THE CHEMISTRY OF NITROGEN FIXATION AND MODELS FOR THE REACTIONS OF NITROGENASE

RICHARD A. HENDERSON, G. JEFFERY LEIGH, and
CHRISTOPHER J. PICKETT

A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton, England

ISBN 0-12-023627-3

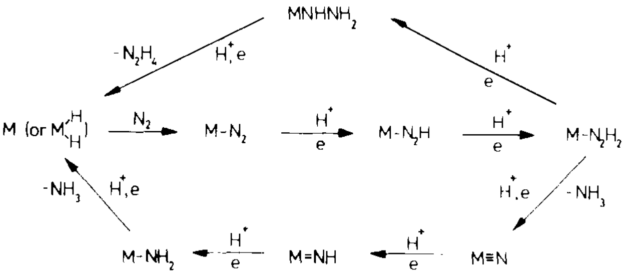
I. Introduction

The interest in nitrogen fixation for the inorganic chemist is to try to understand, using simple compounds, what nature does so comparatively effortlessly within the enzyme, nitrogenase. This is of particular value considering the increasing demand for nitrogenous fertilizers, and the vast industrial expenditure of energy in producing ammonia.

The literature of chemical nitrogen fixation, even excluding that related to the Haber process, is now considerable. In the Unit of Nitrogen Fixation we have assembled a bibliography of chemical nitrogen fixation, starting in 1965, and at present it consists of some 900 papers. It is not our aim to purvey the essence of these 900 papers in the space of this article. There are many reviews covering the whole area, and the reader is referred to them, and particularly to a Chemical Review by our colleagues Chatt, Dilworth, and Richards, for information up to the end of 1976 (*82*). We aim to concentrate on the last 6 years, and to discuss one particular aspect: the way coordinated dinitrogen may break down to give ammonia (or amines) and hydrazine (or organohydrazines) and how this relates to the properties of nitrogenase.

The mechanisms of reaction of coordinated dinitrogen are a matter of dispute. There are several proposals extant, chemical and biological, and these are espoused by their progenitors with varying degrees of fervor. However, there is now sufficient chemistry available for us to make preliminary judgments concerning the validity of the various proposals, and this is one of the aims of the current article. We shall attempt to survey the chemistry relating to nitrogen fixation, and then discuss its relevance to nitrogenase.

In order to provide a basis for the discussion, we shall use Scheme 1. This is based upon the chemistry of dinitrogen complexes as developed in the Unit of Nitrogen Fixation, but it is not intended to exclude consideration of schemes originating elsewhere. Indeed we hope to evaluate all the schemes in the literature. Our basic assumptions are



SCHEME 1. Pathways for the stepwise reduction of dinitrogen to ammonia and hydrazine.

that reduction of dinitrogen to ammonia occurs by the protonation of a coordinated dinitrogen bound at a single metal site, with either one or two protons at a time, and that concomitant electron flow into the coordinated dinitrogen occurs via the metal.

The chemistry associated with each of the intermediate types outlined in Scheme 1 will be discussed in the first three major sections. The first section will deal with the chemistry of dinitrogen complexes, the second with that of N_2R and N_2R_2 complexes, and the third with N_2R_3, NR, and nitrido complexes ($R = H$ or an organic group). Having expounded the chemistry of these putative intermediates in the nitrogen fixation cycle a more detailed discussion of the various proposed chemical mechanisms, and the relation to biological nitrogen fixation, will follow.

II. The Binding of Dinitrogen and Dinitrogen Complexes

It is now evident that dinitrogen will form complexes with all transition elements, and that, at least in matrices at low temperatures, poly(dinitrogen) complexes are common. Dinitrogen can also bind somewhat tenuously to nontransition metals and even to carbon as judged from decomposition reactions of diazoalkane and diazonium salts. The qualities of a metal site for binding, and, moreso, for activating, dinitrogen to protonation and/or alkylation, are not yet defined. Dinitrogen can bind to a "vacant" site, or displace a ligand (in a process which is presumably dissociative) or even displace two ligands (as in hydrides). These aspects will be discussed below. Complexes of dinitrogen discovered since about 1977 and new data on older complexes are detailed in the next section.

A. Dinitrogen Complexes

1. Ti, Zr, Hf, and Th

One of the most interesting species described recently is the 16-electron [$Ti(N_2)_6$]. This is isolated as a yellowish-red solid in a matrix at about 16 K (*56*), and it decomposes above 40 K, being less stable than [$Ti(CO)_6$]. Its IR spectrum shows three bands assigned to N—N stretches in a distorted (actually C_2) local environment, at 2131, 2100, and 2095 cm^{-1}. Its UV spectrum has been interpreted, and is believed to show (once again) that dinitrogen is a poorer σ donor and π acceptor than CO. However, in the excited state bound dinitrogen may carry more charge than carbon monoxide, which suggests that photoactivation to protonation may be worth investigating. 10Dq for [$Ti(N_2)_6$] is 21,370 cm^{-1}, compared with 28,255 cm^{-1} for [$Ti(CO)_6$].

Titanium cyclopentadienyl derivatives form an extensive series of dinitrogen complexes. However, when the titanium-containing precursors are bound to polymers there is no reactivity with dinitrogen comparable to that observed for the analogous derivatives in solution, and fixation is, at best, marginal (*202, 220*).

The reactions of cyclopentadienyltitanium derivatives with dinitrogen are very complex, and some of the most interesting and surprising are due to Pez (*270*). The complex [μ-(η^1,η^5-C_5H_4)(η^5-C_5H_5)$_3$$Ti_2$] reacts rapidly with dinitrogen in hydrocarbon solvents to yield a deep-blue material [{(C_5H_4)(C_5H_5)$_3$$Ti_2$}$_2$$N_2$]. This is of unknown structure, though a symmetrical Ti—N_2—Ti system [no IR active $\nu(N_2)$] has been ascribed to it (*271, 272*). In 1,2-dimethoxyethane, under dinitrogen (10 atm) this compound reacts to produce a dark-green or black complex which could not be definitively characterized, although it shows $\nu(N_2)$ at 1222 cm^{-1}. This material yields a reddish-brown solid with tetrahydrofuran (THF) which has $\nu(N_2)$ at 1296 cm^{-1}, but, again, it could not be characterized. However, reaction of the reddish-brown material with diglyme (diglyme = $C_6H_{14}O_3$) yielded a red-brown crystalline product of formula [μ_3-N_2{(η^5,η^5-$C_{10}H_8$)(η^5-C_5H_5)$_2$$Ti_2$}{($\eta^1$,$\eta^5$-$C_5H_4$)($\eta^5$-$C_5H_5$)$_3$$Ti_2$}]. [$\eta^5$-$C_5H_5$)$_2$($C_6H_{14}O_3$)Ti] · $C_6H_{14}O_3$ [$\nu(N_2)$ = 1282 cm^{-1}] which has the essential structure shown in Fig. 1.

This represents a still unique coordination for dinitrogen which here has a N—N bond length of 1.301(12) Å, somewhat longer than an N—N double bond. It may be that all three of the materials obtained by Pez have this kind of dinitrogen coordination. The dinitrogen is displaced irreversibly by dihydrogen and [(μ-H)$_2$(μ-$C_{10}H_8$)(η^5-C_5H_5)$_2$$Ti_2$] is produced. Hydrogen chloride in diglyme yields, princi-

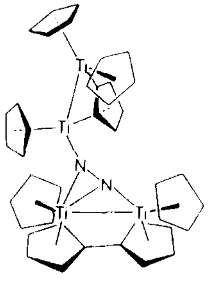


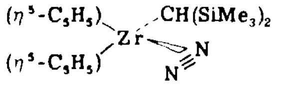
FIG. 1. Structure of the $[\mu_3\text{-}N_2\{(\eta^5,\eta^5\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)_2Ti_2\}\{(\eta^1,\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2\}]$ unit.

pally, dinitrogen, but water in ethereal solution converts over 90% of the dinitrogen to ammonia (principally) and hydrazine. Why and how is not clear. Finally, carbon monoxide in diglyme yields a further dinitrogen complex, of appropriate stoichiometry $C_{28}H_{20}Ti_2N_2(CO)_2$, $\nu(N_2) = 1502\ \text{cm}^{-1}$. This is apparently *not* an analog of $[\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2]$ (see below) since the IR spectra suggest the presence of both terminal and bridging carbonyls.

The compound $[\{(\eta^5\text{-}C_5H_5)_2TiCH_2C(CH_3)_3\}_2N_2]$ has been characterized (*337*). Its homologs are well known. Surface anchoring of titanium complexes to SiO_2 in order to produce heterogeneous, supported dinitrogen complexes has not been successful (*202*).

Zirconium dinitrogen complexes show many unusual features. A detailed NMR study (^1H and ^{15}N) of $[\{(\eta^5\text{-}C_5Me_5)_2ZrL\}_2N_2]$ (L = N_2, CO, or PF_3) has been reported (*237*). It appears that the C_5Me_5 rings undergo exchange in the compound with L = N_2 (the two rings on a given zirconium are not identical) and the terminal dinitrogen molecules exchange with gaseous dinitrogen, but about 10 times faster than the rings exchange. A mechanism involving reversible loss of terminal dinitrogen was postulated to explain this. These exchanges do not occur for L = CO. Of the three dinitrogen complexes, only that with L = N_2 reacts with HCl to yield hydrazine (the other two regenerate only N_2), and the rate of this reaction (which seems to involve scrambling of terminal and bridging N_2) is faster than the rate of dinitrogen exchange. Protonation and exchange are probably not mechanistically related. The NMR behavior of $[\{(\eta^5\text{-}C_5Me_5)_2TiL\}_2N_2]$ (L = N_2) is similar.

There is only one simple type of complex which is still believed to contain side-on dinitrogen. A typical example was obtained by reduction of $[(\eta^5\text{-}C_5H_5)_2ZrCl\{CH(SiMe_3)_2\}]$ with sodium amalgam in tetrahydrofuran under dinitrogen (*181, 204*). The paramagnetic complex has two equivalent nitrogens (EPR, a triplet in the $^{15}N_2$ complex, a quintuplet in the $^{14}N_2$), but neither molecular weight determination nor X-ray structure analysis has proved feasible. There is no IR active band assignable to $\nu(N_2)$, and the compound is best formulated as shown in **1**. It loses dinitrogen at 10^{-3} mm Hg, 20°C to yield $[\{(\eta^5\text{-}C_5H_5)_2Zr\{CH(SiMe_3)_2\}\}_2N_2]$. The compound reacts with HBr to produce dinitrogen, ammonia, and hydrazine but not in reproducible quantities. The homolog $[(\eta^5\text{-}C_5H_4Me)_2Zr\{CH(SiMe_3)_2\}N_2]$ is also known.



1

There is also evidence for an unstable $[\{(\eta^5\text{-}C_5H_5)_2HfN_2\}_2N_2]$ (*23*). A thorium dinitrogen complex is apparently formed when thorium sputtered in argon is exposed to dinitrogen (*177*).

2. *V, Nb, and Ta*

The compound $[V(N_2)_6]$ has been obtained by matrix isolation techniques (*56*), and its UV spectrum analyzed. 10Dq for this compound is 22,460 cm^{-1} (compared with 28,845 cm^{-1} for $[V(CO)_6]$) and the charge-transfer bands are principally of the $t_{2g} \rightarrow \pi^*$ type. This material is analogous to $[Ti(N_2)_6]$. No other vanadium dinitrogen complexes have been isolated.

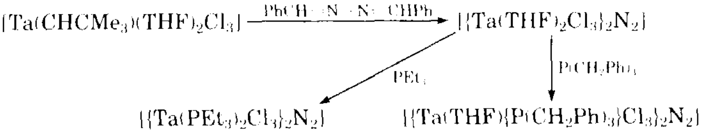
Niobium dinitrogen complexes have proved difficult to tie down. There is a report of a dark-blue, paramagnetic, air-sensitive material isolated from the reaction of $[(\eta^5\text{-}C_5H_5)_2NbCl_2]$ with *n*BuLi in an atmosphere of Ar + 0.1% N_2 + 0.1% O_2. The analysis has been interpreted as indicating the formula $[\{(\eta^5\text{-}C_5H_5)_2Nb\text{-}n\text{Bu}\}_2N_2O_2]$, although this seems to be more in the nature of an inspired guess (*228*). The same applies to another vague formulation, $[\{NbCl(Me_2PCH_2CH_2PMe_2)_2\}_2N_2]$ (*55*). Complexes of the type $[\{NbX_3(THF)_2\}_2N_2]$ (X = Cl or CH_2CMe_3) have been reported, and are very similar to the tantalum analogs (*281*).

Complexes of tantalum with dinitrogen have suddenly become relatively common. The initial synthesis was an indirect one, but direct reduction under N_2 is also possible (*334*).

$$[Ta(CHCMe_3)Cl_3(PMe_3)_2] \xrightarrow[N_2]{Na/Hg} [\{Ta(CHCMe_3)(PMe_3)_2Cl\}_2N_2] \xrightarrow{LiR}$$
$$[\{Ta(CHCMe_3)(PMe_3)_2R\}_2N_2] \ (R = Me,\ i\text{Pr or } CH_2CMe_3) \qquad (1)$$

Reduction under $^{15}N_2$ gave the labeled analogs, and comparison of the IR spectra showed a band at 847 (^{14}N) or 820 (^{15}N) cm^{-1} associated with dinitrogen. There is no band assignable to $\nu(N_2)$. Further dinitrogen complexes of similar form can be obtained by reducing $[Ta(PMe_3)_2(C_2H_4)Cl_3]$ under N_2, but $[TaCl_3(PMe_3)_3]$ itself does not pick up dinitrogen, for what are described as kinetic reasons (*282*).

An alternative route to tantalum dinitrogen complexes is shown in Eq. (2).



(2)

This remarkable reaction with azine may be compared to an azine-forming reaction of at least two dinitrogen complexes with acetone.

$$\begin{array}{c}[\{Ta(PEt_3)_2Cl_3\}_2N_2]\\ \text{or}\\ [\{TaCl(PMe_3)_3(C_2H_4)\}_2N_2]\end{array}\xrightarrow[8\ \text{h},\ 25^\circ\text{C}]{Me_2CO} Me_2C{=}N{-}N{=}CMe_2 \qquad (3)$$

All this suggests that the bridging dinitrogen in these materials may best be represented by a structure (*334*) as shown in **2**, and this is confirmed by X-ray structure analysis.

$$Ta{=}N{-}N{=}Ta$$

(**2**)

The complexes $[\{Ta(CHCMe_3)(PMe_3)_2CH_2CMe_3\}_2N_2]$ (*109*) and $[\{Ta(THF)Cl_3\{P(CH_2Ph)_3\}_2\}N_2]$ (*110*) have approximately linear Ta—N—N—Ta systems with the TaN distance of 1.82 Å and rather close to a Ta=N double bond length. The N—N bond lengths are ~1.29 Å, which is close to a N—N single bond. The best representation of the dinitrogen in these ligands would be as formally N^{-2}—N^{2} {or hydrazido(4−)}, this is unusual, and a situation only achieved hitherto in highly reduced dinitrogen complexes, such as one of nickel (*205*).

Consonant with the reduced nature of the bound dinitrogen, the complexes react with aqueous acid to form hydrazine, apparently quantitatively according to the formal reaction shown in Eq. (4) (*282*, *334*).

$$[L_2Cl_3Ta{=}N{-}N{=}TaCl_3L_2] + 4HCl \longrightarrow 2TaCl_5 + N_2H_4 + 4L \qquad (4)$$

3. *Cr, Mo, and W*

a. The Complexes. The dinitrogen complexes of this Group, and especially those of Mo and W, have been especially intensively studied. The dinitrogen complexes of Cr, like those of other First Transition Period elements, are rather labile and not easy to study.

The complex [$Cr(CO)_5N_2$] has been investigated in a matrix at 20 K, and its UV spectrum interpreted (*52, 53*). The related species [$Cr(\eta^6$-$C_6H_6)(CO)_2N_2$] has also been isolated under matrix conditions (*277*). However, this species is stable at normal temperatures and has been prepared by conventional routes (*304*), and its IR spectrum in the matrix [1940, 1898 ν(CO); 2145 $\nu(N_2)$ cm^{-1}] agrees well with that observed under ambient conditions. The other chromium complex relevant to this discussion contains a bridging dinitrogen, [$(\eta^5$-$C_5H_5)(CO)_2MnN_2Cr(CO)_5$] [2138 $\nu(N_2)$ cm^{-1}] (*299*). It was obtained by reaction of [$(\eta^5$-$C_5H_5)(Mn(CO)_2N_2$] with [$Cr(CO)_5$(THF)] or, more surprisingly, by base-catalyzed dihydrogen elimination from [$(\eta^5$-$C_5H_5)(CO)_2MnN_2H_2Cr(CO)_5$]. This latter reaction, which is the converse of a plausible Haber-type route for complexed dinitrogen, is so far unique. The complex [$\{Cr(Ph_2PCH_2CH_2PPh_2)_2\}_2N_2$] has been claimed; it is paramagnetic and has been incompletely described (*315*).

For molybdenum, several new compounds have appeared, and one, namely [$MoX(N_2)(Ph_2PCH_2CH_2PPh_2)_2$] (X = Cl or Br), totters on the edge of extinction. Neither XPS (X-ray photoelectron spectroscopy) (*44*) nor IR (*88*) and Raman (*114a*) spectroscopic data lend any real credence to the integrity of this species, which is probably a cocrystallized mixture of [$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$] and [$MoX_2(Ph_2PCH_2CH_2PPh_2)_2$]. It probably has no more than a transient existence as a reaction intermediate. The compound [$Mo(CO)_5N_2$] has been isolated in a matrix at 20 K, and has $\nu(N_2)$ = 2248 cm^{-1}, higher than the corresponding frequency in either the chromium or tungsten analogs (*52*). Clearly, a monotonic variation of $\nu(N_2)$ down the Group Cr, Mo, W does not occur. The complex [$(\eta^5$-$C_5H_5)Mo(CO)_2(N_2)CH_3$] has been isolated in a dinitrogen matrix at 12 K. It has $\nu(N_2)$ = 2191 cm^{-1} (*236*).

The very labile dinitrogen complex [$Mo(CO)(N_2)(Ph_2PCH_2CH_2PPh_2)_2$] has been described in detail. Its immediate precursor, [$Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2$], is obtained by the reaction of [$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$] with, for example, benzyl propionate under carefully controlled conditions (*283, 322*). This precursor is square pyramidal in the solid state, with carbon monoxide at the apex and an essentially vacant coordination position trans to it. The CO bond length is 1.192(12) Å, and ν(CO) = 1690 cm^{-1}, and the nearest approach of any phenyl hydrogen to the molybdenum is 2.98(11) Å. Upon exposure to dinitrogen, $[Mo(CO)(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ forms. This has a CO bond length of 1.127(20) Å, and NN bond length of 1.09(2) Å, which is rather short. However, coupled with $\nu(CO) = 1799\ cm^{-1}$ and $\nu(N_2) = 2128\ cm^{-1}$ (rather high) this is not unreasonable (*283*). A dinitrogen complex of molybdenum has been anchored to a tin oxide electrode, but it was not possible to reduce the bound dinitrogen past the hydrazido(2−) stage (NNH_2^{2-}) (*226*).

A further interesting complex, synthesized from $[Mo(PMe_3)_6]$, itself obtained by direct reaction of molybdenum atoms and the phosphine, has been alluded to. The action of dinitrogen (15 atm) on a benzene solution generates $[Mo(N_2)(PMe_3)_5]$, $\nu(N_2) = 1950\ cm^{-1}$ (*112*).

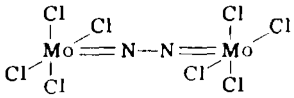
There are many more complexes of the types $[Mo(N_2)_2(\text{neutral ligand})_4]$, though the neutral ligands are all phosphines. One series with $Ar_2PCH_2CH_2PAr_2$ (Ar = p-$CF_3C_6H_4$, p-ClC_6H_4, p-MeC_6H_4, or p-$MeOC_6H_4$) has a range of $\nu(N_2)$ from 1990 cm^{-1} at one extreme to 1956 cm^{-1} at the other. The significance of these data for bonding theories in these compounds has been discussed at length (*195*). Another isolated compound is $[Mo(N_2)_2(PPh_3)\{(Ph_2PCH_2CH_2)_2PPh\}]$ which has an equatorial arrangement of phosphoruses (*18*). This complex reacts with HBr to yield $[MoBr_3\{(Ph_2PCH_2CH_2)_2PPh\}]$, dinitrogen, and ammonia. A general method of synthesizing $[Mo(N_2)_2(\text{diphosphine})_2]$ using $MoCl_5$ as the immediate precursor rather than materials such as $[MoCl_3(THF)_3]$ has been reported (*172*).

The preparation of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ has been described (*64*). Reaction of this complex with ethylene yields $[Mo(C_2H_4)_2(PMe)_4)]$, and exposure to dinitrogen results in equilibria being set up.

$$[Mo(C_2H_4)_2(PMe_3)_4] + N_2 \rightleftharpoons [Mo(C_2H_4)_2(N_2)(PMe_3)_3] + PMe_3 \qquad (5)$$

$$2[Mo(C_2H_4)_2(N_2)(PMe_3)_3] \rightleftharpoons [Mo_2(\mu\text{-}N_2)(C_2H_4)_4(PMe_3)_6] + N_2 \qquad (6)$$

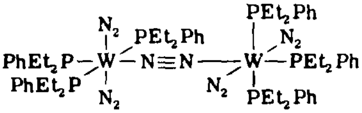
A further dinitrogen complex of a different class may also have been prepared by the action of NCl_3 or IN_3 on $MoCl_5$ (*229*). The product analyzes as $MoNCl_4$ and is apparently dimeric. It shows no $\nu(N_2)$ although bands assigned to $\nu(MoN)$ were observed at 1005 and 1022 cm^{-1}, and were it not for the fact that it is paramagnetic ($\mu_{eff} = 1.63$ BM) it could be satisfactorily formulated as shown in **3**.



3

The compound loses a chlorine to give $MoNCl_3$ when heated in CCl_4 at 100°C, and water produces dinitrogen, ammonia, and molybdenum blue. It is superficially analogous to the tantalum dinuclear species discussed above, but its paramagnetism is still a puzzle.

Tungsten complexes recently reported are generally unexceptional. The series $[W(N_2)_2(Ar_2PCH_2CH_2PAr_2)_2]$ parallel their molybdenum analogs, their values for $\nu(N_2)$ being some 25 cm^{-1} lower, and their oxidation potentials being virtually identical (*195*). It has been evident for some time that not all tertiary phosphines give rise to complexes $[M(N_2)_2(phosphine)_4]$, and that other dinitrogen complexes form in the reductive systems used in the attempted preparations. One of these other complexes has now been characterized, $[\{W(N_2)_2(PEt_2Ph)_3\}_2(N_2)]$, and its structure (**4**) determined (*5*). This is the first bridging dinitrogen complex of tungsten. The complex has $\nu(N_2)$ = 1890 and 1895 cm^{-1} and contains more dinitrogen per metal atom than any stable complex heretofore reported.



4

The complex $[W(CO)_5N_2]$ [$\nu(N_2)$ = 2227 cm^{-1}] has been isolated in a matrix at 20 K (*52*). Some evidence for $[W(CO)_4(N_2)_2]$ and $[W(CO)_4N_2]$ has also been presented. Substitution reactions of $[W(N_2)_2(PMePh_2)_4]$ have led to new species $[W(N_2)_2(PMePh_2)_3L]$ (L = 3-RC_5H_4N or 4-RC_5H_4N; R = Me or CO_2H), $[W(N_2)_2(PMePh_2)_4][FeCl_4]$ (rather unstable) and $[M(N_2)_2(PMePh_2)_2(Ph_2PCH_2CH_2PPh_2)]$ (M = Mo or W) have also been described (*100*).

b. Reactions of Dinitrogen Complexes (Mo and W). The protonation and acylation of Mo and W complexes containing dinitrogen were fundamental discoveries which gave the first definitive evidence that mononuclear coordinated dinitrogen could indeed be involved in the reactions of nitrogenase. The mechanisms of such protonations are not clear, although firm evidence for some of the initial steps has now been obtained.

The complexes $[M(N_2)_2(tertiary\ phosphine)_4]$ (M = Mo or W) react with acids in different ways. For example $[W(N_2)_2(PMe_2Ph)_4]$ with HCl or H_2SO_4 in methanol produces 1 mol dinitrogen and up to 2 mol ammonia, whereas the molybdenum counterpart gives only ~1 mol of ammonia and 1.5 mol of dinitrogen. Many data have been collected on the yields of ammonia from the reactions of these substrates with a variety of acids in a range of solvents (*82, 107, 190, 258*). It is impossible as yet to analyze the various influences that the acid and solvent have on the yields of ammonia. The solvent will never act merely as an inert medium in which the reaction takes place; it can affect the strength of the acid, and if it is a sufficiently good nucleophile it can enter the coordination sphere of the complex and thus influence the rate and/or position of subsequent protonations.

The reactions of complexes of the type *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ with acids in general proceed only as far as the hydrazido(2−) stage, *trans*-$[M(NNH_2)X(R_2PCH_2CH_2PR_2)_2]^+$ (Section VI,B). This also happens when these are attached to an electrode surface (*226*). Under certain rather specific conditions protonation can occur at the metal rather than the dinitrogen, to yield $[MH(N_2)_2(R_2PCH_2CH_2PR_2)_2]^+$ (R = Ph). The mechanisms of these reactions are discussed in more detail in Section VI,D,2. There is nothing unique about the hydrazido(2−) state for the complexes containing chelating phosphine ligands; ^{15}N-NMR spectroscopy has shown this to be a key intermediate stage in the reactions of $[M(N_2)_2(PMe_2Ph)_4]$ with H_2SO_4 in tetrahydrofuran (*4*).

Other electrophiles such as Lewis acids, trifluoroacetic anhydride (Section VI,B), and alkyl halides (Section IV,A,6) also react with coordinated dinitrogen. As will be discussed in a later section, the reactions of *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ with alkyl halides are several orders of magnitude slower than the reactions with acid. The reaction with alkyl halides proceeds via initial loss of dinitrogen from the substrate to yield the reactive five-coordinate, 16-electron species $[M(N_2)(R_2PCH_2CH_2PR_2)_2]$, which rapidly reacts with the alkyl halide. It is now clear that substitution reactions of *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ also proceed via rate-controlling loss of dinitrogen (*25, 88*).

All these observations have stimulated a general interest in the factors that control the rate of dinitrogen loss from a variety of bis(dinitrogen) species. The electronic absorption spectrum of $[Mo(N_2)_2(PPh_2CH_2CH_2PPh_2)_2]$ has been analyzed in terms of the expected *d–d* and d–$\pi^*(N_2)$ charge-transfer transitions, all of which weaken the Mo—N_2 bond and enhance dinitrogen loss (*171*). Photodissociation can occur solely upon populating low ligand field excited states (*7*). The compound $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ is photoluminescent (*63*), and the observed spectrum agrees with that cited in (*171*). The flash photolysis of the same compound in THF by tungsten light leads to the species $[W(Ph_2PCH_2CH_2PPh_2)_2]$, which picks up two dinitrogen molecules (*326*) in successive steps. Observed rate constants in dinitrogen-saturated THF are $k_1 = 4.6\ (\pm 0.8) \times 10^2\ \text{sec}^{-1}$ and $k_2 = 3.9\ (\pm 0.6)\ \text{sec}^{-1}$.

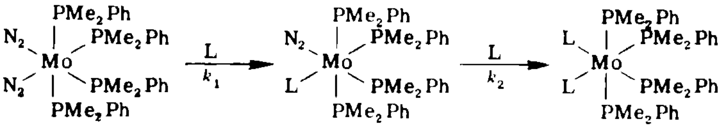
Replacement of dinitrogen has been studied both quantitatively and qualitatively. In a qualitative sense, $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ reacts with H_2 to give only $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ and there is no sign of earlier reported species such as $[MoH_2(Ph_2PCH_2CH_2PPh_2)_2]$ and $[\{MoH_2(Ph_2PCH_2CH_2PPh_2)\}_2(Ph_2PCH_2CH_2PPh_2)]$ (*8*). The complex $[Mo(CO)(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ reacts with a range of bases, L, which displace dinitrogen (*323*). These experiments have yielded an affinity series for the various potential ligands in competition with dinitrogen for the dinitrogen-binding site in $[M(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ (*88*).

$$\text{RNC, CO} > \text{PhCN} > n\text{PrCN} > N_2 > \text{MeCN} > \text{SCN}^- > \text{CN}^- > N_3^- > NH_3 > \text{PhC}_2$$
$$> H_2O,\ C_5H_5N,\ \text{halide (the last three bind very weakly)}$$

The fact that dinitrogen can displace "good" ligands such as azide and ammonia from a good dinitrogen-binding site clearly shows that the site is uniquely fitted for binding a ligand with the peculiar characteristics of dinitrogen (a very weak σ donor power but a considerable π acceptor power).

The replacement of dinitrogen by a range of other π bonding ligands has enabled a study to be made of the effect of the new ligands on the oxidation potential. In general, there is a linear correlation between $E^{\text{ox}}_{1/2}$ and $\nu(N_2)$ and this kind of relationship has been used, together with data from other series of complexes, to develop quantitative estimates of parameters describing ligand and metal interactions. On this basis, it was concluded that a metal site for binding dinitrogen strongly should be at once electron rich and polarizable (*95, 97*). It was also shown how the mechanism of alkylation of coordinated dinitrogen, via loss of dinitrogen prior to coordination of alkyl halide, changed to an outer-sphere electron-transfer mechanism with the most electron-rich dinitrogen complexes such as $[W(N_2)(SCN)(Ph_2PCH_2CH_2PPh_2)_2]^-$ (*97*) (Section IV,B). Complexes such as the last are very electron rich ($E^{\text{ox}}_{1/2} = -1.16$ V vs saturated calomel electrode, sce), and bind the dinitrogen very strongly. Even the neutral tungsten(I) species is indefinitely stable in air (whereas the bromo analog disproportionates rapidly) and the cationic tungsten(II) species has a half-life of ~15 sec in THF solution, whereas its bromo analog decomposes under similar conditions and is undetectable.

