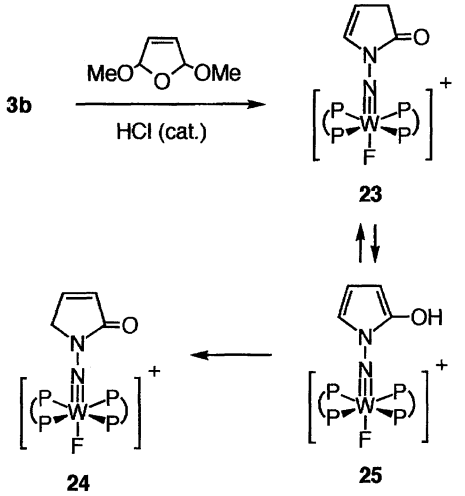
Prototropy and thermodynamic stability of 2-hydroxypyrrole and dihydro-2*H*-pyrrol-2-ones have been attracting considerable attention, because these structures have been found in tetrapyrrole pigments and the tautomerization of these compounds are thought to play certain roles in biologically important processes.[33] However, unsubstituted and N-substituted 1,3-dihydro-2*H*-pyrrol-2-ones are thermally labile compounds[34] and their studies have been severely limited. It is noteworthy that such a relatively unstable heterocycle can be prepared on the metal center and fully characterized by X-ray analysis.

Synthesis and Reactivities of (1-Pyrrolyl)imido Ligands via Diazoalkane Complexes. 2,5-Dimethoxytetrahydrofuran, a cyclic acetal of succinaldehyde, also reacts with cationic hydrazido(2-) complexes **3** in the presence of an acid catalyst to form (1-pyrrolyl)imido complexes *trans*-$[MX(\overline{NNCH{=}CHCH{=}CH})(dppe)_2]^+$ (**26a**, M = Mo, X = F; **26b**, M = W, X = F; **26c**, M = W, X = Cl) which have a pyrrole ring containing the terminal nitrogen atom of the original dinitrogen ligand (Scheme 14).[35] The reaction proceeds at room temperature to give the compounds in high yields (up to 90%).

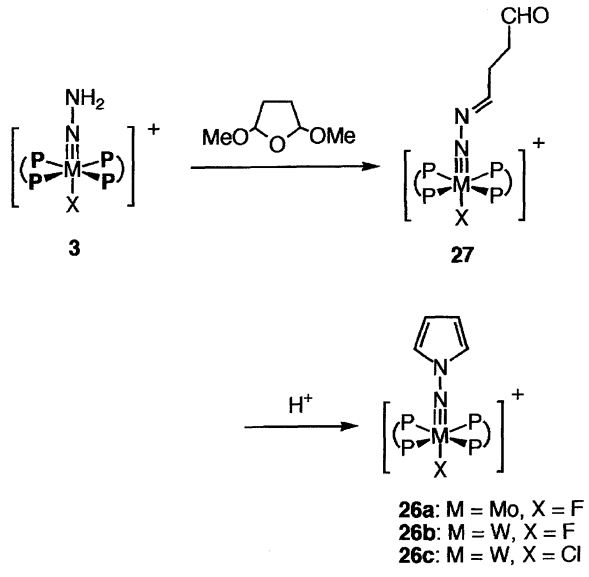
As in the above cases, the pyrrole ring of **26** is considered to be formed via stepwise condensations at the terminal nitrogen. The first step may be the formation of 4-diazobutanal complexes *trans*-$[MX(NN{=}CHCH_2CH_2CHO)(dppe)_2]^+$. In fact, *trans*-$[WF(NN{=}CHCH_2CH_2CHO)(dppe)_2][BF_4]$ (**27**) and its dimethyl acetal complex are isolated from the reaction of **3b** with the furan in the absence of acid. The second step is the ring closure caused by an acid catalyst. This type of pyrrole ring formation is known as modified Paal–Knorr synthesis,[36] but the present reaction is its first application to preparation of metal derivatives containing pyrroles via metallohydrazines.



Scheme 12.



Scheme 13.



Scheme 14.