The rate of substitution reactions can give a measure of the activation energy, and with the usual assumptions of transition state theory, the metal–dinitrogen bond energy. The enthalpy value thus obtained (*88*) for $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ is 116 kJ mol^{-1}. Parallel studies, on the replacement of dinitrogen by PhCN, gave a value of 113 kJ mol^{-1} (*68a*). The corresponding value for M = W is >159 kJ mol^{-1}. In *cis*-$[M(N_2)_2(PMe_2Ph)_4]$, both dinitrogens are replaced in consecutive steps by PhCN, and the ratios k_{Mo}/k_W for each step are ~10^2. This fully accords with the tighter binding of dinitrogen to tungsten compared to molybdenum. A similar study using MeNC suggested two slow reactions for the successive steps where k_2/k_1 ~5 and k_1 (273 K) = 1.2 $\sec^{-1}$. This work revealed a cis-labilizing series in the second step, viz.,



(7)

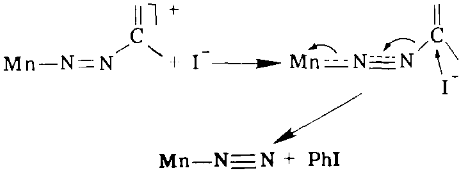
*t*BuNC > MeNC > N_2 > MeCN (*276*). Reaction of $[Mo(N_2)_2(dppe)_2]$ with organic isocyanates to produce $[Mo(OCNR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ has also been reported (*247*).

Variation of phosphine substituents in the series $[M(N_2)_2(Ar_2PCH_2CH_2PAr_2)]$ (Ar = *p*-ClC_6H_4, *p*-$CF_3C_6H_4$, Ph, *p*-MeC_6H_4, or *p*-$MeOC_6H_4$) shows that there is no longer a quasilinear relationship between $E_{1/2}^{ox}$ and $\nu(N_2)$. In fact, an inductive cis influence of the substituent makes itself felt at the metal (as shown by $E_{1/2}^{ox}$ which correlates linearly with Hammett σ_p) whereas the values of $\nu(N_2)$ correlate best with σ^+ which suggests through conjugation between the phosphorus and dinitrogen. The values for the activation energy for dinitrogen loss correlate roughly with simplistic ideas of the relative donor powers of the phosphines (all the values are in the range 90–105 kJ mol^{-1}) and upon oxidation to the corresponding $[Mo(N_2)_2(\text{diphosphine})_2]^+$ species ΔG^* drops by ~20 kJ mol^{-1} (*195*). Clearly analogous Mo(II) species would not be expected to be thermodynamically stable.

4. *Mn, Tc, and Re*

Manganese forms two kinds of stable dinitrogen complex, containing either terminal or bridging dinitrogen ligands (both homodinuclear and heterodinuclear). The complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$ [$\nu(N_2)$ = 2155 cm^{-1}] is obtained from the reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$ with dinitrogen. This compound has a high value of $\nu(N_2)$, and the dinitrogen itself would be expected to be rather positive. It reacts with LiMe or LiPh in THF at −20°C to generate a compound formulated as a novel derivative of diazene (*305*, *306*) (Section V,C,4).

An alternative route to the mononuclear dinitrogen complex is by the reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2Ar)]^+$ and its rhenium homologs with nucleophiles such as Cl^-, Br^-, I^-, Cn^-, and SCN^-. This has potential for the synthesis of asymmetrically labeled dinitrogen complexes (*15, 16*). The reaction even occurs with the nucleophile PPh_3. The reaction sequence shown in Eq. (8) has been proposed. (The representa-



(8)

tion Mn—N≡N for a dinitrogen complex, and similarly elsewhere, simply portrays a metal dinitrogen interaction. It is not a canonical form.) An excess of PPh_3 yields $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(PPh_3)]$ (*15*). The complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$ is reduced irreversibly at scan rates up to 100 V sec^{-1} at -2.08 V vs sce, more easily than the tricarbonyl (-2.34 V, reversible) but the irreversibility is not due to dinitrogen loss (*354*).

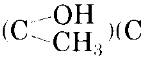
Dinuclear complexes have generally been obtained by indirect routes. Thus, $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(THF)]$ reacts with CF_3CHN_2 to give $[\{(\eta^5\text{-}MeC_5H_4)Mn(CO)_2\}_2N_2]$ with $\nu(N_2)$ at 1971 cm^{-1}. X-Ray analysis reveals that despite the IR-active band there is a linear, symmetrical dinitrogen bridge between two manganese atoms, with N—N = 1.118(7) Å, by no means an unusual separation (*350*). The reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_4)]$ with $[Cr(CO)_5(THF)]$ produces the complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_4)Cr(CO)_5]$ with a bridging hydrazine. This can be oxidized by H_2O_2/Cu^{2+} at -25°C to give the bridging diazene complex and finally the bridging dinitrogen complex (*299, 300*). In fact the diazene complex decomposes spontaneously with loss of dihydrogen in the presence of base to yield the bridging dinitrogen complex without the need for a specific oxidant, but the mechanism is not clear.

The complexes $[Mn(CO)_3(N_2)(NO)]$, $[Mn(CO)_2(N_2)(NO)]$, and $[Mn(N_2)(NO)_3]$ have been characterized in an argon matrix (*122, 124*).

There is one report of a technetium complex, $[Tc(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$, obtained by reduction of $[TcCl_4(PPh_3)_2]$ with Na/Hg under dinitrogen in the presence of the diphosphine (*208*). The apparently paramagnetic complex has $\nu(N_2) = 2046$ cm^{-1}, but the evidence for the formulation and the paramagnetism is not entirely satisfactory. The technetium complex would have been expected to be diamagnetic $[TcCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ by analogy with rhenium chemistry.

The chemistry of rhenium complexes with dinitrogen is quite extensive. It was earlier shown (*73*) that complexes such as $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ contain a rather basic dinitrogen and that this can react with Lewis acids to form adducts, although few of these have been characterized in detail. The adduct from the reaction of $[\mathrm{ReCl(N_2)(PMe_2Ph)_4}]$ and $[\mathrm{MoCl_4(THF)_2}]$ in methanol has $\nu(\mathrm{N_2}) = 1660\ \mathrm{cm}^{-1}$, and the paramagnetic ($\mu_{\mathrm{eff}} = 1.85$ BM) compound, of formula $[\mathrm{MoCl_4(OCH_3)(\mu\text{-}N_2)ReCl(PMe_2Ph)_4}]$, has a linear Mo—N—N—Re system with N—N = 1.18 Å (*106*). Diamagnetic $[\{\mathrm{ReCl(PMe_2Ph)_4}\}_2\{\mathrm{MoCl_4(N_2)}\}_2]$ has a relatively long N—N separation of 1.28 ± 0.05 Å (*106*), and two further adducts characterized are $[\{\mathrm{MoCl_3(THF)_2}\}\mathrm{N_2}\{\mathrm{ReCl(PMe_2Ph)_4}\}]$ [$\nu(\mathrm{N_2}) = 1558\ \mathrm{cm}^{-1}$, $\mu_{\mathrm{eff}} = 3.5$ BM] and diamagnetic $[\{\mathrm{WCl_4(PMe_2Ph)}\}\mathrm{N_2}\{\mathrm{(ReCl(PMe_2Ph)_4}\}]$ [$\nu(\mathrm{N_2}) = 1740\ \mathrm{cm}^{-1}$] (*106*).

The complex $[\mathrm{ReH_3(Ph_2PCH_2CH_2PPh_2)_2}]$, upon irradiation at 366 nm in benzene, loses dihydrogen to produce a five-coordinate species $[\mathrm{ReH(Ph_2PCH_2CH_2PPh_2)_2}]$, analogous to $[\mathrm{Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2}]$ (*278*). Similarly, it binds donor molecules in the vacant site, particularly carbon monoxide, acetylene, and dinitrogen, the last to give $[\mathrm{ReH(N_2)(Ph_2PCH_2CH_2PPh_2)_2}]$, but few further details are available.

Four rather unusual rhenium compounds, of the form $[\mathrm{(ReR_4)_2N_2}]$ (R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2CMe_3}$, Me, or $\mathrm{CH_2CMe_2Ph}$), can be obtained from reaction of $[\mathrm{ReCl_4(THF)_2}]$ with $\mathrm{MgR_2}$ in THF under dinitrogen (*239*). These red-purple materials show no band assignable to $\nu(\mathrm{N_2})$ and their structures must be regarded as provisional. The complex $[(\eta^5\text{-}\mathrm{MeC_5H_4})\mathrm{Re(CO)_2N_2}]$ can be obtained by the attack of a nucleophile on $[(\eta^5\text{-}\mathrm{MeC_5H_4})\mathrm{Re(CO)_2(N_2)R}]^+$ (R = aryl) (*16*), and also by the reaction of dinitrogen (or $\mathrm{N_2O}$) with compounds such as $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(CO)_2(THF)}]$. A high pressure (100 atm) is required, and $\nu(\mathrm{N_2})$ is also high (2138 cm^{-1}) (*302*). The dinitrogen in this last compound is susceptible to nucleophilic attack (*306*), as it is in the manganese homolog. However, electron richness, as measured by $E_{1/2}^{\mathrm{ox}}$ or $\nu(\mathrm{N_2})$, is not a sufficient criterion for reactivity of dinitrogen to nucleophilic attack, since $[\mathrm{ReCl(CO)_2(N_2)(PPh_3)_2}]$ [$E_{1/2}^{\mathrm{ox}} = 1.1$ V vs sce, $\nu(\mathrm{N_2}) = 2050\ \mathrm{cm}^{-1}$] reacts with LiMe to form, after addition of acid, the carbene complex  $[\mathrm{ReCl(C}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{CH_3}\end{smallmatrix}\mathrm{)(CO)(N_2)(PPh_3)_2}]$, and $[\mathrm{ReCl(CO)_3(PPh_3)_2}]$ ($E_{1/2}^{\mathrm{ox}} = 1.37$ V) reacts with LiMe to yield $[\mathrm{ReMe(CO)_3(PPh_3)_2}]$ (*99*).

The reduction of $[\mathrm{Re(NPh)Cl_3(PPh_3)_2}]$ by sodium amalgam in the presence of an excess of $\mathrm{PMe_3}$ under $\mathrm{N_2}$ leads to $[\mathrm{Re(NHPh)(N_2)(PMe_3)_4}]$. This unusual rhenium(I) species contains a labile $\mathrm{N_2}$, which can be replaced by $\mathrm{H_2}$, and has a high value of $\nu(\mathrm{N_2}) = 2000\ \mathrm{cm}^{-1}$. The N—N distance is short, 1.101(18) Å (*106a*). Irradiation of $[\mathrm{ReH_5(PMe_2Ph)_2}]$ by 366 nm radiation in benzene under $\mathrm{N_2}$ leads to the ortho-metallated species *fac*-$[\mathrm{Re(PMe_2Ph)_3(PMe_2C_6H_4)N_2}]$ which has N—N = 1.117(13) Å (*177a*). There are more dinitrogen complexes of rhenium than of any other element.

5. *Fe, Ru, and Os*

Although iron is one of the principal metals involved in biological nitrogen fixation, its nitrogen (and especially its dinitrogen) chemistry has been relatively little explored. New dinitrogen complexes of iron are relatively few. The complex $[\{(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)\}_2(N_2)]^{2+}$ can be obtained by displacing acetone from $[(\eta^5\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(Me_2CO)]^+$ (*303*). It has $\nu(N_2)$ at 2040 cm^{-1} (IR active, although unexpectedly, and there is no indication of a mononuclear species). IR and NMR data suggest that the iron has a lower electron density than in the CO analog.

A new dinitrogen complex has been obtained by reduction of $[FeBrL]^+$ ($L = Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$) with $Na[BH_4]$ under dinitrogen. This reaction generates $[FeHL]^+$ and then $[FeH(N_2)L]^+$. The bromide salt $[\nu(N_2) = 2130\ cm^{-1}]$ is trans, with $FeH = 1.53(9)$, $NN = 1.076(15)$ Å and $Fe\hat{N}N = 178.5(7)^\circ$ (*173*). The chemistry of this compound has not been explored.

A further as yet uncharacterized dinitrogen complex can be obtained by reduction of $FeCl_3$ with naphthyllithium under dinitrogen. It is not altogether clear how this occurs. The primary product is $Li_2[Fe(naphthyl)_4]$ which is a tetrahedral complex which can be further reduced, with dinitrogen uptake (*11*). However, comparable reduction of $FeCl_3$ with LiPh produces the square-planar compound $[Li_2(Et_2O)]_2[FePh_4]$ which takes up dinitrogen directly (*309*). This system has not yet been completely characterized. The complex $[FeH_2N_2(PEtPh_2)_3]$ reacts with cyclohexene to form $[FeH(C_6H_{11})(PEtPh_2)_2(solvent)]$ (*27*).

The first of all the dinitrogen complexes was $[Ru(NH_3)_5N_2]^{2+}$, and there are now considerable numbers of ruthenium dinitrogen compounds, but none shows chemistry involving transformation of dinitrogen. It has been shown that $[Ru(NH_3)_5N_2]^{2+}$ is formed by many routes, a new one being from $[Ru(NH_3)_5(NO)]^{3+}$ and OH^- under argon. This reaction is believed to involve a kind of diazotization, and in the presence of $[Ru(NH_3)_6]^{3+}$ the dinuclear species $[\{Ru(NH_3)_5\}_2N_2]^{4+}$ is formed (*180*). More unexpected, $[Ru(NH_3)_5(H_2O)]^{2+}$ reacts with 3,3′-pentamethylenediazirine to produce two related products, one of which is a diazirine complex with the N—N system bound side-on (X-ray analysis). The other material has not been characterized, but both react with dioxygen in acid to generate $[Ru(NH_3)_5N_2]^{2+}$ and cyclohexanone (*312*).

New complexes have been isolated from the reaction of $[Ru(Hedta)(H_2O)]^-$ [$edta = (O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2{}^{4-}$] and dinitrogen, and there is also evidence for intermediate species such as $[Ru(Hedta)(N_2)]^-$. The two materials unequivocally characterized were

$(NH_4)_2[Ru(edta)N_2] \cdot 5H_2O$ and $Mg_2[\{Ru(edta)\}_2N_2] \cdot 8H_2O$. The latter loses dinitrogen thermally in a process for which $\Delta H^* = 44$ kJ mol^{-1}, but it is not known what is the rate-limiting step (*139*).

The reaction of $[\{Ru(NH_3)_5\}_2N_2]^{4+}$ with OH radicals has been investigated. The mechanism has been inferred to be as shown in Eq. (9) (*61*).

$$[\{Ru(NH_3)_5\}_2N_2]^{4+} + OH \longrightarrow [(NH_3)_5RuN_2Ru(NH_3)_5(OH)]^{4+} \longrightarrow$$
$$[\{Ru(NH_3)_5\}_2N_2]^{5+} + H_2O \longrightarrow [Ru(NH_3)_5OH]^{2+} + [Ru(NH_3)_5N_2]^{2+} + H^+ \qquad (9)$$

The dinuclear complex can also be reduced by the hydrated electron, but no chemical transformation of dinitrogen was achieved (*19*).

New osmium complexes are few, the air-sensitive $[Os(N_2)(THF)(TPP)]$ (TPP = tetraphenylporphyrinate(2−)) being formed from $[OsO_2(TPP)]$ and hydrazine hydrate. The compound has $\nu(N_2) = 2050$ cm^{-1}, not very different from $\nu(N_2)$ of $[Os(NH_3)_5N_2]^{2+}$ ($\sim$2030 cm^{-1}) (*47*).

One conceivable way of "fixing" nitrogen is to split the N≡N triple bond of dinitrogen bridging two metal atoms as shown in Eq. (10).

$$M{-}N{\equiv}N{-}M \longrightarrow M{\equiv}N + N{\equiv}M \qquad (10)$$

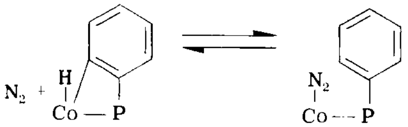
In practice, only the converse has been achieved. For example the oxidation of $[Os(NH_3)_5(CO)]^{2+}$ by Ce(IV) or $K_2S_2O_8$, or even electrolytically, generates $[\{Os(NH_3)_4(CO)\}_2N_2]$ (*49*). It is not altogether clear how, but it is believed that the reaction may proceed via $[Os(NH_3)_4(NH)(CO)]^{2+}$ which dimerizes and is oxidized. The loss of protons would be facile, it having been shown that the pK_a of $[Os(NH_3)_6]^{4+}$ (<0) is at least 15 units less than that of $[Os(NH_3)_6]^{3+}$ (>15) (*51*). A wide range of haloammine dinitrogen complexes has been obtained using this principle (*50*). For example, $[Os(NH_3)_4Cl_2]^{2+}$ is oxidized to $[Os(NH_3)_4Cl_2]^{3+}$ by HNO_2 and reductive diazotization at pH >3 then produces $[Os(NH_3)_3(N_2)Cl_2]^+$, and $[Os(NH_3)_5(N_2)]^{2+}$. The values of $\nu(N_2)$ are all above 2000 cm^{-1}, and for Os(III) compounds approach 2200 cm^{-1}. Consequently, no protonation of coordinated dinitrogen in these complexes is to be expected. The electron-withdrawing power of dinitrogen is shown by the following parameters: $[Os(NH_3)_6]^{3+}$, $pK_a \sim 16$; $[Os(NH_3)_5(N_2)]^{3+}$, $pK_a \sim 6.6$ (*50*).

The photolysis of $[Os(NH_3)_5N_2]^{2+}$ and $[Os(NH_3)_4(N_2)_2]^{2+}$ at 229–366 nm is complex. The mono(dinitrogen) complex loses dinitrogen, aquates, and is oxidized by protons, and the resultant reaction manifold is complicated. The bis(dinitrogen) complex solely photoaquates yielding $[Os(NH_3)_4(H_2O)N_2]^{2+}$ which can also oxidize. For both complexes, charge-transfer is associated with the photooxidation, and ligand field states with the aquation (*240*).

6. *Co, Rh, and Ir*

Compounds at this end of the Transition Series have attracted less interest of late, presumably because their chemistry is not such as to lead to hydronitrogen species.

The cobalt(0) species $[Co(N_2)(PPh_3)_3]$ is a catalyst for the isomerization of α-olefins (*284*). The isomerization is actually accelerated by dinitrogen, and this is believed to be due to the fact that the dinitrogen, which is probably a stronger ligand for cobalt in these materials than the olefins, displaces a metallation equilibrium as shown in Eq. (11).

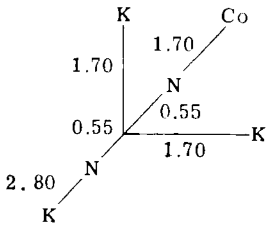


(11)

The cobalt(I) species $K[Co(N_2)(PMe_3)_3]$ (**5**) can be obtained by several routes, the most direct being the following (*182, 212*).

$$[CoCl(PMe_3)_3] \xrightarrow[\text{Ar, then } N_2]{K} K[Co(N_2)(PMe_3)_3] \qquad (12)$$

This orange solid is stable to 140°C under dinitrogen (1 atm.) and has a fairly complex crystal structure in which there is a linear KNNCo system with further potassium ions bonded side-on to dinitrogen as shown (approximate distance in Å) in **5**. The compound has $\nu(N_2)$ at $\sim 1900\ cm^{-1}$.



5

Related species $[Co(N_2)(PR_3)_3Mg(THF)_2]$ can be obtained by reaction of $MgEt_2$ with $[CoH(N_2)(PR_3)_3]$ (PR_3 = PPh_3 or $PEtPh_2$) (*248*). This compound is (surprisingly) diamagnetic and may be incorrectly formulated. With acid it generates dihydrogen, dinitrogen, hydrazine, and ammonia (trace), the precise amounts depending upon the reaction conditions, although no proper material balance has been presented.

The matrix isolated species $[Co(CO)_x(N_2)_y(NO)]$ ($x = 1$ or 2, $y = 2$ or 1) have been reported (*123*).

New rhodium dinitrogen complexes fall into two classes, mononuclear and dinuclear. The mononuclear side-on dinitrogen complex (*60*) $[RhCl(N_2)(P\text{-}i Pr_3)_2]$ has proved to be a conventional end-on material (*327*). The dinuclear species $[\{RhX(PCy_3)_2\}_2]$ ($X = Cl$, Br, or I) react with dinitrogen (fastest for $X = I$) to generate $[RhX(N_2)(PCy_3)_2]$ which has $\nu(N_2)$ at $\sim 2100\ cm^{-1}$ (*339*). A further series of compounds $[RhH(N_2)(PR_3)_3]$ ($PR_3 = P\text{-}t Bu_2Ph$, $P\text{-}t Bu_3$, PCy_3, or $P\text{-}i Pr_3$) has been synthesized as shown in Eq. (13). They all have $\nu(N_2)$ $\sim 2140\ cm^{-1}$ (*357*).

$$RhCl_3 \xrightarrow[N_2,PR_3]{NaHg/THF} [RhH(PR_3)_3] \xrightarrow{H_2} [RhH_3(PR_3)_2] \xrightarrow{N_2}$$

$$[RhH(N_2)(PR_3)_2] \longrightarrow [\{RhH(PR_3)_2\}_2N_2] \tag{13}$$

The dinuclear species for $PR_3 = P\text{-}i Pr_3$ has a linear Rh—N—N—Rh system with N—N = 1.134(5) Å, and $\nu(N_2) = 1827\ cm^{-1}$ (*357*).

There are no new data on iridium dinitrogen species, or on dinitrogen complexes of Ni, Pd, or Pt.

7. *Miscellaneous Dinitrogen Complexes*

Barium nitride, Ba_3N_2, is a catalyst for the scrambling of $^{14}N_2$ and $^{15}N_2$ and is two to three orders of magnitude more effective than iron or ruthenium. The energy of activation is $\sim 40\ kJ\ mol^{-1}$ (*266*). This suggests that it is not necessary for an element to be a transition metal for it to bind dinitrogen or to catalyze the Haber process.

Haber catalysts generally contain promoters such as alkali metals, and mixtures such as $K–Ru–Al_2O_3$ have been investigated as potential Haber catalysts and dinitrogen-complexing agents. This mixture catalyzes $^{14}N_2–^{15}N_2$ isotope scrambling at 270°C, and forms three types of binding to dinitrogen (*335, 336*), variously assigned to dinitrogen bound to Ru, dinitrogen bound to K, and dinitrogen adsorbed within the bulk solid [$\nu(N_2) = 2020\ cm^{-1}$]. Two species with $\nu(N_2) = 1935$ and $1870\ cm^{-1}$, respectively, are formed upon heating the mixture after exposure to dinitrogen (*261*). It is not clear whether these are new or are the Ru and K complexes previously identified. K–Ru absorbs dinitrogen to form an adduct formulated as KN_2Ru. This can be solvolyzed to give ammonia, hydrazine, and dinitrogen, and the air-stable solvolysis residue shows bands at 2160 and 2200 cm^{-1} (*262*). The origin of these bands has not been assigned.

Fe–Al_2O_3 also binds dinitrogen and Fe–MgO can give rise to two interconvertible dinitrogen species, $\nu(N_2)$ = 2050 and 2200 cm^{-1} (*263*).

The species $HgF_2 \cdot N_2$ has been identified in an argon matrix (*325*), and the paramagnetic species $Si(N_2)$ is stable at 4 K. It has $\nu(N_2)$ = 1736 cm^{-1} (*227*).

B. The Condition of Coordinated Dinitrogen

Despite the wealth of evidence confirming that dinitrogen binds end-on to metals in the vast majority of cases, and that it protonates when so bound by a simple reaction with acid, theoretical chemists have continued to calculate new, hypothetical schemes and systems.

Ab initio calculations on $[Ru(NH_3)_5N_2]^{2+}$, $[(CoH(N_2)(PH_3)_3]$, and $[\{Ni(PH_3)_2\}_2N_2]$ are interpreted to show that σ donation by dinitrogen is more important than π acceptance in metal–dinitrogen bond formation. This is at odds with the empirical data and also with Xα calculations on species such as $[Ni(N_2)_4]$, $[Co(N_2)_4]^-$, and $[Fe(N_2)_4]^{2-}$ (*43*). Further, it was inferred that side-on dinitrogen may be more "activated" (weaker N—N bonding) than end-on, although the link to metal is stronger in the latter case (*356*). On the other hand, *ab initio* calculations on $[MN_2]$(M = Fe, Co, or Ni) and $[(\eta^5\text{-}C_5H_5)_2TiN_2]$ argue against side-on coordination (*340*). The wholly hypothetical $[Cr(N_2)(PH_3)_4]$ has also been studied by LCAO–MO–SCF calculations, and apparently falls into the same pattern. The end-on dinitrogen was found to be negatively charged, "consistent with XPS, dipole moment, and other measurements" (*355*). It is predicted that the exonitrogen would be attacked. $H_2\overset{+}{N}{=}\overset{-}{N}$ has been also used as a model for calculations on end-on N_2 (*127*). The matrix-isolated $[Ni(CO)_3N_2]$ is not expected to be thermally stable, according to DVM–HFS calculations (*358*).

Calculations of reaction pathways are always risky, unless adequate mechanistic data are available. An extended Hückel calculation on *cis*- and *trans*-$[Mo(N_2)_2(PH_3)_4]$ suggested that the dinitrogen is overall negative in both cases, but moreso in the cis-isomer, but the site of protonation was not designated (*152*). The complex $[MoCl(N_2)(PH_3)_4]^-$ was predicted to be more susceptible to dinitrogen loss upon photoactivation than in bis(dinitrogen) compounds, but there are no empirical data for systems based upon $\{Mo(Ph_2PCH_2CH_2PPh_2)_2\}$ since $[MoCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^-$ cannot be isolated. On the other hand the discussion presented on the alkylation reactions (*152*), being based on an incorrect mechanism (*98*), is clearly in error.

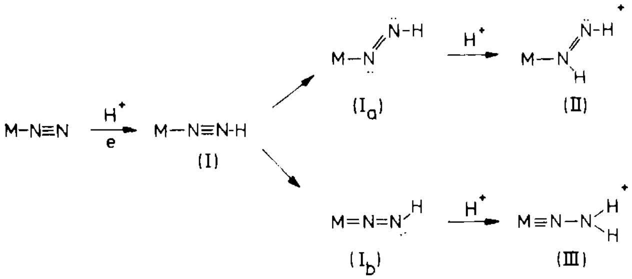
Ab initio calculations on $[Ru(NH_3)_5(N_2)]^{2+}$, $[Mo(N_2)_2(PH_3)_4]$, and other species suggest that the polarization of the dinitrogen molecule changes from species to species, being, in the examples cited, in the sense $Ru—\overset{\delta-}{N}—\overset{\delta+}{N}$, and $Mo—\overset{\delta+}{N}—\overset{\delta}{N}$, respectively (*253*). This accords with experiment: but hypothetical reactivity in metal systems such as $[M(NH_3)_4(N_2)Cl]^{n+}$ (M = Ti, V, Cr, Mn, or Fe) has been related to the degree of π bonding (*33, 34*). Nonmetal systems [N_2 + H·, H^+ or H , (*269*), Second Period hydroxides plus N_2 (*234*)] have also received attention.

ESCA provides a tool for determining the degree of polarization of coordinated dinitrogen (*225*). The relative degrees of polarization in a series of compounds cannot be estimated since experimental errors are large (*254*), but nitrogens in azocompounds etc. carry less negative charge than nitrogens in dinitrogen complexes. The polarization of the dinitrogen residue in diazenido complexes of Rh, Ir, and Ru is less than in the (hypothetical) dinitrogen parents (*111*). The Os($4f_{7/2}$) binding energies of $[Os(NH_3)_4(N_2)_2]^{2+}$ (52.7 eV) and of $[\{Os(NH_3)_4Cl\}_2N_2]^{3+}$ (51.6, 52.8 eV) are difficult to comprehend. The latter shows two Os signals although the Os should be equivalent (valence delocalization) (*17*). However, on that basis, the former ought to contain Os(III) which is clearly not the case and the data and conclusions have been disputed (*222*). Clearly ESCA data should be treated with caution, even where they accord with experiment (*44*), as with the demonstration that the putative $[MoCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ is likely to be (*88*) a mixture of $[MoCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ and $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$.

^{15}N-NMR chemical shifts in complexes such as $[ReCl(N_2)(PMe_2Ph)_4]$ and its adducts promise to be of value in assessing the electronic condition of bound dinitrogen, but the significance of a given chemical shift, even when one can distinguish between endo- and exo-nitrogens, is not clear (*87, 144*).

III. The Activation of Dinitrogen toward Ammonia Formation

Although the next reaction to yield ammonia from dinitrogen and dihydrogen is exothermic ($\Delta H^\circ_{f(g)}$ = −92.6 kJ mol^{-1}), the major thermodynamic problem in dinitrogen fixation is overcoming the unfavorable formation of diazene ($\Delta H^\circ_{f(g)}$ = +203.6 kJ mol^{-1}). As originally described by Chatt (*72*) the binding of the dinitrogen molecule to a transition metal assists the formation of ammonia. For the specific example of protonation of coordinated dinitrogen (an aspect in which we have a dominant but not exclusive interest in this article), the binding of



SCHEME 2. Initial stages in the reduction of coordinated dinitrogen.

dinitrogen to a transition metal polarizes the ligand and increases its basicity (greater contribution from π backbonding than σ donation), thus facilitating attack of the first proton, as shown in Scheme 2.

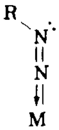
For dinitrogen bound at a mononuclear site, the placing of the first proton on the coordinated dinitrogen gives the diazenido ligand (N_2H, I). In order for further protonation to occur at a nitrogen atom, rearrangement of the diazenido ligand is necessary to generate a basic site at either $N_\alpha(I_a)$ or $N_\beta(I_b)$. By allowing increased metal–nitrogen bond order at the expense of the nitrogen–nitrogen multiple bond, the metal assists in the second protonation. Depending upon whether N_α or N_β is the position of subsequent protonation, either a diazene (HNNH, II) or a hydrazido(2−) ligand (NNH_2, III), respectively, is obtained.

In this section the reactivity of complexes containing the diazenido, diazene, and hydrazido(2−) ligands will be described. It is pertinent to discuss not only complexes containing these ligands but also the analogous compounds containing alkyl, aryl, or acyl substituents (e.g., N_2Me, N_2Ph, or N_2COPh). This is warranted in the context of the unsubstituted diazenido ligand, which is a particularly elusive beast and is authenticated for mononuclear complexes only in *trans*-$[M(N_2H)X(dppe)_2]$ (M = Mo, X = F or Br, M = W, X = F, Cl, Br, or I) (*102*). Substituted derivatives can give valuable information which is otherwise unavailable.

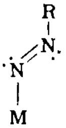
IV. The Diazenido Ligand

It can be envisaged that, depending upon the electronic requirements of the metal, the diazenido ligand can adopt one of the following geometries.

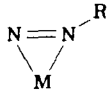
6



7



8



9

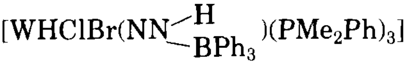
Neither the linear configuration (**6**) nor the sideways bonded form (**9**)[1] has been authenticated to date, although $[Ru(N_2Ar)Cl(bipy)_2]PF_6$ (bipy = $C_{10}H_8N_2$) has been tentatively assigned the linear form (**6**) on the basis of the very high $\nu(NN)$ (*41*) [Ar = p-MeC_6H_4, $\nu(NN) = 2080\ cm^{-1}$; Ar = p-$MeOC_6H_4$, $\nu(NN) = 2095\ cm^{-1}$]. Of the remaining two forms, the doubly bent structure (**8**) is represented only in the complexes of the later transition metals, where electron-rich metals and the 18-electron rule preclude the diazenido ligand acting as a three-electron donor (**7**). Thus structure (**8**) is authenticated only in the complexes, $[RhCl_2(N_2Ar)(PPh_3)_2]$ (Ar = C_6H_5 or p-$O_2NC_6H_4$) (*218*) and $[Rh\{PhP[(CH_2)_3PPh_2]_2\}(N_2Ph)Cl]$ (*169*) together with the single series of platinum complexes $[Pt(PEt_3)_2L(N_2Ar)]^{n+}$ (L = Cl, NH_3, py, PEt_3, or EtNC; n = 0 or 1) (*267*). All the remaining diazenido complexes are believed to adopt the singly bent configuration (**7**), or have unambiguously been shown by crystallography to do so.

As a point of interest, a recent *ab initio* calculation (*145*) indicates that the sideways bonded form of LiN_2H is the most stable configuration.

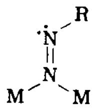
^{15}N-NMR spectroscopy promises to be of great utility in distinguishing the singly and doubly bent forms of the diazenido ligand. The ^{15}N-enriched complexes, *trans*-$[M(N_2R)X(dppe)_2]$ (M = Mo or W, X = Cl or Br, R = Et or COMe) which contain the singly bent form of the diazenido ligand (**7**) exhibit resonances [relative to $C^2H_3NO_2$) at ($-28 \rightarrow -60$ ppm) and ($-123 \rightarrow -165$ ppm) for the N_α and N_β atoms, respectively, the latter showing a large Nuclear Overhauser Effect. In contrast $[RuCl_2(N_2Ar)(PPh_3)_2]$ (Ar = C_6H_5 or p-$O_2NC_6H_4$), which adopts the doubly bent form (**8**), has a resonance attributed to N_α 350 ppm downfield from that of the singly bent structures (*146*). This technique has already been applied to a structural problem. Electrochemical studies (*95*), and the anomalously high $\nu(NN)$ ($\sim 1880\ cm^{-1}$) of the complexes *trans*-$[W(N_2H)X(dppe)_2]$ (X = F, Cl, Br, or I) compared with their alkyldiazenido counterparts ($\sim 1540\ cm^{-1}$) (*76*), suggested that these might be the seven-coordinate hydrides, $[W(H)X(N_2)(dppe)_2]$. However the ^{15}N-NMR spectra of the fluoro and bromo complexes are consistent with a singly bent diazenido ligand (X = Br, $N_\alpha = -25.9$

---

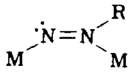
[1] This form has now been dectected in $[Ti(C_5H_5)Cl_2(N_2Ph)]$, Dilworth *et al.* (unpublished observations).

ppm, $N_\beta = -187.1$ ppm; X = F: $N_\alpha = -24.6$ ppm and $N_\beta = -182.6$ ppm). Furthermore, the N_α resonance is inverted due to the Nuclear Overhauser Effect demonstrating that the proton resides on the terminal nitrogen (*144*). Although no crystal structure is available for a diazenido complex, the structure of  $[WHClBr(NN{<}^{H}_{BPh_3})(PMe_2Ph)_3]$ (*319*) has been determined, and can be considered to be the BPh_3 adduct of a diazenido complex.

Of the two possible modes of bonding for bridging diazenido ligands, form **10** has been authenticated in $[\{Mn(N_2Ph)(CO)_4\}_2]$ (*1*) and



10



11

$[\{Pt(N_2H)(PPh_3)_2\}_2]$ (*154*). The platinum complex is the only diazenido complex other than *trans*-$[M(N_2H)X(dppe)_2]$.

A. METHODS OF PREPARATION

There are six principal routes available to prepare diazenido complexes and these have been reviewed before (*143, 154, 275, 317*), although for convenience the relevant routes will be outlined here. Other routes such as the reaction of nitrosyl complexes with an aniline (*41*), or the reactions of 1,3-diaryltriazenes in acid (ready cleavage to yield diazonium ions *in situ*) with transition metal complexes (*317*), are of much less general utility.

1. *Reactions with Diazonium Salts*

Following in the wake of the first reaction shown to yield diazenido complexes (*210*) many workers have investigated the reactions of diazonium salts with transition metal complexes. This category involves two distinct subsections.

1. Substitution in 16-electron or 18-electron species to replace a 2-electron ligand by RN_2^+ [Eq. (14)].

$$[RuCl_2(PPh_3)_3] + ArN_2^+Cl^- \xrightarrow{\text{EtOH–acetone}} [RuCl_3(N_2Ar)(PPh_3)_2] + PPh_3 \qquad (14)$$

2. Oxidative addition of diazonium ions ($d^8 \rightarrow d^6$ or $d^{10} \rightarrow d^8$) [Eq. (15)].

$$[\mathrm{Pt(PPh_3)_3}] + \mathrm{ArN_2^+} \xrightarrow{\mathrm{EtOH{-}Et_2O}} [\mathrm{Pt(N_2Ar)(PPh_3)_3}]^+ \qquad (15)$$

These two types of reaction have been used extensively in the preparation of aryldiazenido complexes of the 4*d* and 5*d* metals: Mo and W (*129, 130, 203, 210, 243, 244, 255, 332, 333*), Rh and Ir (*126, 168, 169, 183, 218*), Re (*14, 15*), Ru and Os (*70, 218, 219, 241, 243*), and Pt (*71*). To a much lesser extent aryldiazenido complexes of the 3*d* metals have been isolated: Cr (*115, 185*), Mn (*15*), Fe (*68, 197*), and Co (*68*).

2. *Insertion of Diazonium Ions into Metal Hydride Bonds*

In 1965 it was shown that diazonium salts apparently could be "inserted" into Pt—H bonds (*267*). The diazene complex thus formed can subsequently be deprotonated by base to yield the corresponding diazenido complex [Eq. (16)].

$$[\mathrm{Pt(H)Cl(PEt_3)_3}] \xrightarrow{\mathrm{ArN_2}} [\mathrm{Pt(NHNAr)Cl(PEt_3)_2}]^+ \xrightarrow{\mathrm{base}} [\mathrm{Pt(N_2Ar)Cl(PEt_3)_2}] \qquad (16)$$

More recently this route has been employed for complexes of Mn and Re (*14, 159*), Ru (*243, 244*), and Ir (*218*).

3. *Reaction with Hydrazine and Substituted Hydrazines*

This category also involves two distinct sections.

1. The *in situ* oxidation of the hydrazine in the presence of certain Mo (*178*) and Re (*81, 153*) complexes [Eq. (17)].

$$[\mathrm{ReCl_3(PMe_2Ph)_3}] + \mathrm{PhNHNH_2} \longrightarrow [\mathrm{ReCl_2(NH_3)(N_2Ph)(PMe_2Ph)_2}] + [\mathrm{ReCl_2(N_2Ph)(PMe_2Ph)_3}] \qquad (17)$$

The ammine complex is a minor product.

2. The condensation of metal-oxo species with hydrazines [Eq. (18)] (dtc = $\mathrm{S_2CNMe_2^-}$).

$$[\mathrm{MoO_2(dtc)_2}] + \mathrm{PhNHNH_2} \xrightarrow{\mathrm{Nadtc}} [\mathrm{Mo(N_2Ph)(dtc)_3}] \qquad (18)$$

Such reactions have been employed with complexes of Mo (*28, 29*), and a variety of benzoyldiazenido complexes of Re have been prepared by this route (*81, 96*). Hydrazine itself can give rise to dinitrogen complexes (*48*), so that the process is restricted to derivatives of substituted hydrazines.

4. *Reaction with Diazenes*

The reaction of $Me_3SiNNPh$ with a transition metal halide complex has been used to prepare diazenido complexes of the early transition metals (*1, 107*).

$$[(\eta^5\text{-}C_5H_5)TiCl_3] + Me_3SiNNPh \longrightarrow [(\eta^5\text{-}C_5H_5)TiCl_2(N_2Ph)] + Me_3SiCl \qquad (19)$$

5. *Hydride or Carbanion Attack on Diazoalkane Complexes*

Treatment of diazoalkane complexes with $Li[AlH_4]$ or LiR gives diazenido complexes (*22*) (dppe = $Ph_2PCH_2CH_2PPh_2$). For example,

$$[Mo(NN{=}CH_2)F(dppe)_2]^+ + Li[AlH_4] \longrightarrow [Mo(NNMe)F(dppe)_2] \qquad (20)$$

6. *Formation from Dinitrogen Complexes*

Treatment of *trans*-$[M(N_2)_2(dppe)_2]$ with 1 mol equivalent of HBr in THF gives a mixture of diazenido, hydrazido(2−), and parent dinitrogen complexes which cannot be separated. However diazenido complexes can be prepared cleanly by deprotonation of the corresponding hydrazido(2−) complexes with triethylamine or aqueous potassium carbonate (*102*), in a medium in which the products are insoluble. For example,

$$trans\text{-}[W(N_2)_2(dppe)_2] \xrightarrow[-N_2,THF]{2HBr} trans\text{-}[W(NNH_2)Br(dppe)_2]^+$$
$$\xrightarrow[MeOH]{Et_3N} trans\text{-}[W(N_2H)Br(dppe)_2] \qquad (21)$$

Direct acylation or alkylation of dinitrogen complexes has proved possible only in a limited number of cases. The reaction of $[ReCl(N_2)(PMe_2Ph)_3L]$ (L = PMe_2Ph or py) with benzoylchloride gives $[ReCl_2(N_2COPh)(PMe_2Ph)_3]$ (*90*) and the Group VI dinitrogen complexes react with a variety of alkyl halides (*39, 57, 76, 88, 97, 138, 171*) and acylating reagents (*114, 324*). Equation (22) represents an example.

$$trans\text{-}[Mo(N_2)_2(dppe)_2] + MeI \xrightarrow[C_6H_6]{} trans\text{-}[Mo(N_2Me)I(dppe)_2] + N_2 \qquad (22)$$

There is some degree of stereospecificity in this reaction since use of the complex *trans*-$[Mo(N_2)_2(S,S\text{-}Ph_2PCH(Me)CH(Me)PPh_2)_2]$ and 2-octyl bromide leads to an accumulation of the *S*-diastereoisomer in the recovered octyl bromide (*38a*).

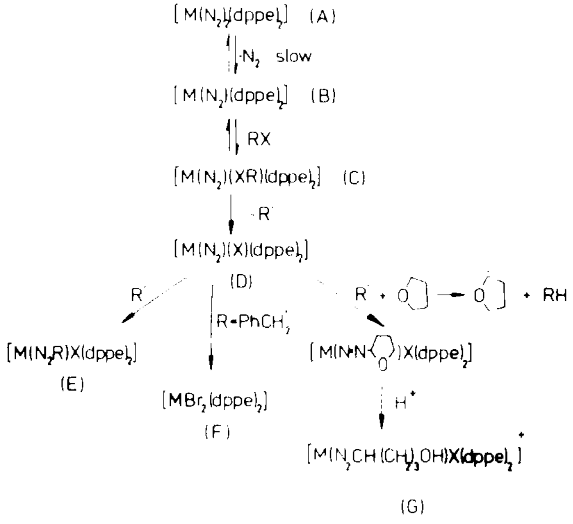
Simple alkyl chlorides react with these dinitrogen complexes to give only *trans*-[$MCl_2(dppe)_2$]. "Activated" alkyl chlorides such as ethyl chloroacetates react to give the corresponding diazenido complexes (*58*, *59*).

B. MECHANISMS OF FORMATION OF ALKYL- AND ACYLDIAZENIDO COMPLEXES

Of the several methods of making diazenido complexes, the only one which has been investigated mechanistically is the reaction between *trans*-[$M(N_2)_2(dppe)_2$] and alkyl bromides or iodides (*88*, *89*). This, of course, is the most important from our point of view, since the product is formed directly by a reaction of coordinated dinitrogen.

Kinetic studies on the reaction between *trans*-[$M(N_2)_2(dppe)_2$] ($M = Mo$) with alkyl, acyl, or aroyl halides, in the dark, show that the rate of the reaction is independent of the concentration and nature of the alkyl halide, but has a first-order dependence on the concentration of the complex ($k_{obs} = 1.3 \pm 0.2 \times 10^{-4}$ sec^{-1}). The tungsten reaction requires light.

This is consistent with rate-limiting loss of dinitrogen from the substrate (A) as shown in Scheme 3. The 16-electron, 5-coordinate intermediate thus generated (B) is rapidly attacked by alkylhalide, RX, which coordinates through the halogen to yield *trans*-[$M(N_2)(XR)(dppe)_2$], (C). Subsequent homolysis of the carbon–halogen bond



SCHEME 3. Mechanism of the reaction of alkyl halides with *trans*-[$M(N_2)_2(dppe)_2$].

yields *trans*-[$M(N_2)X(dppe)_2$] (D) and the radical R˙ (detected by ESR spectroscopy). Provided R˙ is of the right stability (R = Me, Et, *n*Pr, or *n*Bu) its attack on (D) results in the diazenido product (E). However when R = CH_2Ph the products are dibenzyl and [$MoBr_2(dppe)_2$] (F). In tetrahydrofuran, the tetrahydrofuranyl radical is generated and after acid work-up of the reaction products some diazobutanol complex, *trans*-[$Mo\{N_2CH(CH_2)_3OH\}Br(dppe)_2$]$HSO_4$ (G), was isolated (*26*). Evidently R˙ is sufficiently reactive to abstract a hydrogen atom from tetrahydrofuran, and the derived radical attacks species (D).

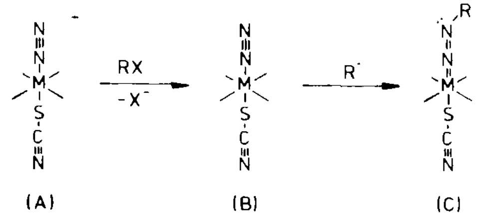
The carbon–chlorine bond is too strong for homolysis to occur, thus rationalizing the lack of a diazenido-forming pathway with alkyl chlorides.

This mechanism, and in particular the coordination of RX to the 16-electron intermediate (B), is further substantiated by the observation that the reaction between *trans*-[$W(N_2)_2(dppe)_2$] and MeI, in the presence of (*n*Bu_4N)Br yields *trans*-[$W(N_2Me)I(dppe)_2$] exclusively.

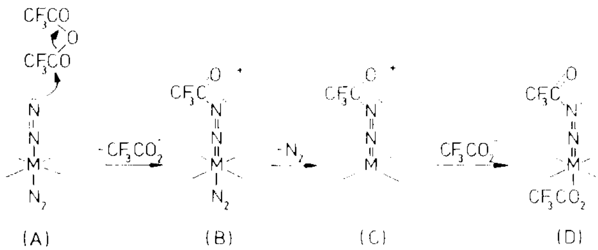
For the above mechanism to be the most favored pathway, the following rules must be obeyed. (1) The complex must be coordinatively unsaturated (or potentially so). (2) The metal must be sufficiently electron releasing to cause homolysis. (3) The metal must be a sufficiently strong π donor to retain the coordinated dinitrogen.

In contrast, the kinetics of the alkylation of *trans*-[$Mo(N_2)(L)(dppe)_2$]$^-$ (L = CN or SCN) with *n*BuI show a first-order dependence upon both the complex and the alkyl halide (*88*). These kinetics and the retention of the ligand, L, in the diazenido product are consistent with the mechanism shown in Scheme 4. The electron-rich complexes (A) undergo rate-limiting, outer-sphere electron transfer to yield the alkyl radical and *trans*-[$M(N_2)L(dppe)_2$] (B). Subsequent, rapid attack of the radical on the coordinated dinitrogen of (B) yields the diazenido product (C).

This latter pathway for the formation of diazenido complexes is sig-



SCHEME 4. Mechanism of the alkylation of electron-rich dinitrogen complexes (phosphine ligands omitted for clarity).



SCHEME 5. Proposed mechanism for the reaction between trifluoroacetic anhydride and *trans*-[$M(N_2)_2(dppe)_2$] (phosphine ligands omitted for clarity).

nificant, since it avoids the slow loss of dinitrogen associated with the former pathway. It has been proposed (*114*), based on the qualitative observation that the reaction of *trans*-[$W(N_2)_2(dppe)_2$] with trifluoroacetic anhydride is faster than the reaction with alkyl halides, that this reaction adopts a third type of mechanism as shown in Scheme 5.

Nucleophilic attack of the coordinated dinitrogen on the carbonyl carbon of trifluoroacetic anhydride yields *trans*-[$W(N_2COCF_3)$-$N_2(dppe)_2]^+$ (B). Acylation of the dinitrogen has the effect of removing electron density from the metal thus labilizing the *trans*-dinitrogen to yield the five-coordinate intermediate [$W(N_2COCF_3)(dppe)_2]^+$ (C). Subsequent attack of the trifluoroacetate group at this vacant site yields the *trans*-[$W(N_2COCF_3)(O_2CCF_3)(dppe)_2$] product (D). This reaction mechanism bears close resemblance to that for the protonation reactions (see Section VI,D) and it is possible that the reaction with trifluoroacetic anhydride is acid catalyzed. Although the addition of triethylamine does not markedly affect the reaction rate, which is inconsistent with the acid-catalyzed pathway, it may well be that the triethylammonium ion is sufficiently acidic to perform the catalysis.

C. SITE OF PROTONATION IN DIAZENIDO COMPLEXES

A qualitative molecular orbital study, using extended Hückel calculations (*152*), predicts that singly bent diazenido ligands (**7**) on d^6 metals have greater electron density on N_β, whereas for the doubly bent ligands (**8**) on d^8 metals there is a large increase in charge on both nitrogen atoms, but particularly on N_α. These predictions are borne out by the results of an X-ray photoelectron spectroscopic investigation (*45*). Direct comparison of the XPS data on the complexes with the arene diazonium ion shows that upon coordination of the latter a large flow of electron density to the ligand occurs, the bulk of the electron density residing on N_α in the singly bent form.

ESCA studies on some diazenido complexes (*111*) show that the separation of the N(1s) energies is less than in the benzenediazonium cation, and markedly less than in dinitrogen complexes. The diazenido ligand has a relatively low polarity, with a charge difference between nitrogen atoms of about 0.1 units on the CNDO charge scale. This study has also shown that the N(1s) binding energy for ruthenium and osmium aryldiazenido complexes is greater than for rhodium complexes, consistent with the former being singly bent and the latter doubly bent. Similarly the aryldiazenido complexes of ruthenium show a significant correlation between the Hammett σ_p for the substituent in the aryl group and the $3p_{3/2}$ or $3d_{5/2}$ binding energies, whereas the rhodium complexes show little, again supporting the formulation of a singly bent diazenido ligand in the former compounds and doubly bent diazenido ligands in the latter. The spectrum of $[RuCl(N_2C_6H_4Me)_2(PPh_3)_2]^+$ consists of a single N(1s) signal with a shoulder on either side. This has been ascribed to a molecule containing inequivalent aryldiazenido groups (i.e., one singly and one doubly bent).

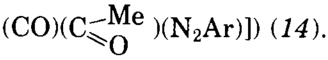
With the authenticated singly bent diazenido complexes, protonation (or, more generally, electrophilic attack) does occur at N_β as predicted by the studies described above, to yield hydrazido(2−) complexes (*39, 57–59, 72, 97, 114, 324*) and protonation of doubly bent species gives diazene complexes (*201, 218*).

D. Nucleophilic Attack in Diazenido Complexes

A natural extension to the observations that nucleophiles such as iodide attack the aryl ring of the complexes $[(\eta^5\text{-}C_5H_5)M(CO)_2(N_2Ar)]^+$ (M = Mn or Re) (*15, 16*) (Section II,A,4) is the reaction of these substrates with hydride or carbanions.

The reaction of sodium borohydride with $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2C_6H_4R)]^+$ gives $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NHNC_6H_4R)]$ (as well as some $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2)]$) (*14*). Thus just as doubly bent diazenido complexes protonate to give aryldiazene complexes, hydride attack on singly bent diazenido complexes gives aryldiazene complexes.

Reaction of methyllithium with $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2Ar)]^+$ gives predominantly the hydrazido(2−) complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NNMeAr)]$ (together with some dinitrogen complex and $[(\eta^5\text{-}C_5H_5)Re(CO)(C{\scriptstyle\genfrac{}{}{0pt}{}{\diagup Me}{\diagdown\!\!\diagdown O}})(N_2Ar)]$) (*14*).



$[(\eta^5\text{-}C_5H_5)Re(CO)(C(=O)Me)(N_2Ar)]$

V. The Diazene Ligand

In an article concerned with coordinated dinitrogen residues in nitrogen fixation reactions, the diazene moiety occupies a somewhat ambiguous position. No complex containing diazene has been shown to yield ammonia. In a series of publications (*285*, *286*), however, Schrauzer has invoked diazene as a crucial intermediate in a variety of nitrogen-fixing reactions. Evidence for this is circumstantial and comes from a comparison with nitrogenase of the various model-fixing systems. The detailed arguments have been reviewed earlier (*82*).

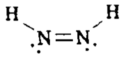
Besides the proposals of Schrauzer, other systems have been postulated to proceed via free diazene. Thus the reaction of $[\{(\eta^5\text{-}C_5H_5)_2Ti\}_2N_2]$ with HCl in methanol yields hydrazine and dinitrogen in about equal quantities. These are believed to result from a disproportionation of diazene (*38*). In the reaction of the similar complex $[\{(\eta^5\text{-}C_5H_5)_2TiR\}_2N_2]$ ($R = Ph$) with sodium naphthalene, ammonia is obtained after acid work-up, but if the reaction is quenched after short reaction times some hydrazine is produced. It is proposed that this hydrazine results from the destruction of a bridging diazene intermediate, releasing diazene which subsequently disproportionates (*338*). The hydrolysis of $[\{(PhLi)_6Ni_2(N_2)(Et_2O)_2\}_2]$ in tetrahydrofuran is proposed to proceed via diazene (*205*), and diazene has been considered to be a plausible intermediate in the hydrolysis of $[(\eta^5\text{-}C_5H_4R')Zr(\eta^2\text{-}N_2)R]$ ($R' = H$, Me, or OR; $R = (Me_3Si)_2CH$) (*204*). Finally, the intermediacy of coordinated diazene has been invoked in the reaction of $[\{Fe(PPh_3)_2H(i\text{Pr})\}_2N_2]$ with HCl, which gives low yields of hydrazine (*36*), and in the formation of $[Ru(NH_3)_5N_2]^{2+}$ from $[Ru(NH_3)_6]^{2+}$ and hydrazine (*249*).

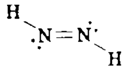
Clearly, to evaluate these proposals for the intermediacy of diazene, it is important to understand the properties of this highly reactive molecule.

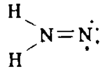
A. Diazene in the Free State

In the free state diazene can occur in three isomeric forms *cis*- and *trans*-diazene (**12** and **13**, respectively), and *iso*-diazene (**14**).

These molecules have been the subject of several theoretical (*69*) and

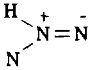

12


13


14

gas-phase spectroscopic studies (*69, 167, 348*). Diazene was first detected by mass spectroscopy during the decomposition of hydrazoic acid or hydrazine in an electrical discharge (*164*), but has subsequently been prepared by a variety of methods (*193*), including, most recently, the thermal decomposition of alkali-metal tosylhydrazines. Depending upon the nature of the alkali metal and the reaction conditions these can give *cis*-, *trans*-, or *iso*-diazene (*348*).

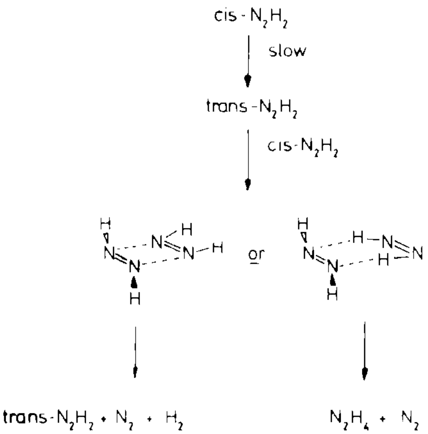
Although extended Hückel (*3*) and INDO calculations (*176*) predict the cis isomer to be the most stable configuration, all *ab initio* methods now predict the trans form (**13**) to be the ground state of the species (*256, 321*). The energy difference between (**12**) and (**13**) may be greater than 18.0 kJ mol^{-1} (*224, 345*), and *iso*-diazene is richer in energy by about 54.8 kJ mol^{-1} (*348*). The ground and excited states of isodiazene (**14**) have been studied using generalized valence-bond and configurational-interaction wave functions. The ground state was calculated to be a singlet ($^1A_1$), with the triplet ($^3A_2$) lying 62.9 kJ mol^{-1} higher (*69, 127*), the singlet state being stabilized due to a large contribution from the form (**15**). This result again differs from that obtained using the Hartree–Fock treatment which predicts the triplet to be at least 21 kJ mol^{-1} *below* the singlet state (*2, 345*).



15

In the gas phase, the kinetics of the decomposition of *trans*-diazene (**13**) exhibit a first-order dependence on the concentration of diazene (*351, 352*) $k_{obs} = 2.45\ (\pm 0.1) \times 10^{-3}\ sec^{-1}$, $T = 23°C$ (after allowing for self-heating and surface catalysis). The major products of this decomposition are hydrazine and dinitrogen. The kinetics have been interpreted in terms of rate-limiting trans to cis isomerization. The reactive *cis*-diazene then interacts with *trans*-diazene to give the major products via a cyclic N_4H_4 intermediate (Scheme 6). This mechanism is preferred to a surface-initiated radical-chain pathway as suggested for methyldiazene (*341*) because (1) oxygen has virtually no effect on the rate, (2), the generation of a radical chain by photoinitiation gives only dinitrogen and hydrogen as products, and (3) the reaction of diazene with olefins is not compatible with a radical mechanism (*353*). The detailed mechanism of the isomerization step is not clear. Theoretical estimates put this barrier at about 252.0 kJ (*12*), so clearly this step is not simple passage over the potential barrier.

Besides hydrazine and dinitrogen, dihydrogen is also observed as a product of the decomposition of diazene. Originally this was believed to

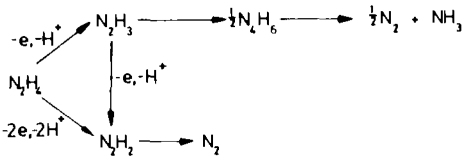


SCHEME 6. Competitive pathways in the gas phase decomposition of diazene.

arise from the competitive decomposition of *cis*-diazene. However this unimolecular reaction is forbidden on symmetry grounds, and the competition between the major pathway and the decomposition of *cis*-diazene would result in the ratio $[H_2]/[N_2]$ varying from 1 to 0, depending upon the pressure of diazene. When the pressure of diazene exceeds 0.03 atm, the ratio is essentially invariant with $[H_2]/[N_2] = 0.46$. This, it is proposed, arises because of the bimolecular decomposition of *cis*-diazene. The essential difference between this reaction pathway and the hydrazine-forming pathway is the relative orientation of the two molecules, the hydrogen atoms on *cis*-diazene pointing either toward (hydrazine-forming pathway) or away from (dihydrogen-forming pathway) *trans*-diazene. This clearly is a discrimination which only the cis isomer can employ. It is, however, difficult to see how these two competitive pathways would exhibit the pressure dependence upon $[H_2]/[N_2]$.

Although *trans*-diazene is thermodynamically unstable with respect to its decomposition, the rate of this reaction is surprisingly slow. This is because of orbital symmetry and the sterically unfavorable trans configuration. Thermal conversion to the more reactive cis isomer is necessary for the reaction to occur. It has also been noted that *trans*-diazene reacts surprisingly slowly with HCl in the gas phase (*167*).

Little is known of the stabiity of diazene in solution. In general the species is generated *in situ* and its presence is shown by the hydrogenation of carbon–carbon multiple bonds. Direct detection has so far proved unsuccessful (*193*). Despite this, the formation of diazene has been invoked in several studies (besides those in nitrogen fixation).

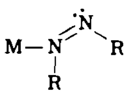


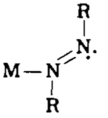
SCHEME 7. Alternative pathways for the oxidation of hydrazine.

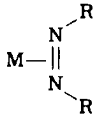
Probably the most extensive of these is the rationalization of the various products obtained from oxidation of hydrazine. One-electron oxidants give rise to ammonia and dinitrogen via dimerization of the hydrazinyl radical. In contrast two-electron oxidants give rise to dinitrogen by further oxidation of the hydrazinyl radical to diazene, which subsequently disproportionates to dinitrogen and hydrazine (*250*) (Scheme 7).

B. COMPLEXES OF DIAZENE

Upon coordination, the diazene ligand can adopt one of three potential configurations (**16–18**).


16

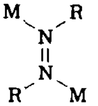

17

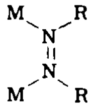

18

The trans structure (**17**) has not been authenticated to date, but the cis form (**16**) has been observed in $[ReCl_2(HN_2C_6H_4F)(PEt_3)_2]^+$ (*201*) and $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2]^+$ (*184*) (i.e., doubly bent diazenido ligands protonate at N_α). The sideways bonded form (**18**) has been observed in $[Ni(tBuNC)_2(N_2Ph_2)]$ (*140*).

Both ^{1}H-NMR and Raman spectroscopy have been used to identify aryldiazene complexes (*184, 218, 268*). However, fluorescence of $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2]$ leads to poor quality of Raman spectra, and rapid exchange in polar solvents of the nonaromatic diazene proton does not allow its detection by NMR spectroscopy.

Of the two possible structures for bridging diazenes, only the less hindered trans structure (**19**) has been authenticated, in $[\{Cr(CO)_5\}_2N_2H_2] \cdot 2THF$ (*196*).