The molecular structure of the (1-pyrrolyl)imido complex **26b** has been confirmed by X-ray analysis. The structure is shown in Figs. 1 and 2. The geometry around the tungsten is distorted octahedral with the (1-pyrrolyl)imido ligand and the fluorine atom in trans positions. The bond lengths in the pyrrole ring are similar to those of free pyrrole except that the distances between the α- and β-carbons (C(1)–C(2), 1.32(1) Å C(3)–C(4) = 1.34(1) Å) are somewhat shorter than free pyrrole (1.382 Å). The W≡NNCH=CHCH=CH moiety is essentially planar as expected, and the W–N(1)–N(2) linkage is nearly linear. It should be pointed out that the N(1)–N(2) distance (1.362(7) Å) is relatively long compared with those of organohydrazido(2-) complexes such as [WBr(NNHMe)(dppe)$_2$]Br (1.32(2) Å),[37] [WCl(py)(NNHCOCHPh$_2$)(PMe$_2$Ph)$_3$]Cl (1.344(11) Å),[38] and [Mo(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$] (1.30(1) Å).[39] In organohydrazido(2-) complexes, the lone pair on the terminal nitrogen atom is delocalized over the N–N–M moiety, and the N–N bond has substantial multiple bond character. In contrast, the lone pair of the pyrrole nitrogen atom in complex **26** is mainly delocalized over the pyrrole ring to form the 6π aromatic system, and the multiplicity of the N–N bond is reduced.

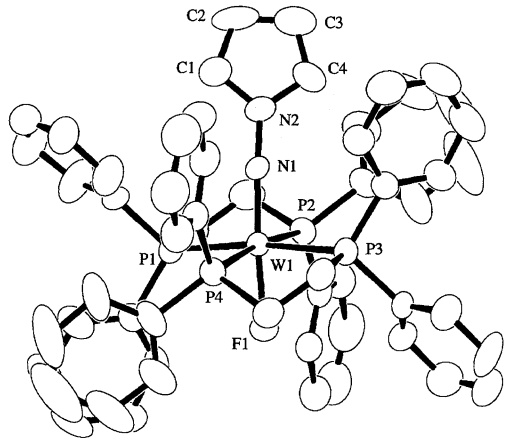


Fig. 1. ORTEP drawing for the cationic part of *trans*-[WF(NNCH=CHCH=CH)(dppe)$_2$][PF$_6$] (**26b**). Hydrogen atoms are omitted for clarity.

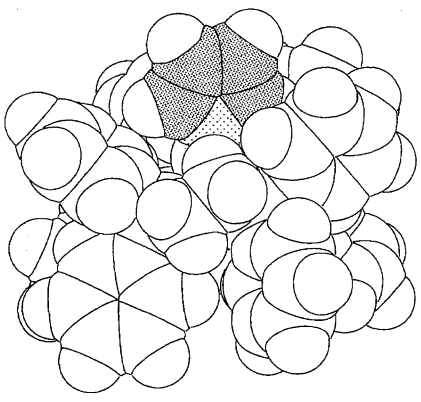


Fig. 2. Space filling view of complex **26b**.

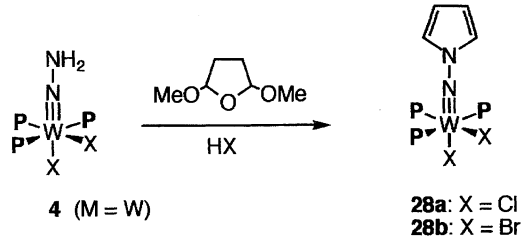
In the ^{1}H NMR spectra of **26**, considerable high field shifts are observed in comparison with those of free pyrrole. Thus, signals for the α- and β-protons of the pyrrole ring in **26b** appears as two broad triplets at about δ = 4.8 and 5.4, respectively, while free pyrrole shows the corresponding signals at δ = 6.7 and 6.2. These high-field shifts are due to the shielding effect of the phenyl groups of the dppe ligands, which has been substantiated by the space filling view of the X-ray structure of **26b** (Fig. 2). The ^{13}C chemical shifts of the (1-pyrrolyl)imido carbons in **26** (about δ = 120 and 106 for α- and β-carbons, respectively) are closely comparable to those of free pyrrole.

Tungsten hydrazido complexes **4a** and **4b** (X=Br) are similarly transformed into the corresponding (1-pyrrolyl)imido complexes *cis,mer*-[WX$_2$(NNCH=CHCH=CH)(PMe$_2$Ph)$_3$] (**28a**, X = Cl; **28b**, X = Br) by reaction with 2,5-dimethoxytetrahydrofuran in the presence of a catalytic amount of aqueous HX (Scheme 15). The molecular structure of **28b** has been unambiguously determined by X-ray diffraction analysis, which shows the structure of the (1-pyrrolyl)imido ligand closely related to that in **26b**.

It is well-known that pyrrole readily undergoes substitution reactions on the ring with a variety of electrophiles with exclusive α-position selectivity.[40] However, the pyrrole ring directly coordinated to a metal species is expected to react in different ways owing to the electronic and steric effects caused by the metal center and ancillary ligands. Actually, several interesting reactivities of the ligating pyrroles have recently been found in η^1-*N*-pyrrolyl–Re(III),[41] η^2-pyrrole–Os(II),[42] η^5-pyrrolyl–Re(III),[43] or η^5-pyrrolyl–Ru(II) and Os(II)[44] complexes.

In contrast, the pyrrole ring of the (1-pyrrolyl)imido complexes **26** and **28** is separated from the metal center by one nitrogen atom. The X-ray analysis and spectroscopic data (vide supra) indicate that the pyrrole ring in complexes **26** and **28** still has an electron-rich aromatic nature, and undergoes electrophilic substitution reactions. On the other hand, the space-filling view of **26** (Fig. 2) clearly envisions that the α-position of the pyrrole ring is completely protected by the phenyl groups of the dppe ligands, while the β-position sticks out of the hindered region. These lead to the expectation that the electrophilic substitution of the pyrrole ring in **26** occurs selectively at the β-position in sharp contrast to that of free pyrrole.

The predicted unique reactivity of the (1-pyrrolyl)imido ligand in **26** has been actually confirmed with various elec-

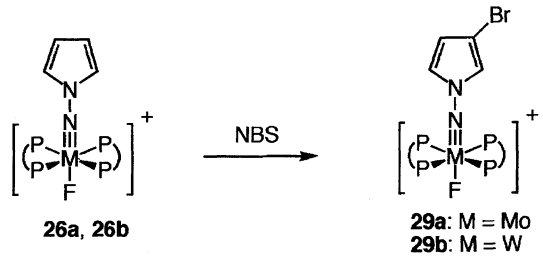


Scheme 15.

trophiles. For example, the tungsten complex **26b** undergoes bromination by treatment with *N*-bromosuccinimide (NBS) in THF even at −78 °C (Scheme 16). The selectivity of the β-monobromination is essentially 100% below −50 °C, and the corresponding (β-bromopyrrolyl)imido complex **29b** can be isolated in a high yield. Molybdenum complex **26a** also gives the corresponding β-monobrominated complex **29a** in a good yield.

Furthermore, exclusive β-cyanation, sulfonation, formylation, and acylation have been achieved by treatment of complex **26b** with chlorosulfonyl isocyanate (CSI) and DMF, SO_3–pyridine complex, $[CHCl{=}NMe_2]Cl$ followed by hydrolysis, and acid chloride (or anhydride)/$AlCl_3$, respectively, although the last reaction is accompanied by the exchange of the fluoride anion on the metal with chloride anion (Scheme 17). In these reactions, no α-substituted products have been observed at all, indicating that the steric protection by the phenyl groups works very effective.

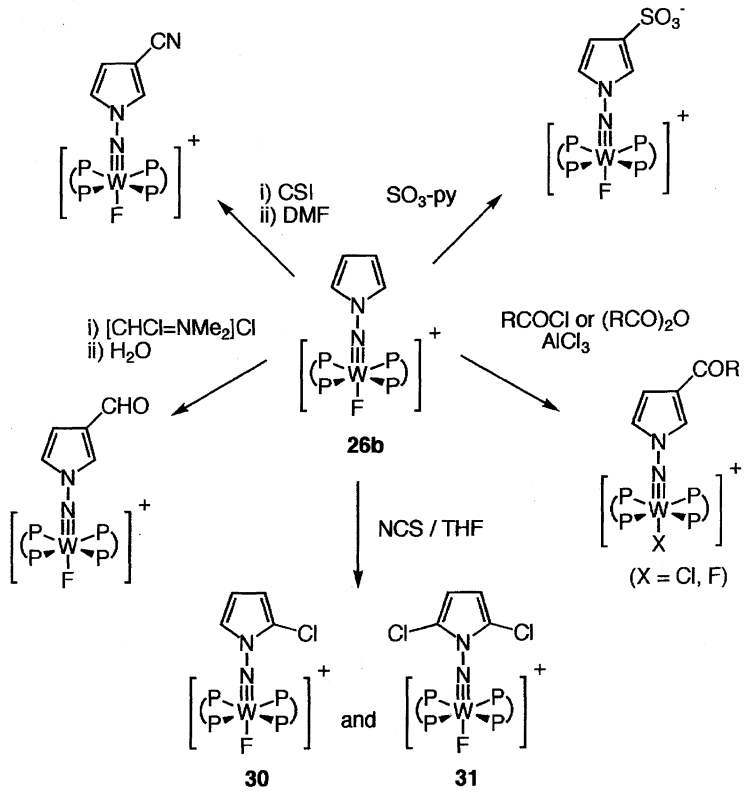
The only exception for the β-selective substitution we have observed is chlorination. Treatment of **26b** with 1.05 equivalent of *N*-chlorosuccinimide (NCS) in THF gives a mixture of the α-monochloro complex **30** and the α,α'-dichloro complex **31**, and addition of 2 equivalent of NCS yields **31** in a high yield. Use of DMF as solvent changed the selectivity and the β-chloro complex is obtained as the major product, but satisfactory selectivity of the β-chlorination has not been achieved by controlling the reaction temperature.