19


20

C. PREPARATION OF MONONUCLEAR DIAZENE COMPLEXES

There are four pathways leading to diazene complexes. These routes have been reviewed before (*143, 275, 317*) and therefore will only be outlined here, with pertinent examples.

1. *Insertion of Diazonium Salts into Metal Hydride Bonds*

The original work in this area was the insertion of diazonium salts into the Pt—H bond of $[Pt(H)Cl(PEt_3)_2]$ to yield $[Pt(NHNAr)Cl(PEt_3)_2]^+$ (*267*). Although this strategy occasionally results in the formation of diazenido complexes if the resulting diazene is sufficiently acidic (see Section IV,A,2), it has been extended to the metal hydrides of Ru (*175, 218*), Os (*218*), Rh (*218*), and IR (*52, 331*) as exemplified in Eq. (23).

$$[IrHCl_2(PPh_3)_3] \xrightarrow{ArN_2^+} [IrCl_2(NHNAr)(PPh_3)_3]^+ \xrightarrow{LiCl} [IrCl_3(NHNAr)(PPh_3)_2] \quad (23)$$

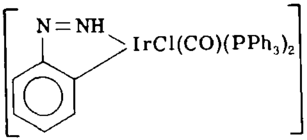
The reaction of $[RhHCl_2(PPh_3)_3]$ with aryldiazonium salts in the presence of LiCl gives complexes that were originally formulated as solvated rhodium "arylazo complexes" (*21*), but these have subsequently been shown by ^1H NMR and ^{15}N-labeling studies to be the diazene complexes $[RhCl_3(NHNAr)(PPh_3)_2]$ (*218*).

Treatment of polyhydrido complexes with diazonium salt, even in an excess, never results in the formation of more than a mono(diazene) complex (*62, 218, 331*) [Eq. (24)].

$$[RuH_2(CO)(PPh_3)_2] + ArN_2^+ \xrightarrow{PPh_3} [RuH(NHNAr)(CO)(PPh_3)_3]^+ \quad (24)$$

Two major problems can occur using this route: (1) treatment of some metal hydrides with diazonium salts decomposes the diazonium salt to dinitrogen (*218*) and (2) facile ortho metallation of the aryl group.

Ortho metallation has been observed in the reactions of diazonium salts with $[IrH_3(PPh_3)_3]$ (*21*) and $[IrH(CO)(PPh_3)_3]$ (*65*). Although the reaction of $[IrCl(CO)(PMe_2Ph)_2]$ with diazonium salts in the presence of lithium chloride gives $[IrCl_2(N_2Ph)(CO)(PMe_2Ph)_2]$ (*131*), the reaction of $[IrCl(CO)(PPh_3)_2]$ with $(p\text{-}XC_6H_4N_2)BF_4$ (X = F or Br) gives a deep red solution which contains a tetrazene complex (*157, 160, 174*). Removal of the solvent, freeze-drying, and recrystallization of the benzene-insoluble fraction from acetone–ether gives the ortho metallated diazene complex (**21**) (*158*), whose structure has been verified by X-ray crystallography (*161*).



21

2. *Reactions with Hydrazines*

The reaction of phenylhydrazine with copper(II) chloride in aqueous solution gives $[Cu_4Cl_4(PhNNH)]$ (*13*) and the reactions of 1,2-disubstituted hydrazines with copper(II) salts give complexes such as $[Cu_2Cl_2(MeNNMe)]$ (*46, 142*). The reaction of substituted hydrazines (or lithiated, substituted hydrazines) with halido complexes of the transition metals can yield diazene complexes. Complexes of Ni, Pd, Pt (*147, 199, 213*), and Rh (*209*) have been prepared in this manner [Eq. (25)].

$$[PtX_2(L)_2] + PhNHNHPh \xrightarrow{Na_2CO_3} [Pt(PhN_2Ph)(L)_2] + 2HX \qquad (L = PPh_3 \text{ or } n\text{BuNC}) \qquad (25)$$

The reaction of transition metal oxo complexes with substituted hydrazines yields the diazene complexes, containing the $\overline{\text{M—NRNC(R)O}}$ chelate.

$$[MoOCl_2(PMe_2Ph)_3] \xrightarrow{PhCONHNH_2} [\overline{\text{MoNHNC(Ph)O}}(PMe_2Ph)_2(N_2COPh)Cl] \qquad (26)$$

Complexes of Mo (*32, 77*) and Os (*80*) have been prepared in this way.

3. *Reaction with Diazenes*

The relative instability of free diazenes (*215*) often precludes the direct reaction of these species with transition metal complexes. However azobenzene reacts with Ni^0 (*264*) species to yield materials such as $[Ni(t\text{BuNC})_2(PhN_2Ph)]$ (*140, 265*). Similarly, ditolyldiazene reacts with $[Ni(\text{cyclooctadiene})_2]$ in the presence of tritolylphosphine to give $[Ni(N_2Ar_2)(PAr_3)_2]$ ($Ar = p\text{-}CH_3C_6H_4$) (*200*).

4. *Reaction of Dinitrogen Complexes*

The reaction of phenyllithium with $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$ is unique (*305*) [Eq. (27)]. It has been proposed that the phenyl anion attacks the α-nitrogen atom, and subsequent protonation of the β-nitrogen gives the diazene product.

$$\begin{tikzcd}
{[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]} \arrow[dr, "LiPh"'] & & {[(\eta^5\text{-}C_5H_5)Mn(CO)_2(PhN{=}NH)]} \\
& {[(\eta^5\text{-}C_5H_5)Mn(CO)_2(PhN{=}N)]} \arrow[ur, "H^+"'] &
\end{tikzcd} \qquad (27)$$

However, the evidence for this product which contains the bulky substituent on the α-nitrogen is not entirely convincing and the compound may be a hydrazido(2−) species.

The reaction of methyllithium with the "electron-poor" $[ReCl(CO)_2N_2(PPh_3)_2]$ followed by treatment with acid gives the carbene complex (*99*), $[Re(C\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown OH})Cl(CO)N_2(PPh_3)_2]$ (i.e., CO is attacked in preference to N_2).

As discussed in Section IV,D, hydride attack on $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2C_6H_4R)]^+$ gives $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NHNC_6H_4R)]$ (*14*).

D. Binuclear Diazene Complexes

Binuclear diazene complexes have been prepared in the meticulous and elegant work of Sellman and co-workers. The basis of the preparative route used in these studies is the oxidation of coordinated hydrazine [by copper(II)–hydrogen peroxide mixtures] to yield dinitrogen complexes (*291*, *292*).

$$[(\eta^5\text{-}C_5H_5)M(CO)_2(N_2H_4)] \xrightarrow[THF]{Cu^{2+}/H_2O_2} [(\eta^5\text{-}C_5H_5)M(CO)_2N_2] \qquad (28)$$

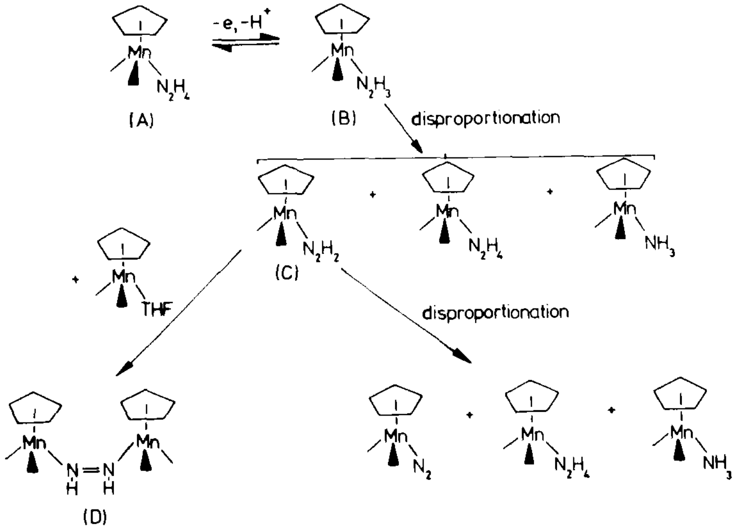
$$(M = Mn \text{ or } Re)$$

Controlled oxidation can give rise to the intermediate diazene complexes in low yield (*293*).

$$[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_4)] \xrightarrow[THF]{Cu^{2+}/H_2O_2} [\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2N_2H_2] \qquad (29)$$

Electrochemical studies (*354*) on this reaction have shown that the one-electron oxidation of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_4)]$ (A) gives $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_3)]$ (B) (Scheme 8), which disproportionates to the very reactive $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2H_2]$ (C). This reacts with $[(\eta^5\text{-}C_5H_5)Mn(CO)_2THF)]$ to yield (D).

The rhenium analog can be prepared by a similar route (*302*). However, unlike the manganese complex, $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2H_4)]$ readily disproportionates to the dinitrogen and ammonia complexes at room temperature.



SCHEME 8. *Reactions of* $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_4)]$ (CO ligands omitted for clarity).

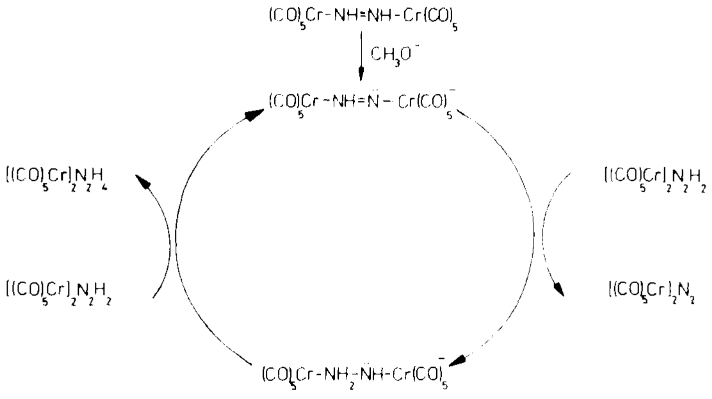
The complex $[\{Mo(CO)_5\}_2N_2H_2]$ can be prepared by a route similar to that described above, by initial preparation of the bridging-hydrazine complex followed by oxidation (*294*).

$$[Mo(CO)_5(THF)] + N_2H_4 \longrightarrow [(CO)_5MoNH_2NH_2Mo(CO)_5] \xrightarrow{Cu^{2+}/H_2O_2} [(CO)_5MoNH{=}NHMo(CO)_5] \qquad (30)$$

The preformation of the bridging-hydrazine complex is a strategy which has been extended to the analogous chromium (*295, 296*) and tungsten (*297*) complexes, although the latter is best prepared by the oxidation of $[W(CO)_5(N_2H_4)]$.

The dark red needles of $[\{Cr(CO)_5\}_2N_2H_2] \cdot 2THF$ have been the subject of a crystal structure determination (*196*). The bridging diazene is trans and the nitrogen–nitrogen bond distance is 1.25 Å, corresponding to the N=N length in organic azo complexes.

$[\{Cr(CO)_5\}_2N_2H_2]$ undergoes rapid proton exchange with $^2H^+$, the exchange rate being faster ($t_{1/2}$ = 45 sec) than that of the similar hydrazine ($t_{1/2}$ = 15 min) or ammine ($t_{1/2}$ > 60 h) complexes (*298*). In the presence of catalytic amounts of strong base this diazene complex disproportionates to the hydrazine and dinitrogen complexes. The proposed mechanism for this disproportionation is shown in Scheme 9.



SCHEME 9. Base-catalyzed disproportionation of $[\{Cr(CO)_5\}_2N_2H_2]$.

Finally, the heterodinuclear diazene complex, $[(\eta^5\text{-}C_5H_5)Mn(CO)_2NHNHCr(CO)_5]$, has been prepared (*299, 300*) by the pathway outlined in Eq. (31).

$$\begin{array}{c} [(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2H_4)] + [Cr(CO)_5(THF)] \\ \text{THF}\Big\downarrow 20^\circ C \\ [(\eta^5\text{-}C_5H_5)Mn(CO)_2NH_2NH_2Cr(CO)_5] \\ \Big\downarrow O_2 \text{ or } H_2O_2 \\ [(\eta^5\text{-}C_5H_5)Mn(CO)_2NH{=}NHCr(CO)_5] \end{array} \qquad (31)$$

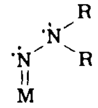
The ^{1}H-NMR spectrum of this product shows $^3J_{HH} = 23.5$ Hz for the bridging diazene which is very similar to that for ethylene ($^3J_{HH} = 19.1$ Hz).

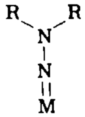
VI. The Hydrazido(2−) Ligand

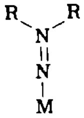
In contrast to the diazene complexes, the hydrazido(2−) complexes are well-authenticated intermediates on the pathway leading to ammonia in the reactions of compounds of the type $[M(N_2)_2(P)_4]$ (M = Mo or W; P = monotertiary phosphine) (*103*).

Upon coordination at a single metal site, the hydrazido(2−) ligand can adopt two possible configurations, the linear, coplanar form (**22**) and the singly bent form (**23**). The delocalized nature of form **22** permits two limiting forms of this configuration, the hydrazido(2−) form (**22a**) and the *iso*-diazene form (**22b**).


22


23


22a

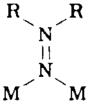

22b

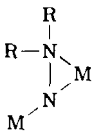
The structures of many hydrazido(2−) complexes have been determined by X-ray crystallography. However, to date only three have been shown to adopt the singly bent form (**23**), $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2HC_6H_4OMe)]$ (*14*) (M$\hat{N}$N = 138.1°), $[(\eta^5\text{-}C_5H_5)_2W(N_2HC_6H_4F\text{-}p)]^+$ (*66, 67, 159, 207*) (M$\hat{N}$N = 146.4°), and $[MoO(NNMe_2)L_2]$ (L = quinolin-8-olate) (*75*) (M$\hat{N}$N = 155.5°). In all these complexes linearity of the hydrazido(2−) ligand would result in a formal 20-electron species, and this is relieved by bending of the ligand at N_α. However, the isoelectronic $[MoO(NNMe_2)(S_2CNMe_2)_2]$ contains a totally linear hydrazido(2−) ligand and thus simple electron counting does not appear to be the exclusive reason for the alternative modes of bonding of this ligand.

Of all the hydrazido(2−) complexes whose structure has been authenticated only one has been shown to adopt the *iso*-diazene form (**22b**), $[Ph_4P]_3[Mo_3S_8(NNMe_2)_2]$ (*149*). The Mo—N bond distance in this complex (2.13 Å) is significantly longer than is observed in complexes containing ligand type **22a** (~1.79 Å), and the N—N distance is significantly shorter (1.16 Å compared with ~1.3 Å), clearly indicative of form **22b**, as is the eclipsed configuration of the hydrazido(2−) ligands. (The maximization of metal–nitrogen orbital overlap by shortening the Mo—N bond is clearly not dominant.) No doubt the strong "electron-attracting" nature of the $[MoS_4]^{2-}$ in complexes plays an important role in defining the ligand form in this case. The complex $[S_2MoS_2Mo(NNMe_2)_2(PPh_3)]$ contains hydrazido(2−) ligands of form **22a** (*150*).

As a bridging ligand the hydrazido(2−) species can be visualized as adopting two forms. Form **25** has been observed only in the complex $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2(NNMe_2)]$ (*211*).

Samples of *trans*-$[M(NNH_2)F(dppe)_2]BF_4$, $[M(NNH_2)Cl(py)(PMe_2Ph)_3]Cl$, and $[M(NNH_2)L(PMe_2Ph)_3]Cl$ (L = quinolin-8-olate) highly


24


25

enriched in ^{15}N have been the subject of an NMR study (M = Mo or W) (*86, 87*). The N—H spin–spin splitting identifies the N_β resonance at high field; replacement of hydrogen by alkyl groups on N_β leads to small downfield shifts. More recently this technique has been employed to follow the hydrazido(2−) intermediates formed in the reactions between *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and H_2SO_4 in tetrahydrofuran, on the pathway leading to ammonia (*4*) (Section VI,B).

A. PREPARATION OF HYDRAZIDO(2−) COMPLEXES

Despite the fact that hydrazido(2−) complexes are in general restricted to the metals molybdenum, tungsten, and rhenium, a great variety of coordination sites (various coligands) have been realized. Four general routes have been employed to yield this class of compounds (*143, 275, 317*).

1. *Reactions of Substituted Hydrazines*

1,1-Dimethylhydrazine reacts with copper(II) halides in dilute aqueous acidic solution at 0°C to give $[Cu_3(NNMe_2)_2X_3]$ (X = Cl or Br) (*13, 35*). The condensation reactions between 1,1-disubstituted hydrazines and $[MoO_2(S_2CNR'_2)_2]$ (R′ = Me, Et, or Ph) yields $[MoO(NNR_2)(S_2CNR'_2)_2]$ (*29, 31*). Only when the hydrazine is $H_2NN(Me)Ph$, H_2NNMe_2, or H_2NNPh_2 can the bis-derivatives $[Mo(NNMePh)_2(S_2CNR_2)_2]$ (*78*), $[Mo(NNMePh)_2(S_2CNMe_2)_2]$, $[Mo(NNPh_2)_2(S_2CNMe_2)_2]$, $[MoCl(NNMe_2)_2(PPh_3)_2]BPh_4$, and $[Mo(NNMe_2)_2(bipy)_2][BPh_4]_2$ (*74*) be prepared. The complex $[MoO(N_2Ph_2)L]$ [L = *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)ethylenediamine] has similarly been prepared (*125*).

Monosubstituted hydrazines $RNHNH_2$ (R = Me, Ph, or PhCO) react with $[MoO_2(S_2CNR'_2)_2]$ to give diazenido complexes which can be protonated or alkylated to give hydrazido(2−) complexes (*29*).

The reaction of the hydrazines $RR'NNH_2$ (R = R′ = Me or Et; R = Me, R′ = Ph) with $[\{(\eta^5\text{-}C_5H_5)Mo(NO)X_2\}_2]$ gives the novel asymmetrically bridged hydrazido(2−) complexes $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2N_2RR']$ (*166, 211*).

2. *Reactions of Trimethylsilyl Derivatives of Hydrazines and Diazenes*

Trimethylsilylated, mono- and disubstituted hydrazines react with complexes containing a metal–halogen bond (*84, 85, 121*).

$$[\mathrm{MoCl_4(PPh_3)_2}] \xrightarrow[\mathrm{NaBPh_4}]{\mathrm{Me_3SiNHNMe_2}} [\mathrm{MoCl(NNMe_2)_2(PPh_3)_2}]\mathrm{BPh_4} \qquad (32)$$

The above reaction, as others employing this route, illustrates the lability of hydrogen on an N_α. The fates of the hydrogens are often unknown, but this route cannot be used generally to prepare hydrazido(1−) complexes (Section V,C,2).

In a remarkable reaction, vanadocene reacts with bis(trimethylsilyl)-diazene to form a bis(trimethylsilyl)hydrazido(2−) complex [Eq. (33)].

$$[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{V}] + \mathrm{Me_3SiN{=}NSiMe_3} \longrightarrow [(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{V{=}N{-}N(SiMe_3)_2}] \qquad (33)$$

The formal 19-electron configuration of the product is accommodated by distortion of the cyclopentadienyl rings (*342, 349*).

3. *Insertion of Diazonium Salts into Metal Hydride Bonds*

The only example to date of the insertion of an aryldiazonium ion into a metal–hydrogen bond to yield a hydrazido(2−) complex is that shown in Eq. (34) (*66, 67*).

$$[\mathrm{WH_2}(\eta^5\text{-}\mathrm{C_5H_5})_2] + \mathrm{ArN_2}^+ \longrightarrow [\mathrm{WH}(\eta^5\text{-}\mathrm{C_5H_5})_2\{\mathrm{NN(H)Ar}\}]^+ \qquad (34)$$

The hydrazido(2−) ligand is bent in this complex, and rearranges to a hydrazido(1−) species (*207*) (Section VII,C,2).

4. *Reactions of Dinitrogen Complexes*

Complexes containing the hydrazido(2−) ligand ($\mathrm{NNH_2}^{2-}$) rather than its substituted analogs have been prepared only by the reaction of the Group VI dinitrogen complexes $[\mathrm{M(N_2)_2(P)_4}]$ [M = Mo or W, P = monotertiary phosphine or $(\mathrm{P})_2$ = chelating diphosphine] and acids HX (X = Cl, Br, I, $\mathrm{HSO_4}$, or $\mathrm{BF_4}$) in methanol or tetrahydrofuran (*91, 92, 103, 104*) [Eqs. (35) and (36)].

$$\textit{trans}\text{-}[\mathrm{M(N_2)_2(dppe)_2}] + 2\mathrm{HBr} \xrightarrow{\mathrm{THF}} \textit{trans}\text{-}[\mathrm{M(NNH_2)Br(dppe)_2}]\mathrm{Br} + \mathrm{N_2} \qquad (35)$$

$$\textit{cis}\text{-}[\mathrm{M(N_2)_2(PMe_2Ph)_4}] + 3\mathrm{HBr} \xrightarrow{\mathrm{MeOH}} \textit{mer}\text{-}[\mathrm{M(NNH_2)Br_2(PMe_2Ph)_3}] + \mathrm{N_2} + (\mathrm{PMe_2PhH})\mathrm{Br} \qquad (36)$$

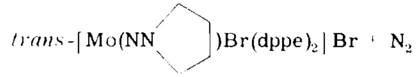
On the basis of infrared evidence, it was originally believed that complexes of the type *trans*-$[\mathrm{M(N_2H_2)X(dppe)_2}]$X were either hydrazido(2−) or diazene complexes depending upon the nature of X. Subsequent crystallographic evidence, however, has shown them all to be of the former type.

Ligand-exchange reactions with complexes of the type *mer*-$[M(NNH_2)X_2(PMe_2Ph)_3]$ and pyridine, substituted pyridines (pyR), or phosphines (e.g., PMe_2Ph) give rise to complexes of the type $[M(NNH_2)X(pyR)(PMe_2Ph)_3]^+$ or *trans*-$[M(NNH_2)X(PMe_2Ph)_4]^+$, respectively (*105*).

The reaction of alkyl halides with *trans*-$[M(N_2)_2(diphos)_2]$ (diphos = chelating diphosphine ligand) can give rise to dialkylhydrazido(2−) complexes via the alkyldiazenido species (*76, 93, 94*) [Eqs. (37) and (38)].

$$\textit{trans}\text{-}[W(N_2)_2(dppe)_2] + 2MeBr \longrightarrow \textit{trans}\text{-}[W(NNMe_2)Br(dppe)_2]Br + N_2 \qquad (37)$$

$$\textit{trans}\text{-}[Mo(N_2)_2(dppe)_2] + Br(CH_2)_4Br \longrightarrow$$



$$\textit{trans}\text{-}[Mo(NN)Br(dppe)_2]Br + N_2 \qquad (38)$$

The reactions of acyl halides (*76*) with *trans*-$[M(N_2)_2(dppe)_2]$ were the first to suggest that a proton could be bound to a dinitrogen ligand. This occurs because of adventitious water, which reacts with acyl halides to generate some hydrohalic acid [Eq. (39)].

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] \xrightarrow[-N_2]{RCOX} \textit{trans}\text{-}[M(NNCOR)X(dppe)_2] \xrightarrow{HX}$$
$$\textit{trans}\text{-}[M\{NN(H)COR\}X(dppe)_2]^+ \qquad (39)$$

In the same manner, the addition of acid to alkyldiazenido complexes of this type gives rise to hydrazido(2−) complexes (*76*) [Eq. (40)].

$$\textit{trans}\text{-}[M(N_2R)X(dppe)_2] + HX \longrightarrow \textit{trans}\text{-}[M(NN(H)R)X(dppe)_2]X \qquad (40)$$
$$(R = \text{alkyl or H})$$

Alkylation of *trans*-$[M(N_2H)X(dppe)_2]$ offers a parallel route through to these same products (*102*), and is a unique pathway to diazenido complexes containing a *trans*-fluoro or chloro group.

$$\textit{trans}\text{-}[W(N_2H)Cl(dppe)_2] \xrightarrow{MeI} \textit{trans}\text{-}[W\{N_2H(Me)\}Cl(dppe)_2]^+ \xrightarrow{Et_3N}$$
$$\textit{trans}\text{-}[W(N_2Me)Cl(dppe)_2] \qquad (41)$$

B. HYDRAZIDO(2−) LIGANDS AS INTERMEDIATES

From the earliest isolation of *mer*-$[M(NNH_2)X_2(PMe_2Ph)_3]$ (M = Mo or W, X = Cl, Br, or I) from the reactions between *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and HX, the intermediacy of the hydrazido(2−) stage on the pathway leading to ammonia has been recognized (*103*). Recently, the direct detection of hydrazido(2−) species in reaction mixtures has been possible using ^{15}N-NMR spectroscopy (*4*). Thus the reactions of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ with a 20-fold excess of sulfuric acid in tetrahydrofuran was followed at 20°C. Periodically the sample was cooled to −30°C and the ^{15}N NMR spectrum was recorded. The necessity to cool to −30°C when recording spectra is a consequence of the long accumulation times necessary. The accumulation time was, however, kept to a minimum by monitoring the more intense Nuclear Overhauser Effect-enhanced resonance assigned to NH_2 rather than the N_α signal. In this manner two hydrazido(2−) complexes were observed in the reaction of the molybdenum complex and six (!) in the reaction of the tungsten analog. It is difficult to rationalize this, even allowing for facile ligand exchange. In this context it is interesting to note that a recent *ab initio* calculation on $MNNH_2^+$ (M = H, Li, B, N, F, or P) indicates that the most favored forms all had a planar arrangement of the five atoms, the angle $M\hat{N}N(\theta)$ depending on M ($M = H$ or F, $\theta = 109°$; $M = B$, $\theta = 120°$; $M = Li$ or N, $\theta = 180°$). Thus some of the hydrazido(2−) complexes observed in the ^{15}N-NMR experiments may represent isomers in which the hydrazido(2−) ligand is bent (**23**).

During the early stages of the turnover of the enzyme, nitrogenase, an intermediate stage of protonation of dinitrogen was detected by quenched-flow experiments (*328*). Analysis of presteady state kinetics (*314*), and comparison with the chemistry outlined above, indicates that this is a hydrazido(2−) stage.

Dialkylhydrazido(2−) complexes have also been shown to be crucial intermediates in the electrochemical reduction of coordinated dinitrogen to substituted hydrazines (*273*). Finally a chromium(III) hydrazido(2−) species has been proposed as an intermediate in the chromium(II) reduction of nitroamine (*192*).

Thus the hydrazido(2−) state represents an important (if not *the* most important) intermediate on the pathway leading to ammonia, both in the biological and abiological fixation of dinitrogen, and a study of the mechanism of formation of these species is of fundamental importance.

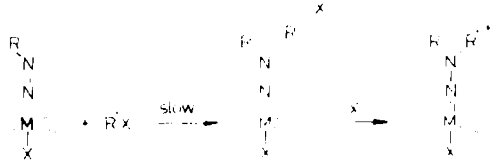
C. THE MECHANISM OF FORMATION OF DIALKYLHYDRAZIDO(2−) COMPLEXES

As described earlier (see Section IV,B) the monoalkylation of coordinated dinitrogen in *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W) is rate limited by dinitrogen dissociation from the substrate (A, Scheme 3) (*88*, *89*).

The kinetics of the reaction between *trans*-[M(N$_2$Me)Br(dppe)$_2$] and methyl iodide in tetrahydrofuran exhibit a first-order dependence in the concentration of complex and first-order in the concentration of methyl iodide. When M = W, the reaction with methyl iodide is 38 times faster than the reaction with ethyl iodide, which is typical of S$_N$2 reactions. Therefore, it is concluded that the secondary alkylation is a bimolecular nucleophilic substitution (Scheme 10) in which nucleophilic attack of the diazenido ligand on the carbon atom of the alkyl halide is the rate-limiting step (*93*).

Comparison of the second-rate order constants for reactions of the molybdenum and tungsten analogs with a given alkyl halide shows that the tungsten complex reacts six times faster than the molybdenum counterpart (Section VI,E,2).

The reaction of *trans*-[Mo(N$_2$)$_2$(depe)$_2$] (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$) with EtBr or MeBr in benzene yields *trans*-[Mo(N$_2$R$_2$)Br(depe)$_2$]$^+$ but no diazenido complex, in circumstances in which the tungsten complex is recovered unchanged. This reflects the relative rates of loss of dinitrogen from these substances (i.e., the strong tungsten–dinitrogen binding precludes formation of the initial diazenido complex). The depe ligand, more basic than dppe, and the greater lability of dinitrogen on the molybdenum results in the reactions with *trans*-[Mo(N$_2$)$_2$(depe)$_2$] proceeding rapidly through to the dialkylhydrazido(2−) complex.



SCHEME 10. Mechanism of alkylation of [M(N$_2$R)X(dppe)$_2$] (phosphine ligands omitted for clarity).

D. THE MECHANISM OF PROTONATION OF DINITROGEN TO FORM HYDRAZIDO(2−) COMPLEXES

Two studies on the mechanism of formation of hydrazido(2−) complexes by the reaction of dinitrogen complexes with acids have been reported (*186, 187*). The salient features of these two mechanisms (one found in methanol, the other in tetrahydrofuran), will be discussed separately, and then compared.

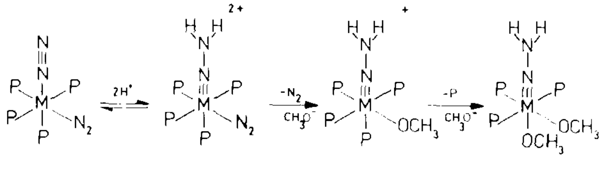
1. *The Reaction of cis-[M(N_2)$_2$(PMe_2Ph)$_4$] with Acids in Methanol*

The kinetics of the reaction between *cis*-[$M(N_2)_2(PMe_2Ph)_4$] (M = Mo or W) and the acids HCl, HBr, or H_2SO_4 in methanol, to yield the common product [$M(NNH_2)(OCH_3)_2(PMe_2Ph)_3$] have been interpreted in terms of the mechanism shown in Scheme 11.

Rapid, but inextensive, diprotonation of a dinitrogen ligand in the substrate (A) gives (B). This protonation removes electron density from the metal, thus labilizing the *cis*-dinitrogen to yield [$M(NNH_2)(PMe_2Ph)_4]^{2+}$. Attack of the solvent at the vacant site yields [$M(NNH_2)(HOCH_3)(PMe_2Ph)_4]^{2+}$. Upon coordination, methanol is rendered sufficiently acidic that a proton is rapidly liberated to yield *cis*-[$M(NNH_2)(OCH_3)(PMe_2Ph)_4]^+$ (C). Subsequent, presumably rate-limiting, loss of a phosphine yields [$M(NNH_2)(OCH_3)(PMe_2Ph)_3]^+$, which is then attacked by methanol to give [$M(NNH_2)(OCH_3)(HOCH_3)(PMe_2Ph)_3]^+$. As before, a proton is rapidly released from the coordinated methanol to yield the [$M(NNH_2)(OCH_3)_2(PMe_2Ph)_3$] product (D).

Thus the 2 mol equivalents of protons which are necessary to diprotonate the coordinated dinitrogen are subsequently regenerated due to the relatively high acidity of coordinated methanol. Protons are consumed only in the neutralization of liberated phosphine.

Although it proved impossible to isolate (D) (in practice dihalides are isolated), other hydrazido(2−) complexes containing alkoxy groups have been obtained (*259*).



SCHEME 11. Mechanism of formation of [$M(NNH_2)(OCH_3)_2(PMe_2Ph)_3$] (M = Mo or W) ($PMe_2Ph$ represented as P).

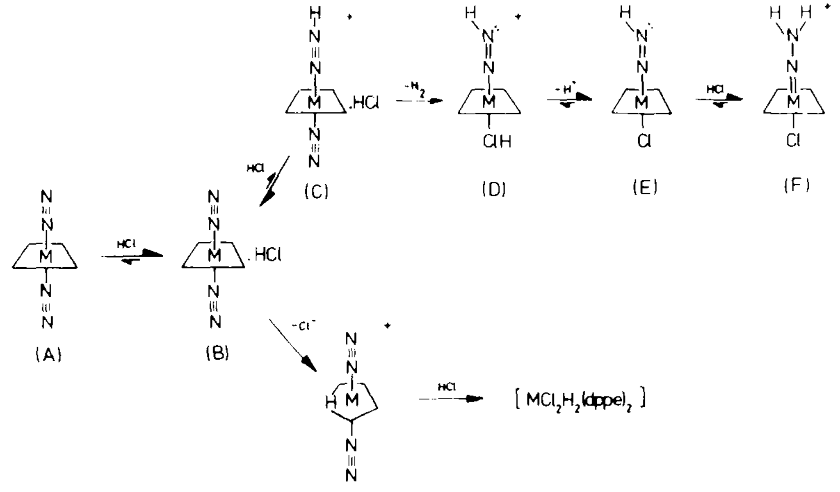
2. *The Reaction of trans-*$[M(N_2)_2(diphos)_2]$ *with Acids in Tetrahydrofuran*

In contrast to the mechanism described above, the reactions of *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ (M = Mo or W, R = Ph or Et) with HCl, HBr, or H_2SO_4 in tetrahydrofuran involve attack by the HX molecule. This is a consequence of the weakly basic nature of tetrahydrofuran (*9*).

In order to accommodate a variety of rate laws obtained in the hydrazido(2−)-forming reactions in tetrahydrofuran, the mechanism shown in the top half of Scheme 12 has been proposed.

Initially, an adduct (B) is rapidly formed between the dinitrogen substrate (A) and a molecule of HX. A dinitrogen ligand is then protonated by a further molecule of HX (C) (other pathways involving diprotonation of dinitrogen are present in the reactions of some substrates). Protonation of the coordinated dinitrogen labilizes the *trans*-dinitrogen, which is lost in the rate-limiting step. The added molecule of HX is now advantageously oriented to enter the coordination sphere (D). Subsequent rapid deprotonation of the coordinated molecule of HX, and rapid protonation of the diazenido ligand (E) results in the hydrazido(2−) product (F).

This mechanism readily rationalizes the formation under certain very specific conditions of hydrido complexes. It was shown some time



SCHEME 12. Mechanism of the reactions between *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) and HCl in tetrahydrofuran (phosphine ligands omitted for clarity).

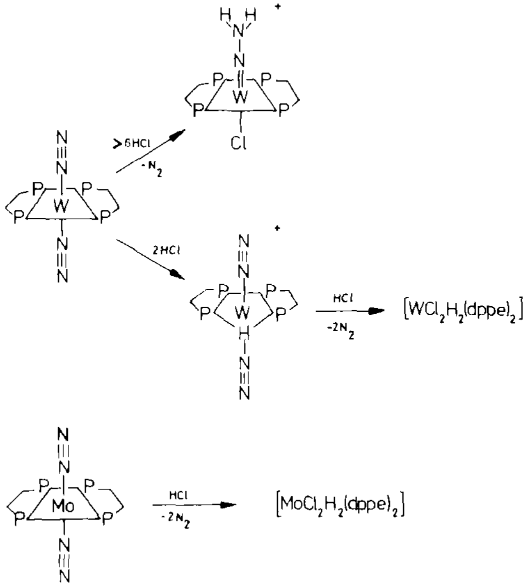


FIG. 2. Products of the reactions between *trans*-[M$(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$] (M = Mo or W) and HCl in tetrahydrofuran.

ago (*92*) that the reaction between *trans*-[M$(N_2)_2$(dppe)$_2$] and HCl can give hydrido complexes. The reaction of *trans*-[W$(N_2)_2$(dppe)$_2$] and HCl yields the hydrazido(2−) complex only at relatively high concentrations of acid. At low concentrations of HCl the predominant product is the seven-coordinate [WH$(N_2)_2$(dppe)$_2$]$^+$ (Fig. 2). This hydrido complex is not an intermediate on the pathway leading to hydrazido(2−) complexes since treatment with an excess of acid results in the loss of both dinitrogen ligands and the formation of [WCl_2H_2(dppe)$_2$]. At all concentrations of HCl, the reaction with *trans*-[Mo$(N_2)_2$(dppe)$_2$] rapidly yields [$MoCl_2H_2$(dppe)$_2$].

Kinetic studies on these hydride-forming reactions have shown that the behavior is readily understood in terms of competing pathways leading to protonation at the metal on the one hand, and formation of hydrazido(2−) complex on the other (Scheme 12).

Of the acids used in these reactions, HCl forms the strongest adduct (B). However HCl is also the weakest acid, and thus the subsequent protonation of dinitrogen (C) is less extensive. Yet this protonation is essential in order that the reaction proceed through to the hydrazido(2−) product (G). Thus with HCl the adduct (B) has the greatest opportunity of decomposing by an alternative route, involving electrophilic attack of the acid on the electron-rich metal center to yield $[WH(N_2)_2(dppe)_2]^+$. Upon increasing the concentration of HCl progressively more of the adduct is protonated, and the hydrazido(2−) complex becomes the major product.

The lower basicity and greater lability of dinitrogen when coordinated to molybdenum results in the reaction of *trans*-$[Mo(N_2)_2(dppe)_2]$ with HCl proceeding rapidly through to $[MoCl_2H_2(dppe)_2]$.

Thus, not only the base strength of the coordinated dinitrogen, but also the acid strength of HX, define the reaction pathway(s): attack at nitrogen versus attack at metal.

3. *Comparison of the Two Mechanisms: Influence of Solvent*

The two mechanisms for the formation of hydrazido(2−) complexes outlined above allow an appreciation of the role of the solvent in the mechanism.

A protic solvent such as methanol ($\varepsilon = 32.6$), renders HCl, HBr, and H_2SO_4 all strong monobasic acids. Furthermore, protic solvents are uniquely advantageous, since the facile release of a proton upon coordination of a solvent molecule (Scheme 11) results in protons being consumed only in the neutralization of liberated phosphine.

In contrast, an aprotic solvent such as tetrahydrofuran ($\varepsilon = 7.4$) is insufficiently basic ($pK_a = -2.05$) to level HCl, HBr, and H_2SO_4. Thus these acids are correspondingly weaker than in the protic solvent. This, together with the lower dielectric constant which favors the formation of adducts, can, under certain very specific conditions, result in the preferential formation of hydrido complexes (i.e., attack of acid at the metal rather than dinitrogen).

E. Influence of the Phosphine Ligands and the Metal upon Nitrogen Ligand Lability and Basicity

The mechanistic studies which have been described so far in this article allow some important conclusions to be made about the influence the phosphine coligand and metal have upon the nitrogen ligands.

1. *Influence of the Phosphine Ligand*

The more basic the phosphine coligand the greater the electron density imparted to the metal. This has two major effects on a coordinated dinitrogen: a decreased lability to dissociation, and an increased basicity. In the formation of hydrazido(2−) complexes in tetrahydrofuran, the two effects conflict. However, the reactions of *trans*-$[M(N_2)_2(depe)_2]$ with a given acid are faster than those of *trans*-$[M(N_2)_2(dppe)_2]$ (*187*), so clearly the basicity effect dominates.

2. *Influence of the Metal*

The increased basicity of a ligand when coordinated to the heavier metals in a transition metal triad has been appreciated for some time (*311*). This is manifest in (1) the rate of alkylation of alkyldiazenido complexes ($k_W/k_{Mo} = 5.4$) (*93*), and (2) the rate of formation of hydrazido(2−) complexes by the reaction of dinitrogen complexes with acid, in methanol ($k_W/k_{Mo} = 9.2 \times 10^2$) (*186*), and in tetrahydrofuran ($k_W/k_{Mo} = 29–85$, dependent upon the acid and substrate employed) (*187*). Clearly the electron-releasing capability of the metal has conflicting influences on the rate, but as in Section VI,E1 the basicity influence dominates.

Early studies attempted to determine, semiquantitatively, the basicity of coordinated dinitrogen, by measuring the formation of adducts between dinitrogen complexes and trimethylaluminium (*73*). However, the results were somewhat anomalous (the adduct formation constant was greater for a molybdenum complex than for its tungsten analog). This clearly does not reflect the proton basicity of the dinitrogen complexes and probably π donation from the dinitrogen to vacant aluminium *d*-orbitals contributes to the adduct formation constant.

Studies on the base-catalyzed substitution of halide for methoxide in complexes *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo or W) have shown (for X = F or Cl) that the imido group in the tungsten complexes is some 1000-fold less acidic than in the molybdenum ones (*188*).

VII. Reactions of Hydrazido(2−) Complexes

A. INTRODUCTION

In the ammonia-forming reactions of tungsten(0) and molybdenum(0) dinitrogen complexes, the only intermediates which have been identified with certainty are hydrazido(2−) species. The number of hydrazido(2−) complexes formed in this way is relatively small. Despite considerable study, the mechanism(s) by which an $Mo{=}NNH_2$ or $W{=}NNH_2$ group is converted to ammonia or hydrazine is unknown, although various pathways have been postulated. Nevertheless, reactions of coordinated hydrazido(2−) ligands have provided a primary basis for discussion of possible modes of action of nitrogenase at the molecular level.

Organohydrazido(2−) complexes are more numerous than hydrazido(2−) complexes and their coordination environments are more diverse. Some of these organohydrazido(2−) complexes can be prepared from dinitrogen, although many have been synthesized indirectly (Section VI,A). The chemistry of organohydrazido(2−) complexes provides information that sheds light on the chemistry of hydrazido(2−) species and that extends to further species. In particular, protonation and insertion reactions of organohydrazido(2−) complexes afford stable organohydrazido(1−) compounds which may bear upon as yet undetected intermediates formed in the conversion of coordinated hydrazide(2−) to ammonia and/or hydrazine.

B. HYDRAZIDO(2−) COMPLEXES

1. *As Intermediates in Ammonia or Hydrazine Yielding Reactions of N_2 Complexes*

Complexes such as *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ react with protic acids in nonaqueous solvents to give ammonia and hydrazine in yields which depend upon the complex, the solvent, and the acid employed (*18, 103, 190, 320*), for example, reaction (42).

$$\underset{1\ \text{mol}}{cis\text{-}[Mo(N_2)_2(PMe_2Ph)_4]} \xrightarrow[\text{HCl}]{\text{dimethoxymethane}} \underset{0.32\ \text{mol}}{NH_3} + \underset{0.31\ \text{mol}}{NH_2NH_2} \tag{42}$$

An *in situ* ^{15}N-NMR study of the protonation reactions of molybdenum and tungsten dinitrogen complexes has shown that signals arise in the early stages of the reaction which can be assigned to relatively stable hydrazido(2−) species (*4*). With careful choice of acid and conditions, thermally stable hydrazido(2−) complexes can be isolated. They often yield ammonia and/or hydrazine upon further protonation (*4, 105*), for example, reaction (43).

$$\underset{1.0\ \text{mol}}{[WCl_2(NNH_2)(PMe_2Ph)_3]} \xrightarrow[\text{MeOH}]{H_2SO_4} \underset{1.54\ \text{mol}}{NH_3} + \underset{0.06\ \text{mol}}{N_2H_4} \tag{43}$$

This is not always the case because *trans*-$[Mo(N_2)_2$-(triphos)$(PPh_3)]$ (**26**) reacts with anhydrous HBr in THF to give ammonia (*18*), but $[MoBr_2(NNH_2)$(triphos)] (triphos = Ph_2PCH_2-

$CH_2PPhCH_2CH_2PPh_2$) may be isolated under modified conditions from **26** and HBr, and is inert to further protic attack by anhydrous HBr (*40*).

Dinitrogen bound to early transition metals in various ways, such as in $[\{TaCl_3(THF)_2\}_2N_2]$, $[\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2]$, and $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}N_2)\{CH(SiMe_3)_2\}]$, yields hydrazine upon protonation with acids. The mechanisms are generally unknown, but the intermediacy of hydrazido(2−) species cannot be excluded.

2. *Stoichiometries and Mechanisms*

The apparent stoichiometries of the protonation reactions of the dinitrogen and hydrazido(2−) complexes of Mo and W are somewhat diverse and rarely have mass balances been established. Reactions (44)–(49) are illustrative. A particular problem has been the identification of the final metal product(s). Reactions (44)–(46) represent stoichiometries for maximum empirical ammonia yields from W(0) and Mo(0) dinitrogen complexes.

$$[Mo(N_2)_2(PMe_2Ph)_4] \xrightarrow{(i)} \tfrac{2}{3}NH_3 + \tfrac{5}{3}N_2 + (Mo^{IV}?) \qquad (44)$$

$$[MoCl_2(NNH_2)(PMe_2Ph)_3)] \xrightarrow{(i)} \tfrac{2}{3}NH_3 + \tfrac{2}{3}N_2 + (Mo^{IV}?) \qquad (45)$$

$$[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{(i)} 2NH_3 + N_2 + W^{VI} \qquad (46)$$

$$[WCl_2(NNH_2)(PMe_2Ph)_3] \xrightarrow{(i)} \tfrac{3}{2}NH_3 + (N_2?) + N_2H_4(\text{trace}) + \text{metal products} \qquad (47)$$

$$[Mo(N_2)_2(PMe_2Ph)_4] \xrightarrow{(ii)} NH_3 + \tfrac{3}{2}N_2 + Mo^{III} \qquad (48)$$

$$\underset{\mathbf{(26)}}{[Mo(N_2)_2(triphos)(PPh_3)]} \xrightarrow{(ii)} NH_3 + \tfrac{3}{2}N_2 + [MoBr_3(triphos)] \qquad (49)$$

$$[MoBr_2(NNH_2)(triphos)] \xrightarrow{(ii)} \text{no reaction} \qquad (50)$$

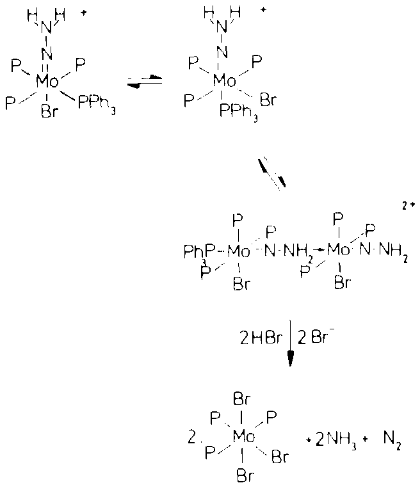
(i) MeOH, excess of H_2SO_4; (ii) THF, excess of HBr.

Protonation of dinitrogen or hydrazido(2−) ligands to yield ammonia [reactions (44)–(50)] is not coupled to electron transfer from an external reductant. Electrons for (new) N—H electron pair bonds must therefore come from the metal as is the case in reaction (46), or from ligand-centered oxidation or disproportionation reactions, as appears to be the case in reaction (49).

Only those Mo(0) and W(0) dinitrogen complexes which possess at least one (labile) monotertiary phosphine ligand give ammonia upon protonation: complexes such as *trans*-$[WF(NNH_2)(dppe)_2]^+$ are inert to further protic attack. It has been suggested (*82*) that the substitution of a phosphine ligand by an anion increases the basicity of the hydrazido(2−) group and that this is an essential step for further protic attack on that group.

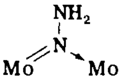
Reaction (49) has been studied (*18*) in some detail. The time course for this reaction is biphasic: 1 mol of dinitrogen per mole of complex is released rapidly whereas the remaining dinitrogen is evolved more slowly with concomitant ammonia formation. ^{31}P-NMR studies suggest that the first phase involves the formation of two isomeric hydrazido(2−) complexes, paralleling the ^{15}N NMR observation of two sets of hydrazido(2−) signals in the protonation reactions of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (*41*). The complexes $[MoF(NNH_2)(triphos)(PPh_3)][BF_4]$ (*170*) and $[MoBr_2(NNH_2)(triphos)]$ (*40*) have been isolated from the reactions of **26** with $[PPh_3H][BF_4]$ and HBr, respectively, but neither gives ammonia upon treatment with HBr under the conditions of reaction (49). Ammonia and dinitrogen are formed if $[MoBr_2(NNH_2)(triphos)]$ is allowed to react with LiBr and CF_3CO_2H in THF.

The reasons for this are not clear (*40*). ^{15}N-Labeling studies on the protonation reaction between HBr and $[Mo(N_2)_2(PPh_3)(triphos)]$ show that the dinitrogen released in both fast and slow stages is formed without new N—N bonds being formed. These observations together with the prerequisite for a monotertiary phosphine and the stoichiometry of reaction (49) have been rationalized by an intramolecular redox reaction such as is represented by Scheme 13 (*40*). However, certain aspects of this Scheme have yet to find empirical support.

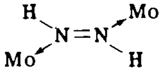


SCHEME 13. Proposed mechanism for the formation of ammonia in the reaction of $[Mo(NNH_2)Br(PPh_3)(triphos)]^+$ with HBr in tetrahydrofuran [triphos ligand represented by phosphorus donor atoms (P) only].

Although no complexes containing a bridging hydrazido(2−) moiety are known, diazene- and organohydrazine-bridged molybdenum complexes have been characterized and suggest possible structures for bridging $\{N_2H_2\}$ (**27, 28**) (*166, 301*).



27



28

Hydrazido(2−) complexes of Mo and W exhibit nucleophilic behavior and condense with aldehydes and ketones to give diazoalkane complexes (*22*), but the mechanism of these condensations has not been determined. Loss of tertiary phosphine from hydrazido(2−) intermediates to accommodate a binuclear interaction, as in Scheme 13, or to allow anion coordination are not incompatible.

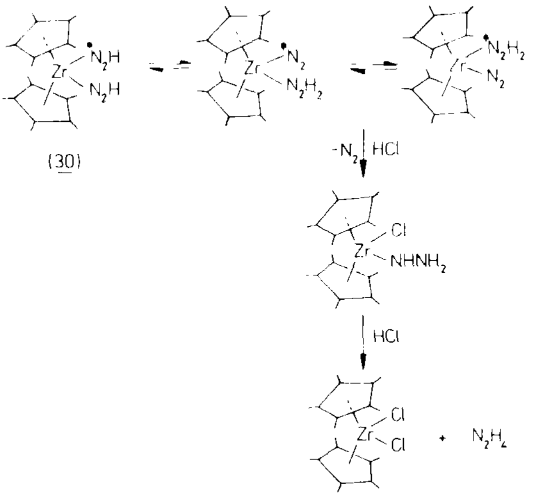
The formation of ammonia and/or hydrazine by protonation of binuclear bridging dinitrogen complexes of Groups IV and V is well established and has been reviewed elsewhere (*82, 148*). In general, stoichiometries are fairly well defined [Eq. (51)], although as with mononuclear complexes, mechanisms are not clearly understood (*282*).

$$[\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2] \xrightarrow{4HCl} 2[(\eta^5\text{-}C_5Me_5)_2ZrCl_2] + N_2H_4 + 2N_2 \qquad (51)$$

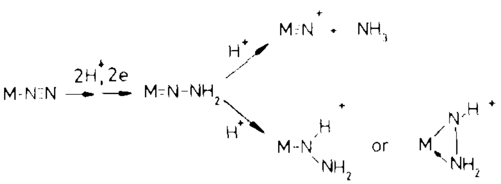
The protonation of $[\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2]$ (**29**) which gives hydrazines derived in equal amounts from both terminal and bridging dinitrogen has been investigated in considerable detail (*238*). The discussion is extended here in the context of hydrazido(2−) chemistry. The complex $[\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2]$ is unreactive toward protic attack by HCl and it was therefore concluded that the initial site of protonation in the reaction of **29** with this acid is a terminal dinitrogen. This need not be the case: replacement of one dinitrogen by chloride may be necessary to activate the remaining bridging or terminal dinitrogen toward a protic attack (cf. necessity for a labile tertiary phosphine ligand in reactions of molybdenum and tungsten dinitrogen complexes). An intermediate of type **30** [Eq. (52)] has been proposed and might yield diazene upon further protonation. Disproportionation of the diazene produces dinitrogen and hydrazine (*238*).

$$\underset{(\mathbf{30})}{[(\eta^5\text{-}C_5Me_5)_2Zr(NNH)_2]} \xrightarrow{2HCl} [(\eta^5\text{-}C_5Me_5)_2ZrCl_2] + 2\,NH{=}NH$$

$$2NH{=}NH \longrightarrow N_2 + NH_2NH_2 \qquad (52)$$



SCHEME 14. Proposed mechanism for the decomposition of $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2H)_2]$.



SCHEME 15. Alternative pathways for the decomposition of hydrazido(2−) complexes.

An equally plausible pathway involves hydrazido(2−) intermediates (Scheme 14); this avoids invoking disproportionation of free diazene.

It is by no means certain that simple protonation of a hydrazido(2−) ligand at a *mononuclear* Mo(IV) or W(IV) site to give, for example, hydrazido(1−) or imido species (Scheme 15) can take place at all, particularly in view of reactions (45) and (47). Nevertheless, protonations of hydrazido(2−) groups to give imido, nitrido, or hydrazido(1−) species remain attractive pathways and indirect evidence from the reactions of *organo*hydrazido(2−) complexes gives them some plausibility. These are discussed below.

C. ORGANOHYDRAZIDO(2−) COMPLEXES

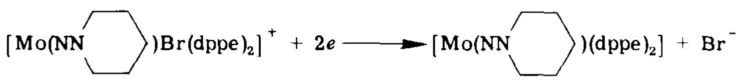
1. *Reductive Activation: Formation of Amines and Hydrazines*

The complexes *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) react with alkyl halides RX (X = Br or I) to give compounds *trans*-$[MX(NNR_2)(dppe)_2]X$

(**31**) by mechanisms which are well understood (Section VI,C). These cations, like the parent nonsubstituted hydrazido(2−) homologs, are inert toward protic attack. Monotertiary phosphine analogs of **31**, although they would be very useful, are as yet unknown.

Although complexes **31** are unreactive toward electrophiles, the organohydrazido(2−) ligand can be degraded to give an amine (HNR_2) by electrophilic attack under forcing conditions. For example, heating (**31**, M = W; X = Br; R = Me) for 2–3 days with $Li[AlH_4]$ in diethylether in a sealed tube at 120°C gives ~1 mol of NMe_2H per atom of tungsten upon acid-quench work-up. The nature of the metal product(s) and the fate of the other nitrogen atom are unknown, hence the stoichiometry of such reactions and mechanisms of degradation are unclear. Nevertheless, these reactions show that coordinated dinitrogen can be converted to organonitrogen products via organohydrazido(2−) complexes.

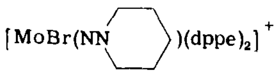
Electrochemical reduction of the complex (**31**, M = Mo; X = Br; R_2 = —$CH_2(CH_2)_3CH_2$—) under an atmosphere of argon in a THF electrolyte at about −2.0 V vs sce at Pt or Hg cathodes is diffusion controlled and clean. The reduction involves the irreversible addition of two electrons and affords the thermally stable, although highly reactive Mo^{II} dialkylhydrazido(2−) complex (**32**) according to Eq. (53). This reduction can also be effected by Li*t*Bu and recently it has been possible to isolate **32** as a black microcrystalline solid using this reductant.



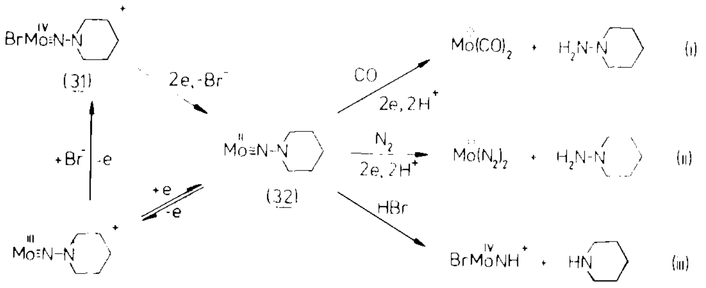
32

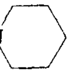
(53)

The Mo(II) complex has a remarkable chemistry which is summarised in Scheme 16. Thus reduction of the parent



under an atmosphere of carbon monoxide proceeds via the formation of **32** to give the *dialkylhydrazine* *N*-aminopiperidine and $[Mo(CO)_2(dppe)_2]$ (cis and trans isomers) in ~60–70% yields of each, in an overall four-electron reduction process (i, Scheme 16). Similarly, reduction under dinitrogen releases the *N*-aminopiperidine and gives *trans*-$[Mo(N_2)_2(dppe)_2]$, in ~65 and 25% yields, respectively (ii, Scheme 16). Complex **32** also reacts rapidly with anhydrous HBr to give the amine, piperidine, and the imido complex, *trans*-$[MoBr(NH)(dppe)_2]^+$,



SCHEME 16. Reactions of [Mo(NN)(dppe)$_2$] (dppe ligands omitted for clarity).

all in 60–70% yields (iii, Scheme 16). Other reactions not directly involving the NNR$_2$ group are also shown in Scheme 16. Related molybdenum and tungsten dialkylhydrazido(2−) complexes show a similar electrochemical behavior although these have yet to be studied in detail (*194, 273*).

The HBr cleavage of the Mo=NNR$_2$ group is important as it demonstrates a reaction pathway analogous to that proposed as a step in the conversion of dinitrogen to ammonia by the enzyme. Two further points regarding these organohydrazine- and amine-forming reactions are worth noting. First, the conversion takes place at a single mononuclear site with retention of four ligands in a square plane. Second, such reactions may form the basis of a cycle by which dinitrogen is converted to organonitrogen products (*194, 273, 274*).

Organohydrazido(2−) complexes of Mo$^{(VI)}$ with dithiocarbamato coligands (dtc) have a reduction chemistry which in some respects parallels that of the lower oxidation state di(tertiary phosphine) complexes discussed above. Complexes such as [Mo(NNRR′)(dtc)$_3$]$^+$, (R′ and R = alkyl, aryl) have been obtained by indirect routes (Section VI,A,1), but not from dinitrogen complexes as these are unknown. Their high formal oxidation states and sulfur, rather than phosphorus, ligand environments, offer an additional dimension to hydrazido(2−) ligand chemistry. The complex [Mo(NNMePh)(S$_2$CNMe$_2$)$_3$]$^+$ (**33**) is closed-shell and inert to protic attack. Electrochemical reduction of **33** in nonaqueous electrolytes proceeds in two successive, reversible, 1-electron steps which give a relatively stable paramagnetic 19-electron species and an unstable 20-electron anion, respectively. Preparative electrolyses yield the hydrazine NH$_2$NMePh (55–60% yield) after quenching the catholyte with anhydrous HCl and base work-up, via a pathway which is believed to involve the formation of a stable hydrazido(1−) intermediate [Eqs. (54) and (55)] (*120*).

$$\underset{(18e)}{[\mathrm{Mo(NNMePh)(S_2CNMe_2)_3}]^+} \underset{-e}{\overset{e}{\rightleftharpoons}} \underset{(19e)}{[\mathrm{Mo(NNMePh)(S_2CNMe_2)_3}]^0} \underset{-e}{\overset{e}{\rightleftharpoons}} \underset{(20e)}{[\mathrm{Mo(NNMePh)(S_2CNMe_2)_3}]^-} \qquad (54)$$

$$\underset{(20e)}{[\mathrm{Mo(NNMePh)(S_2CNMe_2)_3}]^-} \xrightarrow{\mathrm{H^+}} \underset{(18e)}{[\mathrm{Mo(NHNMePh)(S_2CNMe_2)_3}]} \xrightarrow[\text{(2) base work-up}]{\text{(1) HCl}} \mathrm{NH_2NMePH} + \text{unidentified metal product(s)} \qquad (55)$$

The complex $[\mathrm{Mo(NNMePh)_2(S_2CNMe_2)_2}]$ is an unusual, stable, 20-electron species which has been characterized by an X-ray structure determination (*78*) and shown to possess essentially linear hydrazido(2−) ligands. It reacts with an excess of anhydrous HCl to liberate the hydrazine stoichiometrically [Eq. (56)].

$$\underset{(20e)}{[\mathrm{Mo(NNMePh)_2(S_2CNMe_2)_2}]} \xrightarrow{\mathrm{HCl}} \underset{(18e)}{[\mathrm{MoCl_2(NNMePh)(S_2CNMe_2)_2}]} + \mathrm{NH_2NMePh} \qquad (56)$$

With one equivalent of HCl, $[\mathrm{Mo(NNMePh)_2(S_2CNMe_2)_2}]^+$ gives the stable hydrazido(1−) complex $[\mathrm{Mo(NHNMePh)(NNMePh)(S_2CNMe_2)_3}]^{2+}$ which has also been subjected to an X-ray crystal structure determination and thereby shown to possess a sideways-bound hydrazido(1−) group (**34**) (Fig. 3) (*78, 79*). Thus it appears that hydrazido(2−) complexes of molybdenum which are formally reduced to a 20-electron configuration [although in a high metal oxidation state, (IV) or (VI)] possess an incipient lone pair of electrons on a nitrogen atom adjacent to the metal (N_α). Complexes in which an organohydrazido(2−) ligand possesses a bent geometry are now fairly well established (Section VI) and these species, usually protonate at N_α.