Scheme 16.

Since β-substituted pyrroles are widely found in natural products and biologically active compounds as important units,[45] electrophilic substitution reactions of several N-substituted pyrroles have been extensively investigated for the purpose of achieving the β-substitution of the pyrrole ring.[46] However, even the highly bulky *N*-triisopropylsilyl (TIPS) group,[46a] which is one of the most effective directing groups of pyrrole for the β-selective substitution, has failed to show satisfactory directing ability in the cyanation. The excellent steric protection of the α-position of the pyrrole ring by the dppe ligands in **26** is outstanding, and the β-selective substitution of the (1-pyrrolyl)imido complexes may be used as a method for the synthesis of β-substituted pyrroles.

Liberation of Pyrrole and *N*-Aminopyrrole from (1-Pyrrolyl)imido Complexes. Liberation of pyrrole derivatives from the (1-pyrrolyl)imido complexes accomplishes the synthetic process for pyrroles from dinitrogen. Since pyrroles are highly desirable target molecules in organic synthesis, this reaction has been investigated in detail. Needless to say, the selective liberation of pyrrole and *N*-aminopyrrole by the fission of the N–N and metal–N bonds of the (1-pyrrolyl)-imido complexes, respectively, is of great importance, and



Scheme 17.

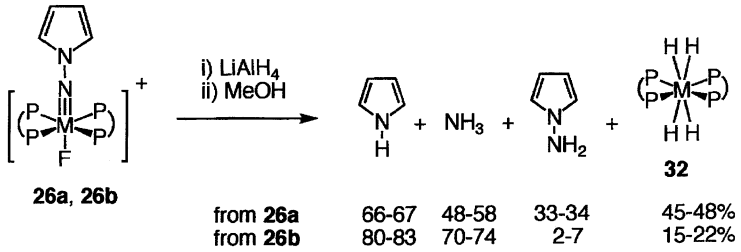
much attention has been paid for this point.

Reaction of **26a** and **26b** with $LiAlH_4$ followed by work-up with MeOH has been found effective for the formation of pyrrole and *N*-aminopyrrole, and the total yields of pyrrole and *N*-aminopyrrole after the reaction at room temperature are essentially quantitative (Scheme 18). Pyrrole is obtained as the major product from both complexes, but it is noteworthy that the tungsten complex **26b** liberates pyrrole much more selectively than the molybdenum analogue **26a**. In addition to pyrrole and *N*-aminopyrrole, ammonia has been detected in almost comparable yields to those of pyrrole. Thus, when pyrrole is liberated by the N–N bond cleavage of the (1-pyrrolyl)imido ligand, the nitrogen atom directly bound to the metal center is released as ammonia after protonolysis.

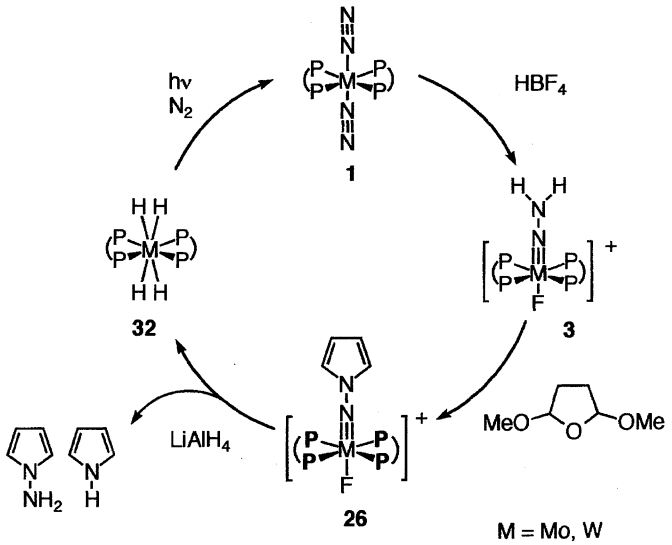
Previously it was reported that the hydride reduction of related alkylhydrazido(2-) complexes of molybdenum and tungsten requires much more drastic conditions and longer reaction times (80 °C, 65 h) to yield amines.[47] In contrast, the reaction of **26** with $LiAlH_4$ proceeds quite smoothly at room temperature. Complex **26a** reacts with $LiAlH_4$ even at −78 °C to give pyrrole and *N*-aminopyrrole in 49 and 28%, respectively, after 20 h. Obviously the reactivity of the N–N bond in complex **26** is remarkably enhanced. This is compatible with the finding by X-ray analysis that the multiplicity of the N–N bond in **26b** is lower in comparison with alkylhydrazido(2-) complexes (vide supra).

From the $LiAlH_4$ reduction of **26a** and **26b**, the tetrahydrido complexes $[MH_4(dppe)_2]$ (**32a**, M = Mo; **32b**, M = W) are recovered as the metal products in moderate yields. These complexes **32** are known to be converted to the original dinitrogen complexes **1** by irradiation under a nitrogen atmosphere.[48] In fact, the molybdenum complex **32a** recovered after the reduction of **26a** is transformed back to **1a** in 95% yield by irradiation with a tungsten lamp under dinitrogen. Thus, a synthetic cycle for the formation of pyrrole and *N*-aminopyrrole from dinitrogen has been accomplished starting from dinitrogen complexes **1** (Scheme 19). It should be emphasized that all the steps are conducted under mild conditions, and all the metal species included are fully characterized. Although we must await further study to achieve catalytic production of pyrroles from dinitrogen, we consider that the synthetic cycle in Scheme 19 is of special interest because it envisions the direct synthesis of organonitrogen compounds from dinitrogen as a realistic process.

Another interesting feature of the newly developed synthesis of pyrroles from molecular nitrogen is that it can be extended to the synthetic method for β-substituted pyrroles, which are hardly obtained by conventional electrophilic substitution reactions of pyrrole. This has been exemplified in the synthesis of β-heptylpyrrole. Thus, the heptanoylation of (1-pyrrolyl)imido complex **26c** with heptanoyl chloride selectively gives the (β-heptanoylpyrrolyl)imido complex **33**, and its hydride reduction proceeds with concomitant reduction of the carbonyl group to yield β-heptylpyrrole in a



Scheme 18.

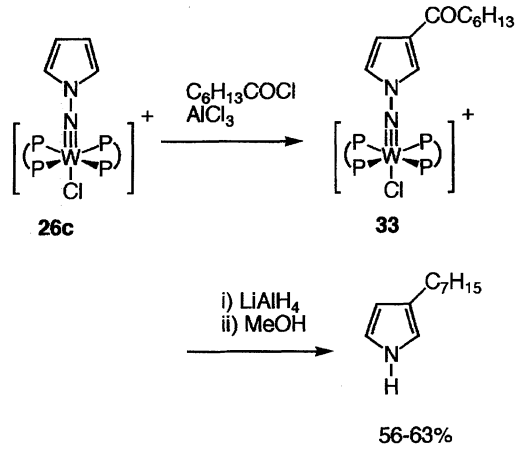


Scheme 19.

Table 2. Synthesis of Pyrrole and *N*-Aminopyrrole from (1-Pyrrolyl)imido Complexes

Complex	Alcohol	Yield/%	
		Pyrrole	*N*-Aminopyrrole
$[WCl_2(NNC_4H_4)(PMe_2Ph)_3]$ (**28a**)	EtOH[a]	56	37
$[WBr_2(NNC_4H_4)(PMe_2Ph)_3]$ (**28b**)	MeOH[b]	27	73
28b	EtOH	11	89
$[WBr_2(NNC_4H_4)(PMe_2Ph)_2(CO)]$ (**34a**)	EtOH	<5	95
34a	Pr^iOH	Trace	100
$[WBr_2(NNC_4H_4)(PMe_2Ph)_2(PhCHO)]$ (**34b**)	MeOH	Trace	100
$[WBr_2(NNC_4H_4)(PMe_2Ph)_2(PhCCH)]$ (**34c**)	MeOH	Trace	100
$[WBr_2(NNC_4H_4)(PMe_2Ph)_2(Bu^tNC)]$ (**34d**)	MeOH[c]	12	75
$[WBr_3(NNC_4H_4)(PMe_2Ph)_2]$ (**35**)	MeOH	36	54

Conditions: complex 0.08—0.09 mmol; KOH, 10 equiv; alcohol 3 ml; at room temperature, 2—4 h.
a) 24 h. b) 0.5 h. c) 50 °C.