2. *Formation of Organohydrazido*(1−) *Complexes from Organohydrazido*(2−) *Complex Precursors*

The first example of complexes with an organohydrazido(1−) ligand were derived from complexes such as $[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{WH(NNHC_6H_4F}$-

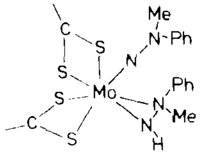


FIG. 3. Structure of $[\mathrm{Mo(NNMePh)(NHNMePh)(dtc)_2}]^+$.

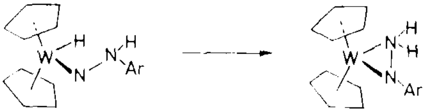
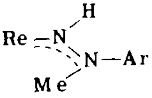


FIG. 4. Thermal transformation associated with $[(\eta^5\text{-}C_5H_5)_2W(H)(NNHAr)]^+$ (Ar = C_6H_4F).

p)]PF_6 which possess an organohydrazido(2−) ligand bound in the unusual bent mode (Section VI). They are unstable thermally and isomerize above ~20°C to give sideways-bound hydrazido(1−) complexes (Fig. 4) (*66, 116*). The protonation reactions of complexes $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NNMeAr)]$ (Ar = $p\text{-}C_6H_4OMe$ or $p\text{-}C_6H_4Me$), which also possess bent hydrazido(2−) ligands, similarly give organohydrazido(1−) complexes; however, it has been suggested that NHNMeAr ligands possess a delocalized bent structure as in **35**, rather than a sideways-bound form.



35

The synthesis (*14*) has been reported of a range of tris(pyrazolyl)borato complexes in which various hydrazido(1−) ligands are coordinated in an end-on mode (*206*). Interestingly, included in this series is the first example of an unsubstituted $NHNH_2$ complex, although the structure of this compound remains to be determined (*242*). A claim that the complex $[W(N_2H_3)Cl_3(PPh_2Me)_2]$ contains the hydrazido(1−) ligand has since been found to be in error. Both ^{15}N-NMR spectroscopy and X-ray structure analysis have shown such species to be $[WH(NNH_2)Cl_3(PPh_2Me)_2]$ (*84*). Treatment of these complexes with acid gives hydrazine in nearly quantitative yields.

The protonation of the quinolin-8-olato complex $[(MoO(NNMe_2)(C_9H_6NO)_2]$ (another "bent" organohydrazido ligand complex) gives NH_3 and $NHMe_2$ as well as NH_2NMe_2. The complex, $[MoO_2(C_9H_6NO)_2]$ is the only isolable metal product, and was formed in 10–20% yield [Eq. (57)]. Presumably an organohydrazido(1−) intermediate is involved (*75*).

$$[MoO(NNMe_2)(C_9H_6NO)_2] \xrightarrow[\text{CH}_2\text{Cl}_2 \text{ or MeOH}]{\text{HX}} NH_3 + NMe_2H + NH_2NMe_2 + \text{metal products} \qquad (57)$$

The chemistry of the hydrazido(1−) ligand is in its infancy. Nevertheless, it is clear that such species can, in certain cases, undergo further reactions with protons to release organohydrazine. Whether or not hydrazido(1−) complexes or their organo analogs are capable of yielding an imido complex and an amine in a clean reaction as shown in reaction (58) remains to be demonstrated.

$$\mathrm{M(NHNR_2)} \longrightarrow \mathrm{MNH} + \mathrm{HNR_2} \tag{58}$$

VIII. Reactions Involving Ligated Diazenes

The formation of metal-bound diazene from dinitrogen and its subsequent disproportionation is a plausible mechanism of action of nitrogenase (*54*). The disproportionation of free diazene is well established (Section V,A) although such reactions of metal-bound diazene are as yet unknown. The enzymatic release of a reactive species such as *cis*-, *trans*-, or *iso*-diazene would be unexpected but cannot be ruled out.

The synthesis of diazene complexes has been described (Sections V,B, C, and D). It is worth reiterating that no diazene complex has been prepared via reactions of coordinated dinitrogen and no stoichiometric conversion to hydrazine or ammonia has been demonstrated.

Organodiazenes show a somewhat richer chemistry. Many years ago it was demonstrated that coordinated phenyldiazene can be catalytically hydrogenated on platinum(0) according to Eq. (59) (*268, 216*).

$$[\mathrm{Pt(HN{=}NPh)(PEt_3)_3}] \xrightarrow{\mathrm{H_2}} [\mathrm{Pt(H_2NNHPh)(PEt_3)_3}] \tag{59}$$

Dinitrogen coordinated to a manganese(I) center can be converted to a coordinated dimethyldiazene by successive attack of methyl carbanions and carbonium ions and solutions of the diazene complex under dinitrogen at high pressure liberate dimethyldiazene. Such a reaction sequence affords a cyclic system for the conversion of dinitrogen to dimethyl diazene (*306, 307*). The isomerization of a diazene (or organodiazene) complex to a hydrazido(2−) or organohydrazido(2−) complex, or vice versa as shown in Eq. (60), has not been achieved.

$$\mathrm{M(NHNH)} \longrightarrow \mathrm{M(NNH_2)} \tag{60}$$

Recent work on the insertion of diazenido ligands into M—H bonds and on the attack of hydride and organolithium reagents upon diazenido complexes suggest that such reactions may be feasible (*14*).

In summary, the chemistry of coordinated diazene and organodiazenes is insufficiently developed to permit a detailed discussion of the role of diazene in the action of nitrogenase.

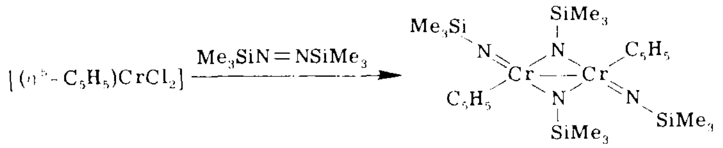
IX. Nitrides, Imides, and Amides

A. AS INTERMEDIATES IN ENZYMATIC NITROGEN FIXATION

The biological fixation of dinitrogen by way of nitrido, imido, and/or amido intermediates has long been recognized as plausible. Such intermediates might arise by one of several possible N—N bond-cleavage reactions. For example, protic attack upon hydrazido(2−) intermediates has been postulated [Eq. (61)] (*83*). The protic cleavage of a dialkylhydrazido(2−) complex in a reaction analogous to Eq. (61) has been discovered (Scheme 16, Section VII,C,1).

$$\mathrm{Mo{=}NNH_2 \xrightarrow{2H^+} Mo{=}NH^{2+} + NH_3} \qquad (61)$$

Coordinated diazene may undergo cleavage to give a bis(imido) species. This cleavage reaction has been authenticated (*260, 348a*) as evidenced by the isolated product, in the reaction between $[(\eta^5\text{-}C_5H_5)CrCl_2]$ and $Me_3SiN{=}NSiMe_3$, as shown in reaction (62).

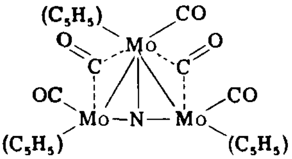


(62)

Polynuclear metal frameworks could also assist in N—N scission. Within this category fall the so-called nitriding reactions of metals (see Section XI). The cleavage of bridging diazene or hydrazine in well-defined reactions of their complexes has not been observed.

B. NITRIDO COMPLEXES

Three classes of nitrido complex have been characterized. The majority of nitrido complexes are monomeric, containing a formal metal–nitrogen triple bond as in $[MNX_4]$ (M = Mo, Re, Ru, or Os; X = halide). However, bridging nitrido complexes are also known. Both symmetric bridges, $M{=}N{=}M'$ (as in $[\{TaBr_5\}_2N]^{3-}$), and asymmetric bridges, $M{\equiv}N{\rightarrow}M'$ or $M{=}\ddot{N}{-}M'$ (as in $[\{MoNCl_3\}]$) have been observed. Finally, triply bound nitrido complexes containing the nucleus M_3N are known. In the anion $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ the nitride is bonded in a planar symmetrical Y-shaped configuration to the three iridium atoms. Similarly, in the recently reported complex **36** the nitrogen atom is bound to three metal (molybdenum) atoms but now in a T-shaped configuration (*132, 163*).



36

The triple bond in terminal nitrides can be formulated as the superposition of one σ bond and two degenerate π bonds. The metal–nitrogen triple bond is extremely short, its length being between 1.57 and 1.66 Å, depending upon the metal, its oxidation state, and the coligands. The strongest metal–nitride bonds are formed by transition metals in their higher oxidation states whereby $d\pi$–$p\pi$ orbital interaction is maximized. Complexes with terminal M≡N bonds normally exhibit strong bands in the 950–1100 cm^{-1} region of the IR spectrum which are assignable to $\nu(M{\equiv}N)$. In structurally comparable species the $\nu(M{\equiv}N)$ increases in frequency from left to right along a Period and also on descending a Group.

The preparative, structural, and bonding aspects of transition metal nitrido complexes have been reviewed in detail recently (*132, 179*). To summarize, there are three principal preparative pathways to yield nitrido complexes and these, with examples, are outlined below.

1. Ammonolysis reactions of oxo complexes with ammonia or alkali metal amides, for example, Eq. (63).

$$Re_2O_7 + 3KNH_2 \longrightarrow K_2[ReO_3N] + K[ReO_4] + 2NH_3 \qquad (63)$$

2. Reaction with hydrazines as shown in Eq. (64).

$$[ReOCl_3(PPh_3)_2] + PhNHNH_2 \longrightarrow [ReNCl_2(PPh_3)_2] + PhNH_2 + HCl \qquad (64)$$

3. Treatment with azido compounds, such as azide ion [Eq. (65)], halidoazide [reaction (66)], or trimethylsilylazide [reaction (67)], which is the most common nitride-forming pathway.

$$MoCl_5 + N_3^- \longrightarrow [MoNCl_4]^- + N_2 + \tfrac{1}{2}Cl_2 \qquad (65)$$

$$\mathrm{MoCl_5 + ClN_3 \longrightarrow [MoCl_5N_3] \longrightarrow [MoNCl_3] + N_2 + Cl_2} \tag{66}$$

$$\mathrm{[Mo(N_2)_2(dppe)_2] + Me_3SiN_3 \longrightarrow [MoN(N_3)(dpe)_2] + \tfrac{3}{2}N_2} \tag{67}$$

An interesting, but currently unique, reaction to form $\mathrm{W(O\text{-}}t\mathrm{Bu)_3N}$ (probably tetrameric) involves the cleavage of the tungsten–tungsten triple bond of $[\mathrm{W_2(O\text{-}}t\mathrm{Bu)_6}]$ by alkyl nitriles as shown in Eq. (68).

$$[(\mathrm{O\text{-}}t\mathrm{Bu})_3\mathrm{W{\equiv}W(O\text{-}}t\mathrm{Bu})_3] + \mathrm{RCN} \longrightarrow [(\mathrm{O\text{-}}t\mathrm{Bu})_3\mathrm{W{\equiv}CR}] + (\mathrm{O\text{-}}t\mathrm{Bu})_3\mathrm{W{\equiv}N} \tag{68}$$

This reaction is formally analogous to organic acetylene metathesis.

The chemistry of the coordinated nitrido group is relatively sparse. The strong trans-labilizing influence of the nitrido group, and the effect this has on the facile exchange and substitution of the trans ligand and the structure of nitrido complexes has been discussed (*132*).

In the context of nitrogen fixation, it has long been known that certain transition metal nitrido complexes yield ammonia on treatment with acid (*45a*). However, this is by no means a general reaction for nitrido complexes. For instance although molybdenum nitrido complexes containing monotertiary phosphine ligands, such as $[\mathrm{MoNCl_2(PMePh_2)_2}]$, react with acid under ambient conditions to give high yields of ammonia (*77a*), the reaction of the analogous *trans*-$[\mathrm{Mo(N)X(dppe)_2}]$ (X = halide) even with an excess of acid (under forcing conditions) yields only the corresponding imido complexes, as shown in Eq. (69) (*189*).

$$trans\text{-}[\mathrm{Mo(N)X(dppe)_2}] + \mathrm{H^+} \longrightarrow trans\text{-}[\mathrm{Mo(NH)X(dppe)_2}]^+ \tag{69}$$

This difference in behavior between formally analogous complexes is reminiscent of that observed with hydrazido(2−) species (Section VII,B), where again only complexes containing monotertiary phosphine ligands protonate through to ammonia. No doubt in both cases the replacement of phosphine by more electron-releasing ligands is essential to increase the basicity of the nitrogen ligand prior to protonation through to ammonia.

The basicity of the nitrido group is a function of the metal and its oxidation state, and of the coligands. However, few systematic or quantitative estimates of this behavior have been made. A quantitative determination of the effect that the metal and the coligands have on the basicity of the nitrido group has been possible for *trans*-$[\mathrm{M(N)X(dppe)_2}]$ (M = Mo or W; X = F, Cl, Br, I, or $\mathrm{OCH_3}$) (*188, 189*). For both metals the basicity of the nitrido group decreases with the trans-ligand along the series $\mathrm{CH_3O > F > Cl > Br, I}$. At least 7 $\mathrm{p}K_\mathrm{a}$ units span the extremes of this series. The somewhat anomalous greater basicity of the nitrido group with the strongly σ-electron-attracting *trans*-methoxy and fluoro groups is a consequence of the greater π electron-releasing capability of these ligands.

For a given trans-ligand the nitride coordinated to tungsten is about 1000 times more basic than when coordinated to molybdenum. This is a consequence of the greater electron-releasing power of tungsten compared to molybdenum and parallels the relative stabilities of the higher oxidation states. The faster rates of formation of hydrazido(2−) complexes from tungsten substrates than molybdenum and the observation that *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ reacts with methanol to yield ammonia whereas the molybdenum counterpart requires the addition of acid (*101*) (Section VII,B,1) are further manifestations of the greater basicity of ligands when coordinated to tungsten. Alkylation rates of organodiazenido complexes to yield dialkylhydrazido(2−) complexes show the same trend. The difference in stoichiometries for ammonia formation between molybdenum and tungsten substrates (Section VII,B,2) may also have its origins in this phenomenon.

Some nitrido complexes of ruthenium, osmium, and rhenium react with phosphines to give phosphineiminato complexes, as shown in Eq. (70).

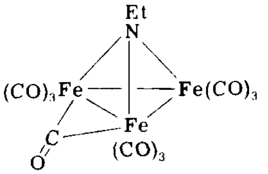
$$[\mathrm{ReNCl_4}] + 2\mathrm{PPh_3} \longrightarrow [\mathrm{Re(NPPh_3)Cl_4(PPh_3)}] \qquad (70)$$

Although it is tempting to envisage this as arising from nucleophilic attack on nitride, this is not unambiguous. The phosphineiminato product may well have been formed by nucleophilic attack of nitride on the phosphine.

C. IMIDO COMPLEXES

An excellent review of transition metal imido complexes appeared in 1980 (*260*). Transition metal imido complexes (NR; R = H, alkyl, or aryl) are most common for Second and Third Row metals, but relatively rare for First Row metals. Three classes of imido complex are known. The majority of imido complexes are monomeric containing a terminal imido group which may adopt either a linear configuration ($\mathrm{M{\equiv}N{-}R}$) containing a formal metal–nitrogen triple bond as in $[\mathrm{Os(N\text{-}\mathit{t}Bu)O_3}]$ and *trans*-$[\mathrm{M(NH)X(dppe)_2}]^+$ (M = Mo or W; X = CH_3O, N_3, F, Cl, Br, or I), or bent configuration ($\mathrm{M{=}N}{\diagup}^{\mathrm{R}}$) in which the MNR angle is in the range 139–167°. The complex $[\mathrm{Mo(NPh)_2(S_2CNEt_2)_2}]$ with a MoNPh angle of 139.4° contains the most bent imido group yet observed. The configuration adopted is a consequence of the 18-electron rule, but in reality the distinction is not clear, since MNR angles differ from the ideal 180 or 120°. However, most compounds structurally analyzed are essentially linear with a metal–nitrogen bond distance varying over the range 1.61–1.79 Å. This short distance is only about 0.05 Å longer than the metal–nitrogen bond length in analogous nitrido complexes and may even be shorter. Surprisingly the imido ligand exerts no strong trans influence.

The other two classes of imido complex contain bridging imido ligands; between two metal atoms as in $[(\mu\text{-NH})(\mu\text{-O})\{Mo(O)[S_2P(OEt)_2]_2\}_2]$, and between three metal atoms as in the iron cluster (**37**).



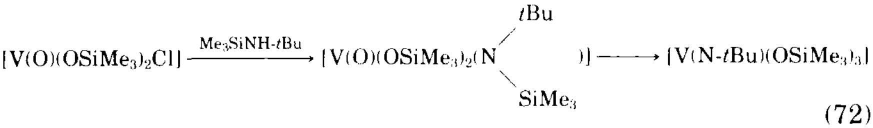
37

A variety of syntheses of imido complexes has been reported. Some are very specific, whereas others are much more general. The more general routes, with specific examples, are listed below.

1. Reaction of halido or oxo complexes with amines or lithium amides as typified by Eq. (71).

$$[Ti(NMe_2)_4] + nPrNH_2 \longrightarrow \{Ti(N\text{-}nPr)_2\}_x + 4Me_2NH \qquad (71)$$

2. Reaction of certain oxo complexes with silylated primary amines as shown in reaction (72).



$$[V(O)(OSiMe_3)_2Cl] \xrightarrow{Me_3SiNH\text{-}tBu} [V(O)(OSiMe_3)_2(N(tBu)(SiMe_3))] \longrightarrow [V(N\text{-}tBu)(OSiMe_3)_3] \qquad (72)$$

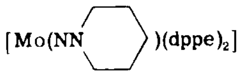
3. Reactions with azides as typified by reaction (73).

$$[Mo(CO)_2(S_2CNEt_2)_2] + 2PhN_3 \longrightarrow [Mo(NPh)_2(S_2CNEt_2)_2] + 2CO + 2N_2 \qquad (73)$$

4. Reactions of alkyl halides or acid with nitrido complexes as illustrated by Eqs. (74) and (69), respectively.

$$[W(N)Br(dppe)_2] + EtI \longrightarrow [W(NEt)Br(dppe)_2]I \qquad (74)$$

A less general route involving the protic cleavage of the dialkylhydrazido(2−) complex



to yield an imido species and an amine is discussed in Section VII,C,1 (*194*). Perhaps related to this, certain higher oxidation state rhenium and molybdenum oxo species react with substituted hydrazines to give imido complexes, as shown in reaction (75).

$$[ReOCl_3(PPh_3)_2] + MeNHNHMe \cdot 2HCl \xrightarrow{PPh_3}$$
$$[Re(NMe)Cl_3(PPh_3)_2] + MeNH_2 \cdot HCl + Ph_3PO \qquad (75)$$

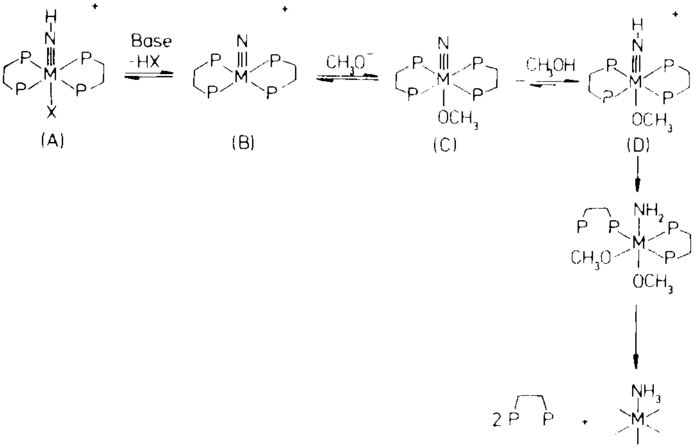
A series of tantalum imido complexes has been synthesized by the addition of imines or nitriles to tantalum neopentylidene complexes as shown in Eq. (76).

$$[Ta(CHCMe_3)Cl_3(THF)_2] + PhN{=}CHPh \longrightarrow$$
$$[Ta(NPh)Cl_3(THF)_2] + Me_3CCH{=}CHPh \qquad (76)$$

This is analogous to the previously described method (Section II,A,2) for making bridging-dinitrogen complexes. Metal chlorides and hydrides also react with nitriles to yield imido complexes, as shown in reaction (77) (*6, 165, 280*).

$$[WCl_6] \xrightarrow[CCl_4]{MeCN} [W(NCCl_2CH_3)Cl_4(CH_3CN)] \qquad (77)$$

Little is known about the reactions of imido complexes. As alluded to in Section IX,B, *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo or W; X = halide) is stable to attack by acid but surprisingly high yields (~70%) of ammonia can be obtained from these complexes by treatment with base (triethylamine or lithium methoxide) in methanol under ambient conditions (*25, 189*). This reaction has been the subject of two mechanistic papers (*188, 189*) and the mechanism is shown in Scheme 17. Initial deprotonation of the imido complex (A) by base generates the strongly trans-labilizing nitrido group. This has the effect in methanol of rapidly liberating the *trans*-halide to yield (B). Subsequent rate-limiting attack of methoxide on the 5-coordinate, 16-electron intermediate gives *trans*-$[M(N)(OCH_3)(dppe)_2]$ (C). The methoxy ligand confers greater basicity on the nitrido group than does the halido ligand (Sec-



SCHEME 17. Mechanism for the formation of ammonia in the reactions of base with *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo or W; X = halide).

tion IX,B). Indeed, a methoxy ligand renders the nitrido group sufficiently basic that it is protonated by methanol to yield *trans*-$[M(NH)(OCH_3)(dppe)_2]^+$ (D). This complex further decomposes slowly by loss of diphosphine to yield ammonia. The details of this decomposition are unknown. However, the kinetics and activation parameters are consistent with rate-limiting diphosphine chelate-ring opening. Furthermore, 2 mol equivalents of diphosphine are liberated per mole of complex during the reaction, and the ammonia formed remains coordinated to the metal. Thus it is believed that successive replacement of diphosphine by methoxy groups increases the basicity of the imido ligand sufficiently for it to be protonated further by methanol. These mechanistic studies have shown that the key step in the ammonia-forming reaction of base with *trans*-$[M(NH)X(dppe)_2]^+$ is the initial deprotonation of the substrate to generate the strongly trans-labilizing nitrido group. This, together with the subsequent substitution of halide for methoxide and the concomitant change in the basicity of the nitrogen ligands with change in the metal's coordination sphere, rationalizes the somewhat anomalous formation of ammonia from *trans*-$[M(NH)X(dppe)_2]^+$ which occurs only under basic conditions and not in acid.

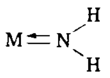
D. AMIDO COMPLEXES

Amido complexes have been known for many years, particularly for First Transition Period elements. These compounds are produced principally by deprotonation of coordinated ammonia. The involvement of the ammonia lone-pair electrons in metal ligand bonding considerably enhances the acidity of the ammonia hydrogens, such that they ionize. The pK_a of coordinated ammonia is a function of the metal, its oxidation state, and the coligands. Apparently small changes in these can lead to enormous changes in the pK_a. Thus, the conversion of $[Os(NH_3)_6]^{3+}$ to $[Os(NH_3)_6]^{4+}$ causes a change in pK_a from >15 to <0, and Os^{IV} ammines persist only in strong acid media (*51*).

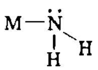
The consequences of this for model "building" are considerable. The conversion of an amido complex to an ammine may not be a thermodynamically favored process. Indeed, the "backward" conversion of ammonia to dinitrogen has been observed. Oxidation of $[Os(NH_3)_5(CO)]^{2+}$ with Ce^{IV} leads to $[Os(NH_3)_5(CO)]^{3+}$, and then to $[\{Os(NH_3)_4(CO)\}_2N_2]^{4+}$. In this context, intermediates such as $[Os(NH_3)_4(CO)N]^{2+}$ have been discussed (*48*). It is ironic that one of the aims of this osmium work had been essentially the converse of these observations, namely, the splitting of bridging dinitrogen to give nitrido complexes. Coordinated nitride may be electrophilic or nucleophilic and it seems reasonable to suppose that a metal must be relatively electron rich to mediate protonation right through to ammonia.

A low oxidation state of the metal would also tend to produce a coordination site at which ammonia would bind weakly and be displaced by the more strongly binding dinitrogen, thus facilitating the next stage of a nitrogen-fixation cycle. This substitution has indeed been observed on the $[Mo(N_2)(dppe)_2]$ site (*95*).

The amido ligand can bind to metals in a terminal position where, formally at least, it may be planar (**38**) or pyramidal (**39**), the latter being the more susceptible to protonation.



38



39

The extensive chemistry of amido complexes, and, more particularly, of alkylamido complexes, reveals that the planar form is almost invariably found, along with bridging amides (*221*). Much attention has been paid to the synthesis of metal amido complexes of early transition metals, lanthanides and actinides. The amido group, particularly where it is bulky, confers unusual low coordination numbers on the metals and can also produce materials with considerable kinetic stability toward attack by nucleophiles (*42, 67*). However, the relevance of this extensive and fascinating chemistry to nitrogen fixation is somewhat problematic.

X. Fixation in Aqueous Solution

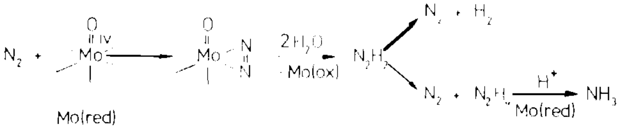
Whether or not water has access to the active site of nitrogenase is not yet clear. However, it would be of value to derive and understand aqueous systems capable of reducing dinitrogen, and at least two general systems are, in fact, known. How they work is still the subject of some controversy.

A. MOLYBDENUM-BASED SYSTEMS

G. N. Schrauzer has developed a series of molybdenum-based systems, which, in the presence of a reductant (generally $Na[BH_4]$) and a buffer (normally borate), convert dinitrogen to ammonia and acetylene to ethylene (and sometimes further to ethane). The general mechanism postulated some years ago is that shown in Scheme 18.

Schrauzer has shown that compounds derived from molybdenum(V)–cysteine derivatives also catalyze the reduction of dinitrogen. Subsidiary experiments confirm that the active species contain molybdenum(IV) rather than molybdenum(III), the latter tending to lead to the production of dihydrogen (*279*). Molybdenum isonitrile derivatives can also lead to dinitrogen-reduction catalysis (*252*). These systems are very difficult to analyze, and they often work best at low molybdenum concentrations ($<10^{-3}$ *M*). The intermediates cannot be isolated or detected directly. Their nature must be inferred on the basis of circumstantial evidence, and this is sometimes difficult to interpret.

The most efficient system of this type is obtained by the reduction of bovine serum albumin in the presence of molybdate. Apparently disulfide links in the peptide are broken and form thiolate groups which then bind molybdenum. In a borate buffer, this system will reduce dinitrogen and acetylene, although not using dithionite as an electron source. The turnover is similar to that of the iron–molybdenum cofactor (see Section XII), and dinitrogen reduction is inhibited by carbon monoxide and stimulated by ATP. The yield of ammonia is linearly dependent upon P_{N_2}, and the yield is also depressed in the presence of fumarate and, more surprisingly, succinate. It is calculated that the



SCHEME 18. Proposed mechanism for catalytic reduction of dinitrogen by "Mo(red)."

activity of these systems (on an atom per atom molybdenum basis) is about 5% of that of nitrogenase (*346, 347*).

More recently the stereochemically specific reduction of cyclopropene to cyclopropane and, in acid solution, to propylene has been demonstrated for the molybdothiol systems (*288*). This also parallels nitrogenase behavior.

It is postulated that all these systems proceed via the diazene mechanism in Scheme 18, although the evidence for side-on dinitrogen is not strong either in this system or in any of the dinitrogen complexes discussed elsewhere.

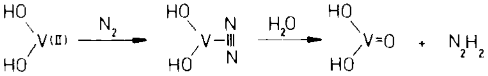
One of the most interesting systems developed recently is due to Schrauzer. Photolysis (mercury arc) of water chemisorbed on anatase yields 2 mol of dihydrogen per mole of dioxygen. In the presence of molecular dinitrogen, dioxygen is still generated, but the chemisorbed dinitrogen is reduced to ammonia and a little dinitrogen. The yields are as yet very small, but the potential may be considerable (*287*).

B. VANADIUM-BASED SYSTEMS

The $V(OH)_2/Mg(OH)_2$ system was discovered by Shilov and co-workers (*134*) but has also been investigated by others. In the heterogeneous vanadium systems there is clearly considerable disagreement as to yields and products, which are a function of reaction conditions that thus need to be defined exactly. The systems are gels in a strong alkaline environment, and the gels apparently age and change their properties. What is not at issue is that this system is one of the best nitrogen-fixing systems known.

Vanadium(II) hydroxide in strong alkali reduces water and generates dihydrogen. If magnesium hydroxide is incorporated by coprecipitation, dihydrogen evolution is depressed and the system is capable of converting dinitrogen to ammonia and hydrazine. Schrauzer's group (*359, 360*) have also studied this system and consider that the dinitrogen is first bound side-on to vanadium(II), and that reduction occurs as shown in Scheme 19.

The diazene then disproportionates to dinitrogen and hydrazine (or dinitrogen and dihydrogen) and the hydrazine may be reduced further



SCHEME 19. Proposed mechanism for the reduction of dinitrogen to ammonia (via diazene) by $V(OH)_2$.

$$2\,V_2^{2+} + N_2 \longrightarrow (V_2^{2+})N_2(V_2^{2+}) \xrightarrow{4H^+} 4V^{3+}(\text{or } 2V_2^{3+}) + N_2H_4$$

SCHEME 20. Proposed mechanism for the reduction of dinitrogen to hydrazine via a tetranuclear intermediate.

to ammonia. In support of this Schrauzer cites the inhibition of hydrazine formation by allyl alcohol, for the reduction of which dinitrogen is also necessary (*360*). Also cited are the inhibition by carbon monoxide and cyanide ion and the formation of ethylene stereochemically cis from acetylene (*359*), the production of vanadium(IV) in dilute systems (*289*), the dependence of the rate of hydrazine formation upon $(P_{N_2})^2$ (*289*), the influence of pH and concentration upon product (high dilution and pH favor hydrazine formation over ammonia) (*290*), and the kinetic isotope effects reported by Shilov *et al.* (*257a*).

In contrast Shilov and his group propose a very different mechanism (Scheme 20), which involves a bridging dinitrogen and four vanadium atoms, each acting as a one-electron reductant (contrasting to Schrauzer's proposal that vanadium acts as a two-electron reductant). The hydrazine may then be reduced to ammonia. On theoretical grounds Shilov considers that d^3 metal ions would make the best dinitrogen reducers in these binuclear systems (*44*), and there is ample evidence to support the formulation of vanadium(II) dinuclear species in aqueous solution. However, Shilov postulates and finds vanadium(III) products, which Schrauzer ascribed to a conproportionation (*289*) as shown in Eq. (78).

$$V^{II} + V^{IV} \longrightarrow 2V^{III}$$

The $V(OH)_2/Mg(OH)_2$ gel is believed to be a solid solution with a lattice similar to CdI_2, and the yield of hydrazine reaches a maximum with the magnesium to vanadium ratio in the range 1:5–10 (*133*). Shilov finds (1) no ^{14}N isotope effect corresponding to the Schrauzer mechanism, (2) that there is no evidence for vanadium(IV), (3) that the reduction of allyl alcohol is independent of, and competitive with, dinitrogen reduction, and (4) a different dependence on P_{N_2} from the square dependence claimed. In short, no evidence for diazene, but much more for a direct reduction to hydrazine (*136*).

It is difficult to understand why this divergence of observations has been found, though altitude (but not yet gravity!) has been suggested as a reason. These systems are heterogeneous and difficult to study.

The disputes are maintained in the studies on the reduction of dinitrogen to ammonia and hydrazine by $Fe(OH)_2$ at pH 9, claimed by

Schrauzer's group (*287*). Denisov has been unable (*137*) to repeat these observations.

Vanadium(II) homogeneous systems reduce dinitrogen to ammonia very cleanly and efficiently, and there is no dispute about them. The original discovery was that vanadium(II) plus polyphenols in homogeneous alkaline solution in a very restricted pH range reduces dinitrogen to ammonia according to Eq. (79) (*198*).

$$6V^{2+} + 6H_2O + N_2 \longrightarrow 6V^{3+} + 2NH_3 + 6OH^- \tag{79}$$

The reaction occurs best at pH 11. The conversion to ammonia is 7% at $P_{N_2} = 1$ atm and 60% at $P_{N_2} = 80$ atm, and pyrocatechol is the best phenol; phenol itself, resorcinol, and hydroquinone are inactive. More recently, it has been shown (*232*) that the stoichiometry is better represented as shown in Eq. (80). This is clearly similar to the currently accepted equation describing the stoichiometry of fixation by nitrogenase.

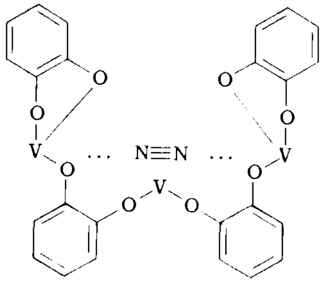
$$8V^{2+} + 8H^+ + N_2 \longrightarrow 8V^{3+} + 2NH_3 + H_2 \tag{80}$$

If a reacting solution is acid quenched then a small amount of hydrazine, derived probably from an intermediate reduction product, is formed. The rate of ammonia formation is linear in P_{N_2} and depends on the square of vanadium concentration, but the actual rate is a function of dioxygen pressure, metal contaminants, etc. The mechanism is believed to follow the pattern discussed above, with dinitrogen bound between two dinuclear pairs of vanadium(II) ions (*232, 233*), but the precise identity of the fixing species remains a mystery.

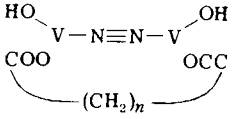
At least four vanadium(II) species have been identified in methanolic aqueous solutions of VCl_2 and catechol (*231*). One is identified as $Na_2[V(C_6H_4O_2)_2] \cdot 2H_2O$, and three contain three vanadium(II) ions on the basis of EPR evidence. One of the compounds is cyclic, and another, which binds dinitrogen, is open chain. This species reaches a maximum concentration when nitrogen fixation is fastest. These results modify the earlier picture to the sequence of reactions in Eq. (81).

$$\begin{tikzcd}
(V_3^{2+}) + N_2 \arrow[r, phantom, "\rightleftharpoons"] & (V_3^{2+})N_2 \arrow[r, "(V_3^{2+})"] & (4V^{3+} \cdots N_2^{4-}) \arrow[d, "V^{2+}"] & + & V_2^{2+} \arrow[d] \\
 & & 2NH_3 + 6V^{3+} & & H_2 + 2V^{3+}
\end{tikzcd} \qquad (81)$$

A preliminary picture of dinitrogen binding is suggested as shown in **40**.



40



41

Independent confirmation of the fixing activity of vanadium(II) stems from the observation that dicarboxylato–vanadium(II) complexes also reduce nitrogen (not very effectively). The putative intermediate is shown in **41** where $n = 5$ or 6 (*163a*).

The reduction is represented as shown in Eq. (82)

$$4V^{2+} + N_2 + 5H^+ \longrightarrow 4V^{3+} + N_2H_5^+ \qquad (82)$$

A second aqueous system due to Shilov uses titanium(III) and molybdenum(III) in aqueous alkali (heterogeneous) or in methanolic solutions when it can be homogeneous. Magnesium ions are a necessary component of the heterogeneous systems. This system is quite venerable in nitrogen-fixing terms, and the mechanism of fixation is not yet completely evaluated. The dry powder isolated from the heterogeneous system is capable of converting dinitrogen to hydrazine when resuspended in alkali, and the conductivity of the powder is of the "activation type." There is no long-range order in the solid (*135*). An ESCA investigation of the solid is claimed to be consistent with the presence of molybdenum(III) in the solid (*37*). This is perhaps open to question since the determination of metal oxidation states by ESCA is notoriously difficult. The importance is that Shilov *et al.* have always believed that molybdenum(III) is the nitrogen-binding agent whereas Schrauzer *et al.* are of the opinion that it is molybdenum(IV).

Molybdenum for fixation can be introduced in a variety of forms, for example, as the graphite–MoCl$_5$ complex (*343*), but molybdenum is not actually necessary for fixation. A mixture of titanium(III) and magnesium ions, when made sufficiently alkaline, produces hydrazine in low yield (0.25% based upon titanium), but only above 140°C, and the reaction is not catalytic (*214*).

Reduction by homogeneous solutions containing molybdenum(III) and titanium(III) in methanol can be mediated by sodium amalgam. The reactions proceed at 20°C, and both hydrazine and ammonia are produced, apparently in parallel reactions (*257*). The Ti/Mo ratio is 10 : 1 and the results are consistent with electron transfer from mercury to titanium to molybdenum to N_2, with the dinitrogen bridging two molybdenum atoms. The parallel reactions are explained by two different kinds of binding site (*257*).

Genuinely catalytic systems were obtained using $MoCl_5$ and sodium amalgam in methanol in a carefully controlled pH range and in the presence of magnesium ions. The yield of hydrazine is linear in P_{N_2} up to 120 atm and the turnover was at best about 4 mol of hydrazine per mole of molybdenum. The amalgam can be replaced by a mercury cathode in a divided cell (*156*), but the systems gradually lose their fixing ability as hydroxide accumulates and precipitation occurs. This can be overcome by adding buffers such as guanidine hydrochloride, and the resultant system reduces dinitrogen to hydrazine with a current efficiency of ~6% at $P_{N_2} = 30$ atm (*217*).

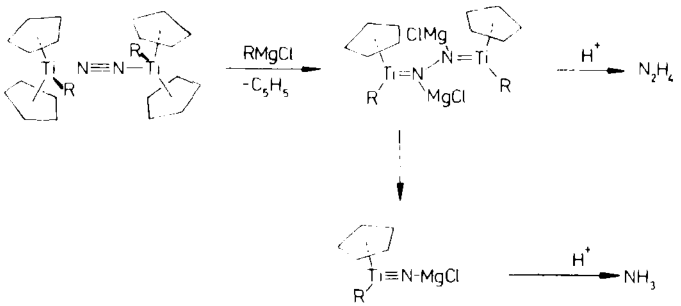
The route generally proposed for these reductions is shown in Eq. (83).

$$2Mo^{III} \longrightarrow Mo^{III}{-}N{\equiv}N{-}Mo^{III} \xrightarrow{4H^+} 2Mo^{V} + N_2H_4 \qquad (83)$$

XI. Other Nitrogen-Fixing Systems

In this section, nonaqueous nitrogen-fixing systems will be discussed. They are all related to the systems described first by Volpin in 1965, namely, a transition metal compound, plus an organometallic reducing agent such as a Grignard reagent, in a nonaqueous solvent such as diethylether. Exposure of such a mixture to dinitrogen causes fixation of the nitrogen on some low-oxidation-state species, the hydrolysis of which generates ammonia. There is probably no single mechanism valid for all systems, but two general classes of mechanism have been propounded, the nitride mechanism, which postulates a reaction of dinitrogen with a metal species to form a nitrido complex, and a bridging mechanism, which postulates dinitrogen binding between two metal atoms. Neither is unequivocally established and recent results have not clarified the situation.

The compound $[\{(\eta^5\text{-}C_5H_5)_2TiCl\}_2]$ reacts with Grignard reagents such as $(CH_3)_3CCH_2MgBr$ to yield $[(\eta^5\text{-}C_5H_5)_2TiCH_2C(CH_3)_3]$ which binds dinitrogen at −90°C (and loses it again at −60°C). The resulting complex $[\{(\eta^5\text{-}C_5H_5)_2TiCH_2C(CH_3)_3\}_2N_2]$ is a bridging dinitrogen complex (*337*), rather like several others $[\{(\eta^5\text{-}C_5H_5)_2TiR\}_2N_2]$ already known. It reacts with more reducing agent, for example, $Na^+C_8H_8^-$ or



SCHEME 21. Ammonia-forming pathway for reaction of $[\{(\eta^5\text{-}C_5H_5)_2TiR\}_2N_2]$.

*i*PrMgCl, as shown in Scheme 21. These results cast some doubt on the details of an alternative route suggested earlier, in which the two cyclopentadienyl residues on the titanium are retained. They also suggest that the bridging and the nitrido mechanisms are not mutually exclusive.

Bridging dinitrogen has also been postulated in the system $CrCl_2$–Mg–$Ph_2PCH_2CH_2PPh_2$–THF–N_2 which generates paramagnetic $[\{Cr(Ph_2PCH_2CH_2PPh_2)_2\}_2N_2]$. In the absence of the diphosphine, the product of the reduction analyzes for $Cr_2N_2Mg_4Cl_4(THF)_5$. Both products hydrolyze to give ammonia and hydrazine, but substantially more of each in the latter case (*315*).

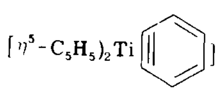
Bridging dinitrogen complexes can be obtained from a terminal dinitrogen ligand by the addition of Lewis acids. An unusual example concerns the reaction of $[CoH(N_2)(PR_3)_3]$ with $MgEt_2$ which yields $[CoN_2(PR_3)_3Mg(THF)_2]$ (PR_3 = PPh_3 or PEt_2Ph only). This reacts with sulfuric acid to give hydrazine (0.29 mol per Co), ammonia (a trace), dinitrogen (0.56 mol per Co), and dihydrogen (0.52 mol per Co). The protonation presumably involves bridging dinitrogen (*248*).

In one other system, however, the situation is less clear than it was believed to be. The kinetics of fixation of dinitrogen in the system $FeCl_3$–LiPh–N_2 (which gives hydrazine upon hydrolysis) have been interpreted in terms of a binuclear iron(I) species bridged by dinitrogen. Upon protonation, this could yield up to four electrons per dinitrogen (*223*). However, it has since been shown that reaction of $FeCl_3$ and an excess of LiC_8H_7 in ether at −30°C forms a material $Li_2[Fe(C_8H_7)_4] \cdot 2Et_2O$. This does not react with dinitrogen, but the tetrahedral species can be reduced by LiPr to yield a species that does bind dinitrogen, and that yields hydrazine (13% yield based upon iron) when solvolyzed with acid. The amount of dinitrogen bound is about 1 mol per Fe (*10*). The crystal structure of a reduced species $Li_4[FePh_4] \cdot$

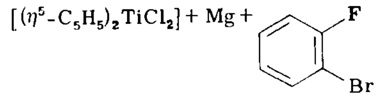
$4Et_2O$, which can bind dinitrogen (but it is not yet known how), has been determined. It is square planar (*10*). Consequently, the binuclear model deduced from the kinetics is far from certain.

The investigation of more typical "nitriding" systems VCl_3, $CrCl_3$, or $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ with $Li(C_8H_8)$ or $Li_2(C_8H_8)$ suggests that reduction to vanadium(I) or vanadium(0) is necessary before fixation can occur (*20*) [evidence discussed above in aqueous systems points to vanadium(II)]. A large excess of the naphthalene ion is necessary, and the lithium also fixes nitrogen in this system. Another "nitriding" system, $AlCl_3$–$Ti(i PrO)_4$–glyme (glyme = 1,2-dimethoxyethane), originally discovered many years ago by Van Tamelen to be suitable for electrolytic reduction, can be made to operate by photoactivation by *p*-gallium phosphide cathode, with a sacrificial aluminium anode. Yields of fixed nitrogen, after hydrolysis, are "several per cent" (*141*).

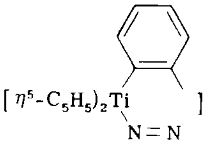
One other system shows potential for the production of ammonia and amines from dinitrogen. It was shown several years ago (*155*) that $[(\eta^5\text{-}C_5H_5)_2TiPh_2]$ decomposes thermally via a benzyne intermediate formulated as **42**. Such species fix nitrogen. The benzyne complex generated by thermal decomposition as above, or from the reaction of **43** with dinitrogen to form a species formulated as **44**. A diphenylacetylene analog has been completely characterized. Reduction and hydrolysis produce small yields of aniline and ammonia (*24, 344*). In fact, there is evidence that titanocene itself can react with aromatics and dinitrogen to generate amines, after hydrolysis. In a similar system, $[(\eta^5\text{-}C_5H_5)_2Ti(C_6H_4CH_3\text{-}p)_2]$ reacts with a 10-fold excess of a reducing metal (Li, Na, or Mg) at 20°C in diethyl ether under dinitrogen (100 atm) to yield *p*-toluidine and ammonia. In the case of the phenyl derivatives, the corresponding yields are aniline, 0.08 mol per Ti, and ammonia, 1.1 mol per Ti. The data are generally consistent with a benzyne mechanism (*313*).



42



43



44

The area of nonaqueous fixation has been reviewed in detail (*344*).

XII. A Summary of the Characteristics of Biological Nitrogen Fixation

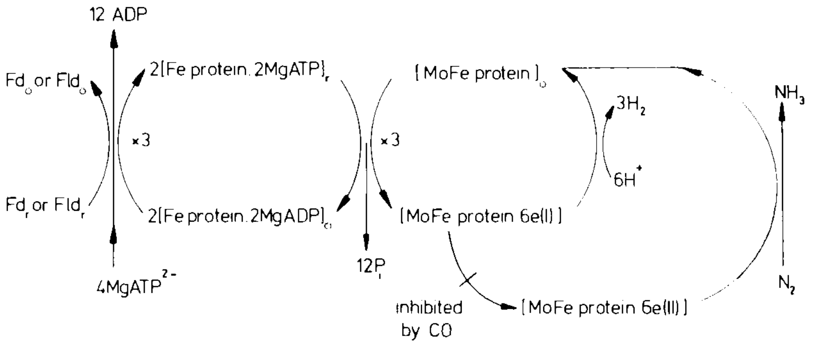
This section is not intended to supply a detailed review of biological nitrogen fixation. For this the reader is referred elsewhere (*316, 230a*). Its aim is to supply a list of those properties of the biological systems that ought to be considered when constructing a model for nitrogenase, based upon the chemical data discussed in the foregoing sections of this article.

All nitrogenases known to date consist of two protein components. (1) A dinitrogen-binding protein containing iron (24–32 atoms), molybdenum (2 atoms), and inorganic sulfur (~28 atoms). This component contains four subunits and has a molecular weight of 220,000–245,000 (depending upon the source). (2) An iron-containing protein which acts as the electron-carrying protein and contains an Fe_4S_4 cluster (*191*). This component consists of two identical subunits, and has a molecular weight of 57,000–73,000. At neutral pH this protein is overall negatively charged, and binds MgATP and MgADP at between two and four binding sites, but only two of these sites are involved in nitrogenase catalysis. The binding of MgATP or MgADP induce different conformational changes in the protein. The binding of MgATP has the effect of rendering the iron protein more oxygen sensitive and of making E_m (the midpoint potential) 120 mV more negative.

A cofactor can be extracted from the iron–molybdenum protein, using *N*-methylformamide. This cofactor (called FeMoCo) has many spectroscopic properties in common with the native protein, especially the EXAFS spectrum, and activates the inactive large protein derived from *Azobacter vinelandii* UW45 mutant which cannot incorporate molybdenum. The cofactor contains no protein or peptide, but does contain molybdenum, iron, and sulfur in atomic ratios of 1 : 6–8 : 4–9. It is believed to contain the dinitrogen-binding site (presumably molybdenum) but there is no definitive proof of this.

The structure of FeMoCo (and the dinitrogen-binding protein) is unknown. The environment of the metals is constituted primarily of sulfur atoms, but the interpretation of the X-ray absorption fine structure (EXAFS) data on both the cofactor and protein (*117–119*) are contentious. It is not known whether the system in any specific part is aqueous or anhydrous, but oxygen destroys the activity. The electron-transfer pathway in the functioning nitrogenase is believed to be as shown in Scheme 22.

The transfer of electrons between proteins is believed to be in single-electron steps and is endoergic, requiring probably three ATP molecules to be hydrolyzed to accomplish the transfer of each pair of electrons.



SCHEME 22. Known reactions during the turnover of nitrogenase (subscript o and r refer to oxidized and reduced forms, respectively; P_i refers to inorganic phosphate).

In the absence of substrate (other than the proton) the final product of electron transfer is dihydrogen. In the presence of dinitrogen, electrons are diverted into the substrate, but dihydrogen is always a product. The limiting stoichiometry for dinitrogen reduction appears to be as shown in Eq. (84).

$$N_2 + 8H^+ + 8e \longrightarrow 2NH_3 + H_2 \tag{84}$$

Carbon monoxide inhibits the system to dinitrogen fixation but not to dihydrogen evolution. If dinitrogen fixation is undertaken in the presence of $^2H_2$ then exchange occurs as shown in Eq. (85), but no ^2H appears in solution.

$$2\,^1H^+ + 2e + {}^2H_2 \longrightarrow 2\,^1H^2H \tag{85}$$

Although dihydrogen inhibits dinitrogen fixation the participation of dinitrogen is necessary for all but about 5% of this $^1H^2H$ production.

There is little definitive information regarding the chemical course of biological nitrogen fixation and it is far from clear whether reduction proceeds via diazene and hydrazine to ammonia or takes some other route. Free hydrazine is reduced to ammonia by nitrogenase, but it is a relatively poor substrate (*54*). The kinetics of this process exclude free hydrazine as an intermediate between dinitrogen and ammonia (*314, 230a*). On the other hand, bound hydrazine cannot be excluded. Quenching of the reacting nitrogenase systems with acid or alkali produces hydrazine, and the source of the hydrazine has been identified as a nitrogen–hydride intermediate, possibly a hydrazido(2−) species such as those isolated from the protonation of coordinated dinitrogen (*314*). On the other hand, studies of the reduction of hydrazine and of $^1H^2H$ formation (*54*) suggest the presence of another intermediate at the hydrazine level, with different properties. The relationship of the two intermediates is not clear.

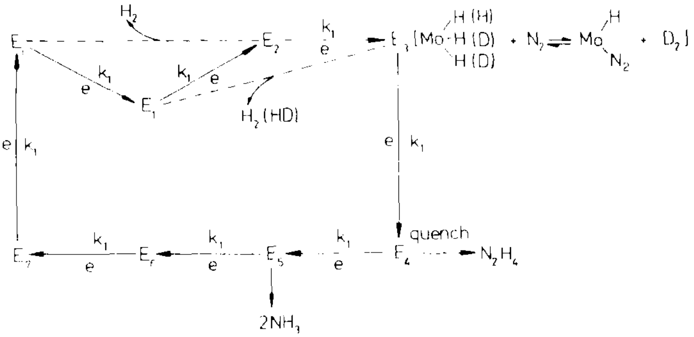
As well as reducing protons and dinitrogen, nitrogenase can reduce a variety of other substrates. The classical example is acetylene, which is reduced stereospecifically (in ^2H_2O) to *cis*-$C_2{}^2H_2{}^1H_2$, and with rather more ease than dinitrogen (with which it can be a competitor). In general olefins are not reduced by nitrogenase, but, exceptionally, *cyclo*propene is reduce stereospecifically cyclo to give cyclopropane, and also, depending upon the pH, propane (*245, 246*).

Other substrates reduced by nitrogenase include azide (which gives ammonia, dinitrogen, and hydrazine) (*151*), diazomethane (ammonia and undisclosed products), nitrous oxide (dinitrogen and water), hydrocyanic acid (methane and ammonia), cyanide (methane and ammonia), methyl isocyanide, and other organoisonitriles (methylamine, methane, ammonia, ethane, and other higher hydrocarbons).

XIII. Biological Mechanisms

With the present state of the art, the biological models for the functioning of nitrogenase generally do not give much information at an atomic and molecular level; they are generally more concerned with the overall reactions of the proteins. It is generally agreed that Scheme 22 (*251*) accommodates most of the observations at a gross level for the functioning of nitrogenase. This, however, gives little information concerning the molecular transformations involved.

By far the most comprehensive mechanism for biological nitrogen fixation is that shown in Scheme 23 (*330*). A study of pre-steady-state



SCHEME 23. Mechanism for the reduction of dinitrogen by nitrogenase.

kinetics for ammonia production, hydrazine production, and dihydrogen evolution yields results that are explained in terms of this scheme. The nitrogen-fixing cycle consists of eight processes of equal rate constant (~5 sec^{-1}) between eight states of the enzyme designated E_0, $E_2 \cdots E_7$. The arrows joining the different enzyme states represent three elementary processes: association of the two protein components, intramolecular electron transfer between the components, and (rate-limiting) protein dissociation. The salient features of this mechanism are listed below.

1. The fixation reaction involves eight single electron-transfer reactions, consistent with the apparent limiting stoichiometry [Eq. (85)]. However, this does not exclude the possibility that the electrons are transferred to dinitrogen within the enzymes in groups of two or more.

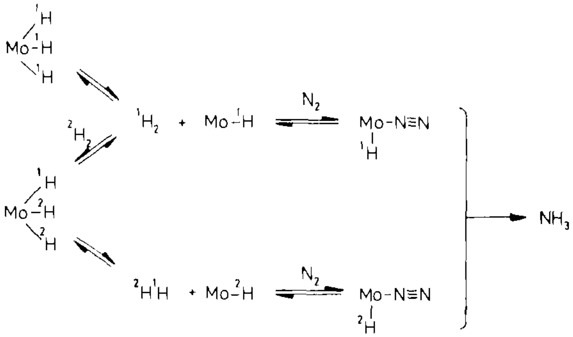
2. Dihydrogen is evolved prior to reduction of dinitrogen, as exemplified by transition metal complexes [Eqs. (86) and (87)].

$$[\mathrm{CoH_3(PPh_3)_3}] + \mathrm{N_2} \longrightarrow [\mathrm{CoH(N_2)(PPh_3)_3}] + \mathrm{H_2} \qquad (86)$$

$$[\mathrm{MoH_4(dppe)_2}] + 2\mathrm{N_2} \longrightarrow [\mathrm{Mo(N_2)_2(dppe)_2}] + 2\mathrm{H_2} \qquad (87)$$

The exchange of dinitrogen and dihydrogen on a trihydride metal site can account for $^1H^2H$ generation (*72a*) (Scheme 24). This particular proposal has been criticized because it does not predict the stoichiometry of $^1H^2H$ formation that has actually been observed with the enzyme (*54*).

3. After five electrons have been transferred (at E_4), then the intermediate state (Mo=NNH$_2$) (see Section VI,B) is formed. This does not,



SCHEME 24. Proposed trihydride molybdenum site of nitrogenase and the reactions resulting in $^1H^2H$ formation.

however, necessarily imply that *only* five electrons have been consumed. More likely six or four have been used at this stage, and the system has become relatively oxidized or reduced. It certainly becomes oxidized as the ammonia is generated.

4. If it is assumed that each state E_n has an equal probability, then the amount of hydrazine produced suggests that the hydrazido(2−) intermediate concentration corresponds to one-eighth the total molybdenum content of the enzyme. This is consistent with one dinitrogen bound per molybdenum, so that dinitrogen does not bridge between the two molybdenum atoms present in the large protein (*329*).

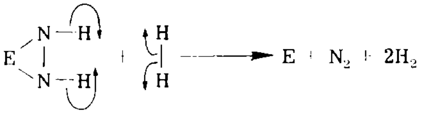
This mechanism is not the only model for nitrogenase function. For example, an analysis of ${}^1H^2H$ formation during turnover of the enzyme has led to a rather different explanation of the reduction pathway, as shown in Eq. (88) (*54*).

$$E + N_2 + 2H^+ + 2e \longrightarrow E{-}N_2H_2 \tag{88}$$

In this equation E represents the active site of the enzyme and $E{-}N_2H_2$ is formulated as a bound diazene, presumably side-on. The next stage is postulated to be formation of a hydrazine-level species, but reaction (89) intervenes in the presence of dihydrogen.

$$E{-}N_2H_2 + H_2 \longrightarrow E + N_2 + 2H_2 \tag{89}$$

Reaction (90) is envisaged in the following terms:



(90)

The details of dinitrogen interaction with E have never been characterized, but the way in which ${}^1H^2H$ could form is clear, and the stoichiometry for this reaction predicted from the model is consistent with observations on the enzyme. The overall reaction, which requires dinitrogen as a "catalyst," is shown in Eq. (91).

$$2{}^1H^+ + {}^2H_2 + 2e \longrightarrow 2{}^1H^2H \tag{91}$$

These two models are the principal attempts to explain nitrogenase function in atomic and molecular terms. There are other suggestions in the biological literature, of course, involving bridging dinitrogen, protonation of dinitrogen by thiolates, etc. They remain hypotheses with no significant empirical basis.

XIV. Conclusions

Despite the many attempts that have been made to interpret the data on the enzyme system in terms of the chemistry, there is no consensus. There are several reasons for this. The major reason is a result of the perverse nature of the coordinated dinitrogen molecule. It became clear, soon after the preparation of the first dinitrogen complex, that merely coordinating dinitrogen to a metal does not necessarily activate it sufficiently for reduction to ammonia or hydrazine. Proton attack at the metal in preference to the dinitrogen ligand can occur, resulting in a stable dinitrogen hydrido complex or labilization of the dinitrogen and its eventual expulsion from the coordination sphere. Even in systems such as *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) (Section VI,D,2) it is clear that, depending upon the conditions, protonation can occur at the metal or dinitrogen. Despite the great advances made in the chemistry of nitrogen fixation over the last two decades we are still far from being able to design a metal site (a metal with its coligands) that will bind dinitrogen and activate it toward, for instance, protic attack.

In this section we attempt to summarize objectively what can clearly be stated concerning the reduction of dinitrogen by metal-based systems. As has been stated earlier, it is sometimes necessary to extrapolate information from analogous complexes containing alkyl or aryl substituents, because of the elusive nature of some of the intermediates.

Dinitrogen has been shown to bind to a variety of sites, although a major goal in this area, the binding of dinitrogen to a metal in an environment of sulfur atoms, has yet to be achieved. This is the only step at which dinitrogen and dihydrogen can conceivably compete, and is one position where the $^1H-^2H$ interaction to form $^1H^2H$ from $^2H_2$ can occur. When dinitrogen binds to a metal it may be end-on or bridged. There is no evidence that is completely unequivocal or that is not circumstantial to suggest that any other mode of binding is likely.

Protonation of coordinated dinitrogen can occur in either end-on or bridging forms. There is no obvious advantage in bridging to achieve activation, at least empirically whatever theory may say, and on the basis of Occam's Razor we prefer the single-metal model for the active site of nitrogenase. Further, bridging, by reducing the negative charge upon what would otherwise be an exo nitrogen, might even inhibit protonation. The advantage of a bridging dinitrogen would appear to be that the electron requirement could be shared between two metal atoms, thus reducing the required range of metal oxidation states.

The first site of protonation in a dinitrogen complex, based on mechanistic studies of complexes, must be the dinitrogen itself, yielding the diazenido species (N_2H). If protonation occurs at the metal then reaction proceeds no further, or results in the loss of coordinated dinitrogen. The formal insertion of dinitrogen into a metal–hydride bond (a popular proposal in the early chemical nitrogen-fixation literature) is unknown.

The first detectable intermediate in both the reactions of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) and the enzyme nitrogenase is the hydrazido(2−) ligand, formed formally by the addition of a proton to the diazenido ligand, although a less direct pathway may be operative. Perhaps, surprisingly, there is no unequivocable evidence that either free or coordinated diazene is present during the nitrogen-fixation process, and certainly there is no known reaction in which a coordinated diazene proceeds stoichiometrically to ammonia or hydrazine.

In the subsequent reactions of hydrazido(2−) complexes, the picture becomes much more woolly, and it is only relatively recently that authenticated complexes containing the hydrazido(1−) ligands [formed formally by protonation of a hydrazido(2−) species] have been isolated. There is considerable structural evidence that hydrazide(1−) prefers a side-on mode of bonding to metals where this is feasible.

Protonation of hydrazido(2−) complexes can occur at the metal and these hydrido–hydrazido(2−) complexes are intermediates on at least one hydrazine-forming pathway.

The reactions of $[Mo(NNH_2)X_2(P)_3]$ (X = halide, P = monotertiary phosphine) on the pathway yielding ammonia apparently involves a bimolecular reaction which avoids the hydrazido(1−) stage completely. This observation may be related to the presence of two molybdenum atoms in the enzyme. It could also be the reason for the stoichiometry of the natural process [Eq. (84)].

The hydrazido(2−) species require four electrons each to form, but each dinitrogen overall requires only six electrons for its reduction. Consequently two electrons are rejected by evolution of dihydrogen.

The conversion of hydrazine (2 mol) to ammonia (2 mol), dihydrogen (1 mol), and dinitrogen (1 mol) by a heterogeneous catalyst in the presence of light has recently been discovered (*263a*). The stoichiometry is clearly reminiscent of Eq. (84), but the reaction does not involve simple disproportionation of hydrazine and its relevance to nitrogenase is an open question.