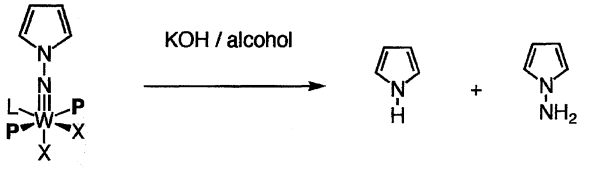


Scheme 20.

good yield (Scheme 20).

The $LiAlH_4$ reduction of the (1-pyrrolyl)imido complex with PMe_2Ph ligands **28b** proceeds at 50 °C to give pyrrole selectively in 75% together with ammonia in 73%. On the other hand, treatment of **28b** with KOH in ethanol at room temperature produces pyrrole and *N*-aminopyrrole in 11 and 89%, respectively (Scheme 21). In order to investigate the ligand effect on the latter reaction, we have prepared a series of ligand substitution[19] derivatives of **28b**, $[WBr_2(NNC_4H_4)(PMe_2Ph)_2(L)]$ (**34a**, L=CO; **34b**, L=PhCHO; **34c**, L=PhCCH; **34d**, L=Bu^tNC) and the W(V) analogue[13] *mer,trans*-$[WBr_3(NNC_4H_4)(PMe_2Ph)_2]$ (**35**). In Table 2 are summarized results of formation of pyrrole and *N*-aminopyrrole from those complexes.[49]

The reactivity of the complexes and the ratio of products



28 (L = PMe_2Ph; X = Cl, Br)
34 (L = CO, PhCHO, PhCCH, Bu^tNC; X = Br)
35 (L, X = Br)

Scheme 21.

are strongly dependent on the nature of the alcohol as well as the ligands on the metal. Essentially quantitative production of *N*-aminopyrrole has been achieved by the reaction of **34a** in Pr^iOH, **34b** in MeOH, or **34c** in MeOH or Pr^iOH. Although the detailed mechanism for formation of *N*-aminopyrrole is under investigation, the above results are extremely interesting in that both pyrrole and *N*-aminopyrrole can be selectively obtained from molecular nitrogen by way of (1-pyrrolyl)imido complexes under mild conditions.

Conclusion

Diazoalkane complexes of molybdenum and tungsten are readily prepared from the dinitrogen complexes **1** and **2** through protonation with acid followed by the condensation of the resultant hydrazido complexes with aldehydes or ketones. This synthetic method is very versatile and the diazoalkane ligands thus formed show intriguing reactivities. Heterocyclic ligands incorporating the coordinated dinitrogen such as (1-pyrrolyl)imido and (phthalimidin-2-yl)imido ligands can also be formed by way of diazoalkane complexes. From these well-characterized complexes, various organonitrogen compounds such as acetone azine, pyrazoles, phthalimidines, pyrroles, and *N*-aminopyrrole are produced in good yields under mild conditions. Further, the β-regioselective electrophilic substitution of the pyrrole ring in (1-pyrrolyl)-imido complexes with dppe ligands has been achieved by taking advantage of the streic effect caused by the ligands. At present, these reactions are stoichiometric with respect to the metal, but we have attained a synthetic cycle to obtain pyrrole and *N*-aminopyrrole from dinitrogen, where the metal species can be recycled as the starting dinitrogen complex. We believe these results would lead to ambitious goal of direct synthesis of various organonitrogen compounds by using dinitrogen as a source of nitrogen atoms.

The authors would like to thank all the dedicated co-workers whose names appear in the references for their outstanding contributions. The grant support by the Ministry of Education, Science and Culture is also gratefully acknowledged.

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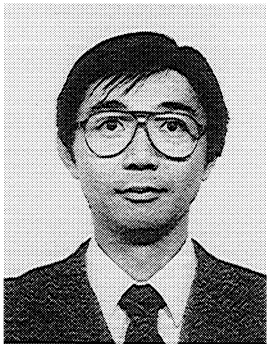

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