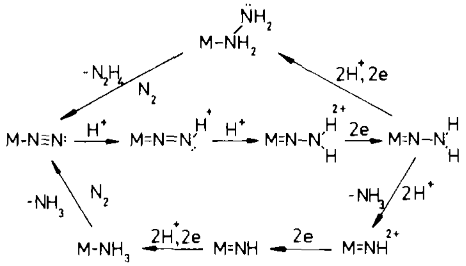
Mechanistically the stage at which nitrogen–nitrogen cleavage can occur is the most poorly understood; it is only recently that this cleavage has been demonstrated unambiguously on a transition metal complex.

Subsequent formation of ammonia from nitrido and imido ligands under a variety of conditions has been demonstrated.

The chemical protonation process probably involves two-electron steps. The kind of electron transfer involved in any disproportionation step is completely unknown. The model enzyme mechanism suggests one-electron steps, but in fact says nothing about how the electrons are used, only about how they are supplied. No current model satisfactorily explains all the features of nitrogenase function. $^1H^2H$ formation during the turnover of nitrogenase under $^2H_2$ has been explained by a model (*72a*) which requires the dinitrogen-binding site to be a potential trihydride as shown in Scheme 24. This has been taken up and significantly elaborated in the model for nitrogenase function illustrated in Scheme 23.

However with the chemical demonstration that diazenido and hydrazido(2−) ligands can "insert" into metal–hydride bonds, the formation of $^1H^2H$ as a consequence of exchange $^2H_2$ with a metal hydride at one of these intermediate stages remains a possibility. This would explain why the exchange is accelerated in the presence of dinitrogen.

The sequence of reactions by which dinitrogen is reduced on a metal is probably that outlined in Scheme 25. This sequence is based on the accumulated data of the chemical systems and is similar to that of Scheme 1, with the important distinction that there is chemical precedence for all the steps shown and others in addition. It seems likely that the mechanism of function of nitrogenase will possess the general features of Schemes 23, 24, and 25 outlined in this article.



SCHEME 25. Reactions for the stepwise reduction of dinitrogen to ammonia or hydrazine.

REFERENCES

1. Abel, E. W., Burton, C. A., Churchill, M. R., and Lin K.-K. G., *J. Chem. Soc. Chem. Commun.* 268 (1974).
2. Ahlrichs, R., and Staemmler, V., *Chem. Phys. Lett.* **37,** 77 (1976).
3. Alster, J., and Burnelle, L. A., *J. Am. Chem. Soc.* **89,** 1261 (1967).
4. Anderson, S. N., Fakeley, M. E., Richards, R. L., and Chatt, J., *J. Chem. Soc. Dalton Trans.* 1973 (1981).
5. Anderson, S. N., Hughes, D. L., and Richards, R. L., *J. Chem. Soc. Chem. Commun.* 1291 (1982).
6. Andrews, M. A., and Kaesz, H. D., *J. Am. Chem. Soc.* **99,** 6763 (1977).
7. Archer, L. J., and George, T. A., *Inorg. Chim. Acta* **44,** L129 (1980).
8. Archer, L. J., and George, T. A., *Inorg. Chem.* **18,** 2079 (1979).
9. Arnett, E. M., *Prog. Phys. Org. Chem.* **1,** 223 (1963).
10. Bagenova, T. A., Gruselle, M., Le Ng, G., Shilov, A. E., and Shilova, A. K., *Kinet. Katal.* **23,** 246 (1982).
11. Bagenova, T. A., Shilova, A. K., Deschamps, E., Gruselle, M., Leny, G., and Tchoubar, B., *J. Organomet. Chem.* **222,** C1 (1981).
12. Baird, N. C., and Swenson, J. R., *Can. J. Chem.* **51,** 3097 (1973).
13. Balch, A. L., Barke, A., and Peiradis, D., *J. Am. Chem. Soc.* **92,** 428 (1970).
14. Barrientos-Penna, C. F., Einstein, F. W. B., Jones, T., and Sutton, D., *Inorg. Chem.* **21,** 2578 (1982).
15. Barrientos-Penna, C. F., Einstein, F. W. B., Sutton, D., and Willis, D., *Inorg. Chem.* **19,** 2740 (1980).
16. Barrientos-Penna, C. F., and Sutton, D., *J. Chem. Soc. Chem. Commun.* 111 (1980).
17. Battistoni, C., Furlani, C., Mattogno, G., and Tom, G., *Inorg. Chim. Acta* **21,** L25 (1977).
18. Baumann, J. A., and George, T. A., *J. Am. Chem. Soc.* **102,** 6153 (1980).
19. Baxendale, J. H., and Mulazzani, Q. G., *J. Inorg. Nucl. Chem.* **33,** 823 (1971).
20. Beelen, T. P. M., and Rummens, C. P. J., *Rec., J. R. Neth. Chem. Soc.* **98,** 8 (1979).
21. Bellon, P. L., Caglio, G., Manassero, M., and Sansoni, M., *J. Chem. Soc. Dalton Trans.* 897 (1974).
22. Ben-Shoshan, R., Chatt, J., Leigh, G. J., and Hussein, W., *J. Chem. Soc. Dalton Trans.* 771 (1980).
23. Bercaw, J. E., personal communication.
24. Berkovitch, E. G., Shur, V. B., Volpin, M. E., Lorenz, B., Rummel, S., and Wahren, M., *Chem. Ber.* **113,** 70 (1980).
25. Bevan, P. C., Chatt, J., Dilworth, J. R., Henderson, R. A., and Leigh, G. J., *J. Chem. Soc. Dalton Trans.* 821 (1982).
26. Bevan, P. C., Chatt, J., Head, R. A., Hitchcock, P. B., and Leigh, G. J., *J. Chem. Soc. Chem. Commun.* 509 (1976).
27. Bianco, V. D., Doronzo, S., and Gallo, N., *J. Organomet. Chem.* **124,** C43 (1977).
28. Bishop, M. W., Butler, G., Chatt, J., Dilworth, J. R., and Leigh, G. J., *J. Chem. Soc. Dalton Trans.* 1843 (1979).
29. Bishop, M. W., Chatt, J., and Dilworth, J. R., *J. Organomet. Chem.* **73,** C59 (1974).
30. Bishop, M. W., Chatt, J., Dilworth, J. R., Hursthouse, M. B., Jayaweera, S. A. A., and Quick, A., *J. Chem. Soc. Dalton Trans.* 914 (1979).
31. Bishop, M. W., Chatt, J., Dilworth, J. R., Hursthouse, M. B., and Motevalli, M., *J. Less Common Metals* **54,** 487, (1977).

32. Bishop, M. W., Chatt, J., and Dilworth, J. R., unpublished results reported in Ref. (*143*).

33. Boca, R., and Pelikan, P., *J. Mol. Catal.* **14,** 121 (1982).

34. Boca, R., Pelikan, P., and Haring, M., *J. Mol. Catal.* **11,** 41 (1981).

35. Boem, J. R., Balch, A. L., and Enemark, J. H., *J. Am. Chem. Soc.* **97,** 501 (1975).

36. Borodko, Y. G., Broitman, M. O., Kachapina, L. N., Shilov, A. E., and Ukhin, L. Y., *J. Chem. Soc. Chem. Commun.* 1185 (1971).

37. Borodko, Y. G., Denisov, N. T., Ioffe, M. S., Korosteleva, A. I., and Moravskaya, T. M., *Dokl. Akad. Nauk SSSR* **238,** 596 (1978).

38. Borodko, Y. G., Ivleva, I. N., Kachapina, L. N., Salienko, S. I., Shilova, A. K., and Shilov, A. E., *J. Chem. Soc. Chem. Commun.* 1178 (1972).

38a. Bossard, G. E., and George, T. A., *Inorg. Chim. Acta Lett.* **53,** L241 (1981).

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

40. Bossard, G. E., George, T. A., Howell, D. B., and Lester, R. K., *Proc. Int. Conf. Chem. Uses Molybd. 4th, 1982.*

41. Bowden, W. L., Little, W. F., and Meyer, T. J., *J. Am. Chem. Soc.* **95,** 5084 (1973).

42. Bradley, D. C., and Chisholm, M. H., *J. Chem. Soc. A* 2741 (1971).

43. Braga, M., Larsson, S., and Leite, J. R., *J. Am. Chem. Soc.* **101,** 3867 (1979).

44. Brant, P., and Feltham, R. D., *J. Less Common Metals* **54,** 81 (1977).

45. Brant, P., and Feltham, R. D., *J. Organomet. Chem.* **120,** C53 (1976).

45a. Brizard. L., *C. R. Acad. Sci.* **123,** 182 (1896); Werner, A., and Dinklage, K., *Chem. Ber.* **34,** 2698 (1901).

46. Brown, I. D., and Dunitz, J., *Acta Crystallogr.* **13,** 28 (1960).

47. Buchler, J. W., and Folz, M., *Z. Naturforsch.* **32b,** 1439 (1977).

48. Buchler, J. W., and Smith, P. D., *Angew. Chem. Int. Ed. Engl.* **13,** 745 (1974).

49. Buhr, J. D., and Taube, H., *Inorg. Chem.* **18,** 2208 (1979).

50. Buhr, J. D., and Taube, H., *Inorg. Chem.* **19,** 2425 (1980).

51. Buhr, J. D., Winkler, J. R., and Taube, H., *Inorg. Chem.* **19,** 2416 (1980).

52. Burdett, J. K., Downs, A. J., Gaskill, G. P., Graham, M. A., Turner, J. J., and Turner, R. F., *Inorg. Chem.* **17,** 523 (1978).

53. Burdett, J. K., Grzybowski, J. M., Perutz, R. N., Poliakoff, M., Turner, J. J., and Turner, R. F., *Inorg. Chem.* **17,** 147 (1978).

54. Burgess, B. K., Wherland, S., Steifel, E. I., and Newton, W. E., "Molybdenum Chemistry of Biological Significance" (W. E. Newton and S. Otsuka, eds.), p. 73 Plenum, London, 1980; Burgess, B. K., Wherland, S., Newton, W. E., and Stiefel, E. I., *Biochemistry* **20,** 5140 (1981).

55. Burt, R. J., Leigh, G. J., and Hughes, D. L., *J. Chem. Soc. Dalton Trans.* 793 (1981).

56. Busby, R., Klotzbücher, W., and Ozin, G. A., *Inorg. Chem.* **16,** 822 (1977).

57. Busby, D. C., George, T. A., Iske, S. D. A., and Wagner, S. D., *Inorg. Chem.* **20,** 22 (1981).

58. Busby, D. C., and George, T. A., *J. Organomet. Chem.* **118,** C16 (1976).

59. Busby, D. C., and George, T. A., *Inorg. Chem.* **18,** 3164 (1979).

60. Busetto, C. D., Alfonso, A., Maspero, F., Perego, G., and Zazzetta, A., *J. Chem. Soc. Dalton Trans.* 1828 (1977).

61. Cabelli, D. E., and Beilski, B. H. J., *J. Phys. Chem.* **86,** 2072 (1982).

62. Caglio, G., and Angoletta, M., *Gazzetta* **102,** 462 (1972).

63. Caruana, A., and Kisch, H., *Angew. Chem. Int. Ed. Engl.* **18,** 328 (1979).

64. Carmona, E., Martin, J. M., Poveda, M. L., Atwood, J. L., Rogers, R. D., and Wilkinson, G., *Angew. Chem. Suppl.* 1116 (1982).

65. Carroll, J. A., Cobbledick, R. E., Einstein, F. W. B., Farrell, N., Sutton, D., and Vogel, P. L., *Inorg. Chem.* **16,** 2462 (1977).

66. Carroll, J. A., and Sutton, D., *Inorg. Chem.* **19,** 3137 (1980).

67. Carroll, J. A., Sutton, D., Cowie, M., and Gauthier, M. D., *J. Chem. Soc. Chem. Commun.* 1058 (1979).

68. Carroll, W. E., and Lalor, F. J., *J. Chem. Soc. Dalton Trans.* 1754 (1973).

68a. Carter, B. J., Bercaw, J. E., and Gray, H. B., *J. Organomet. Chem.* **181,** 105 (1979).

69. Casewit, C. J., and Goddard, W. A., *J. Am. Chem. Soc.* **102,** 4057 (1980).

70. Cenini, S., Porta, F., and Pizzotti, M., *Inorg. Nucl. Chem. Lett.* **10,** 983 (1974).

71. Cenini, S., Ugo, R., and LaMonica, G., *J. Chem. Soc. A* 3441 (1971).

72. Chatt, J., *J. Organomet. Chem.* **100,** 17 (1975).

72a. Chatt, J., *Proc. Phytochem. Soc. Eur. Symp., 18th, 1980* p. 1.

73. Chatt, J., Crabtree, R. H., Jeffrey, E. A., and Richards, R. L., *J. Chem. Soc. Dalton Trans.* 1167 (1973).

74. Chatt, J., Crichton, B. A. L., Dilworth, J. R., Dahlstrom, P., Gutkoska, R., and Zubieta, J., *Inorg. Chem.* **21,** 2383 (1982).

75. Chatt, J., Crichton, B. A. L., Dilworth, J. R., Dahlstrom, P., and Zubieta, J., *J. Chem. Soc. Dalton Trans.* 1041 (1982).

76. Chatt, J., Diamantis, A. A., Heath, G. A., Hooper, N. E., and Leigh, G. J., *J. Chem. Soc. Dalton Trans.* 688 (1977).

77. Chatt, J., and Dilworth, J. R., *J. Less Common Metals* 36 (1974).

77a. Chatt, J., and Dilworth, J. R., *J. Chem. Soc. Chem. Commun.* 517 (1974); Chatt, J., and Dilworth, J. R., *J. Chem. Soc. Chem. Commun.* 983 (1975).

78. Chatt, J., Dilworth, J. R., Dahlstrom, P. L., Gutkoska, R., and Zubieta, J., *Trans. Met. Chem.* **4,** 271 (1979).

79. Chatt, J., Dilworth, J. R., Dahlstrom, P. L., and Zubieta, J., *J. Chem. Soc. Chem. Commun.* 786 (1980).

80. Chatt, J., Dilworth, J. R., and Ito, R., *J. Chem. Soc. Chem. Commun.* 77 (1973).

80a. Chatt, J., Dilworth, J. R., and Leigh, G. J., *J. Chem. Soc. A* 2239 (1970).

81. Chatt, J., Dilworth, J. R., Leigh, G. J., and Gupta, V. D., *J. Chem. Soc. A* 2631 (1971).

82. Chatt, J., Dilworth, J. R., and Richards, R. L., *Chem. Rev.* **78,** 589 (1977).

83. Chatt, J., Eady, R. R., Lowe, D. J., O'Donnell, M. J., Postgate, J. R., Richards, R. L., Smith, B. E., and Thorneley, R. N. F., "Nitrogen Fixation" (W. E. Newton and W. H. Orme-Johnson, eds.), Vol. 1, p. 190. Univ. Park Press, Baltimore, Maryland, 1980.

84. Chatt, J., Fakeley, M. E., Hitchcock, P. B., Richards, R. L., and Tûyet Luong-Thi, N., *J. Chem. Soc. Dalton Trans.* 345 (1982).

85. Chatt, J., Fakeley, M. E., Hitchcock, P. B., Richards, R. L., Luong-Thi, N., and Hughes, D. L., *J. Organomet. Chem.* **172,** C55 (1979).

86. Chatt, J., Fakeley, M. E., Richards, R. L., Mason, J., and Stenhouse, I. A., *J. Chem. Res. S* 322 (1979).

87. Chatt, J., Fakeley, M. E., Richards, R. L., Mason, J., and Stenhouse, I. A., *J. Chem. Res. S* **44** (1979).

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

89. Chatt, J., Head, R. A., Leigh, G. J., and Pickett, C. J., *J. Chem. Soc. Chem. Commun.* 299 (1977).

90. Chatt, J., Heath, G. A., Hooper, N. E., and Leigh, G. J., *J. Organomet. Chem.* **57,** C67 (1973).

91. Chatt, J., Heath, G. A., and Richards, R. L., *J. Chem. Soc. Chem. Commun.* 1010 (1972).

92. Chatt, J., Heath, G. A., and Richards, R. L., *J. Chem. Soc. Dalton Trans.* 2074 (1974).

93. Chatt, J., Hussain, W., Leigh, G. J., Neukomm, H., Pickett, C. J., and Rankin, D. A., *J. Chem. Soc. Chem. Commun.* 1024 (1980).

94. Chatt, J., Hussain, W., Leigh, G. J., and Terreros, F. P., *J. Chem. Soc. Dalton Trans.* 1408 (1980).

95. Chatt, J., Kan, C. T., Leigh, G. J., Pickett, C. J., and Stanley, D. R., *J. Chem. Soc. Dalton Trans.* 2032 (1980).

96. Chatt, J., Leigh, G. J., Morris, R. H., Pickett, C. J., and Stanley, D. R., *J. Chem. Soc. Dalton Trans.* 800 (1981).

97. Chatt, J., Leigh, G. J., Neukomm, H., Pickett, C. J., and Stanley, D. R., *J. Chem. Soc. Dalton Trans.* 121 (1980).

98. Chatt, J., Leigh, G. J., Pickett, C. J., Richards, R. L., and Pombeiro, A. J. L., *Nouv. J. Chim.* **2,** 541 (1978).

99. Chatt, J., Leigh, G. J., Pickett, C. J., and Stanley, D. R., *J. Organomet. Chem.* **184,** C64 (1980).

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

101. Chatt, J., Pearman, A. J., and Richards, R. L., *Nature (London)* **253,** 39 (1975).

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

103. Chatt, J., Pearman, A. J., and Richards, R. L., *J. Chem. Soc. Dalton Trans.* 1852 (1977).

104. Chatt, J., Pearman, A. J., and Richards, R. L., *J. Organomet. Chem.* **101,** C45 (1975).

105. Chatt, J., Pearman, A. J., and Richards, R. L., *J. Chem. Soc. Dalton Trans.* 1766 (1978).

106. Chatt, J., and Richards, R. L., *J. Less Common Metals* **54,** 477 (1977).

106a. Chiu, W. C., Havard, C. G., Rzepa, H. S., Sheppard, R. N., Wilkinson, G., Galas, A. M. R., and Hursthouse, M. B., *Polyhedron* **1,** 37 (1982).

107. Choukroun, R., Gervais, R., and Dilworth, J. R., *Trans. Met. Chem.* **4,** 249 (1979).

108. Ciechanowicz, M., Griffith, W. P., Pawson, D., and Skapski, A. C., *J. Chem. Soc. Chem. Commun.* 876 (1971).

109. Churchill, M. R., and Wasserman, H. J., *Inorg. Chem.* **20,** 2899 (1981).

110. Churchill, M. R., and Wasserman, H. J., *Inorg. Chem.* **21,** 218 (1982).

111. Clark, D. T., Woolsey, I. S., Robinson, S. D., Laing, K. R., and Wingfield, J. N., *Inorg. Chem.* **16,** 1201 (1977).

112. Clarke, F. G. N., Cox, K. P., Green, M. L. H., Bashkin, J., and Prout, K., *J. Chem. Soc. Chem. Commun.* 393 (1982).

113. Cobbledick, R. E., Einstein, F. W. B., Farrell, N., Gilchrist, A. B., and Sutton, D., *J. Chem. Soc. Dalton Trans.* 373 (1977).

114. Colquhoun, H. M., *Trans. Met. Chem.* **6,** 57 (1981).

114a. Colquhoun, H. M., and Head, R. A., *Inorg. Chim. Acta* **45,** L123 (1980).

115. Connelly, N. G., and Demidowicz, Z., *J. Organomet. Chem.* **73,** C31 (1974).

116. Cowie, M., and Gauthier, M. D., *Inorg. Chem.* **19,** 3142 (1980).

117. Cramer, S. P., Hodgson, K. O., Gillum, W. O., and Mortenson, L. E., *J. Am. Chem. Soc.* **100,** 3398 (1978).

118. Cramer, S. P., Gillum, W. O., Hodgson, K. O., Mortenson, L. E., Steifel, E. I., Chisnell, J. R., Brill, W. J., and Shah, V. K., *J. Am. Chem. Soc.* **100,** 3814 (1978).

119. Cramer, S. P., Hodgson, K. O., Steifel, E. I., and Newton, W. E., *J. Am. Chem. Soc.* **100,** 2748 (1978).

120. Crichton, B. A. L., Dilworth, J. R., Pickett, C. J., and Chatt, J., *J. Chem. Soc. Dalton Trans.* 419 (1981).

121. Crichton, B. A. L., Dilworth, J. R., Dahlstrom, P., and Zubieta, J., *Trans. Met. Chem.* **5,** 316 (1980).

122. Crichton, O., and Rest, A. J., *J. Chem. Soc. Dalton Trans.* 208 (1978).

123. Crichton, O., and Rest, A. J., *J. Chem. Soc. Dalton Trans.* 536 (1977).

124. Crichton, O., and Rest, A. J., *J. Chem. Soc. Dalton Trans.* 202 (1978).

125. Dahlstrom, P. L., Dilworth, J. R., Shulman, P., and Zubieta, J., *Inorg. Chem.* **21,** 933 (1982).

126. Dart, J. W., Lloyd, M. K., Mason, R., and McCleverty, J. A., *J. Chem. Soc. Dalton Trans.* 2039 (1973).

127. Davis, J. H., and Goddard, W. A., *J. Am. Chem. Soc.* **99,** 7111 (1977).

128. Day, V. W., George, T. A., and Iske, S. D. A., *J. Am. Chem. Soc.* **97,** 4127 (1975).

129. Deane, M. E., and Lalor, F. J., *J. Organomet. Chem.* **57,** C61 (1973).

130. Deane, M. E., and Lalor, F. J., *J. Organomet. Chem.* **67,** C19 (1974).

131. Deeming, A. J., and Shaw, B. L., *J. Chem. Soc. A* 1128 (1969).

132. Dehnicke, K., and Strähle, J., *Angew. Chem. Int. Ed. Engl.* **20,** 413 (1980).

133. Denisov, N. T., *Kinet. Katal.* **17,** 1044 (1976).

134. Denisov, N. T., Efimov, O. N., Shuvalova, N. I., Shilova, A. K., and Shilov, A. E., *Zhur. Fiz. Khim.* **44,** 2694 (1970).

135. Denisov, N. T., Korosteleva, A. I., Morozov, Y. G., and Kobeleva, S. I., *Kinet. Katal.* **18,** 758 (1977).

136. Denisov, N. T., Ovcharenko, A. G., Svirin, V. G., Shilov, A. E., and Shuvalova, N. I., *Nouv. J. Chim.* **3,** 403 (1979).

137. Denisov, N. T., Zueva, A. F., and Shilova, A. K., *Kinet. Katal.* **19,** 213 (1978).

138. Diamantis, A. A., Chatt, J., Heath, G. A., and Leigh, G. J., *J. Organomet. Chem.* **84,** C11 (1975).

139. Diamantis, A. A., and Dubrawski, J. V., *Inorg. Chem.* **20,** 1142 (1981).

140. Dickson, R. S., and Ibers, J. A., *J. Am. Chem. Soc.* **94,** 2988 (1972).

141. Dickson, C. R., and Nozik, A. J., *J. Am. Chem. Soc.* **100,** 8007 (1978).

142. Diels, O., and Kell, W., *Leibig. Ann.* **443,** 262 (1925).

143. Dilworth, J. R., *Coord. Chem. Rev.* **21,** 29 (1976).

144. Dilworth, J. R., Donovan-Mtunzi, S. D., Kan, C. T., Richards, R. L., and Mason, J., *Inorg. Chim. Acta* **53,** L161 (1981).

145. Dilworth, J. R., Garcia-Rodriguez, A., Leigh, G. J., and Murrell, J. N., *J. Chem. Soc. Dalton Trans.* 455 (1983).

146. Dilworth, J. R., Kan, C. T., Richards, R. L., Mason, J., and Stenhouse, I. A., *J. Organomet. Chem.* **201,** C24 (1980).

147. Dilworth, J. R., Kasenally, A. S., and Hussein, F. M., *J. Organomet. Chem.* **60,** 203 (1973).

148. Dilworth, J. R., and Richards, R. L., "Comprehensive Organometallic Chemistry" (Sir G. Wilkinson, FRS, ed.), p. 1073. Pergamon, Oxford, 1982.

149. Dilworth, J. R., and Zubieta, J. A., *J. Am. Chem. Soc.* **104,** 365 (1982).

150. Dilworth, J. R., and Zubieta, J. A., *J. Chem. Soc. Chem. Commun.* 132 (1981).

151. Dilworth, M. J., and Thorneley, R. N. F., *Biochem. J.* **193,** 971 (1981).

152. Dubois, D. L., and Hoffman, R., *Nouv. J. Chim.* **1,** 479 (1977).

153. Duckworth, V. F., Douglas, P. G., Mason, R., and Shaw, B. L. *J. Chem. Soc. Chem. Commun.* 1083 (1970).

154. Dobinson, G. C., Mason, R., Robertson, G. B., Ugo, R., Conti, F., Morelli, D., Cenini, S., and Bonati, F., *J. Chem. Soc. Chem. Commun.* 739 (1967).

155. Dvorak, J., O'Brien, R. J., and Santo, W., *J. Chem. Soc. D* 411 (1970).

156. Efimov, O. N., Tsarev, V. N., and Brikenshtein, K. M. A., *Zhur. Fiz. Khim.* **51,** 1200 (1977).

157. Einstein, F. W. B., Gilchrist, A. B., Rayner-Canham, G. W., and Sutton, D., *J. Am. Chem. Soc.* **93,** 1826 (1971).

158. Einstein, F. W. B., Gilchrist, A. B., Rayner-Canham, G. W., and Sutton, D., *J. Am. Chem. Soc.* **94,** 645 (1972).

159. Einstein, F. W. B., Jones, T., Hanlon, A. J. L., and Sutton, D., *Inorg. Chem.* **21,** 2585 (1982).

160. Einstein, F. W. B., and Sutton, D., *Inorg. Chem.* **11,** 2827 (1972).

161. Einstein, F. W. B., and Sutton, D., *J. Chem. Soc. Dalton Trans.* 434 (1973).

162. Enemark, J. H., "Nitrogen Fixation" (W. E. Newton and W. H. Orme-Johnson, eds.), Vol. 1, p. 297. Univ. Park Press, Baltimore, Maryland, 1980.

163. Feasey, N. D., Knox, S. A. R., and Orpen, A. G., *J. Chem. Soc. Chem. Commun.* 75, (1982).

163a. Folkesson, B., and Larsson, R., *Acta Chem. Scand.* **33A,** 347 (1979).

164. Foner, S. N., and Hudson, R. L., *J. Chem. Phys.* **28,** 719 (1958).

165. Fowles, G. W. A., Rice, D. A., and Sharton, K. J., *J. Chem. Soc. Dalton Trans.* 1212 (1977).

166. Frisch, P. D., Hunt, M. W., Kita, W. G., McCleverty, J. A., Rae, A. E., Seddon, D., Swann, D., and Williams, J., *J. Chem. Soc. Dalton Trans.* 1819 (1979).

167. Frost, D. C., Lee, S. D., McDowell, C. A., and Westwood, N. P. C., *J. Chem. Phys.* **64,** 4719 (1976) and refs. therein.

168. Gaughan, A. P., Haymore, B. L., Ibers, J. A., Myers, W. H., Nappier, T. E., and Meek, D. W., *J. Am. Chem. Soc.* **95,** 6859 (1973).

169. Gaughan, A. P., and Ibers, J. A., *Inorg. Chem.* **14,** 352 (1975).

170. George, T. A., "Current Perspectives in Nitrogen Fixation" (A. H. Gibson and W. E. Newton, eds.), p. 22. Australia Academy of Sciences, Canberra, 1981.

171. George, T. A., Busby, D. C., and Iske, S. D. A., *Inorg. Organomet. Photochem.* 147 (1978).

172. George, T. A., and Noble, M. E., *Inorg. Chem.* **17,** 1678 (1978).

173. Ghilardi, G. A., Midollini, S., Sacconi, L., and Stoppioni, P., *J. Organomet. Chem.* **205,** 193 (1981).

174. Gilchrist, A. B., and Sutton, D., *Can. J. Chem.* **52,** 3387 (1974).

175. Gill, D. F., Mann, B. E., and Shaw, B. L., *J. Chem. Soc. Dalton Trans.* 311 (1973).

176. Gordon, M. S., and Fisher, H., *J. Am. Chem. Soc.* **90,** 2471 (1968).

177. Green, D. W., and Reedy, G. T., *J. Mol. Spectrosc.* **74,** 423 (1979).

177a. Green, M. A., Huffman, J. C., Caulton, K. G., Rytak, W. K., and Ziolkowski, J., *J. Organomet. Chem.* **218,** C39 (1981).

178. Green, M. L. H., Sanders, J. R., and Whiteley, R. N., *Z. Naturforsch.* **23b,** 106 (1968).

179. Griffith, W. P., *Coord. Chem. Rev.* **8,** 369 (1972).

180. Guengerich, C. P., and Schug, K., *Inorg. Chem.* **17,** 1378, (1978).

181. Gynane, M. J. S., Jeffery, J., and Lappert, M. F., *J. Chem. Soc. Chem. Commun.* 34 (1978).

182. Hammer, R., Klein, H.-F., Friedrich, P., and Huttner, G., *Angew. Chem. Int. Ed. Engl.* **16,** 485 (1977).

183. Haymore, B. L., and Ibers, J. A., *J. Am. Chem. Soc.* **75,** 3052 (1973).

184. Haymore, B. L., and Ibers, J. A., *J. Am. Chem. Soc.* **97,** 5369 (1975).

185. Herberhold, M., and Bernhagen, W., *Z. Naturforsch.* **29b,** 801 (1974).

186. Henderson, R. A., *J. Organomet. Chem.* **208,** C59 (1981).

187. Henderson, R. A., *J. Chem. Soc. Dalton Trans.* 941 (1982).

188. Henderson, R. A., *J. Chem. Soc. Dalton Trans.* 51 (1983).

189. Henderson, R. A., Davies, G., Dilworth, J. R., and Thorneley, R. N. F., *J. Chem. Soc. Dalton Trans.* 40 (1981).

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

191. Holm, R. H., *Chem. Soc. Rev.* **10,** 455 (1981).

192. Hughes, M. N., Okolow-Zubkow, M., and Wallis, H. L., *J. Chem. Soc. Dalton Trans.* 2009 (1981).

193. Hünig, S., Muller, H. R., and Thier, W., *Angew. Chem. Int. Ed. Engl.* **4,** 271 (1965) and refs. therein.

194. Hussain, W., Leigh, G. J., and Pickett, C. J., *J. Chem. Soc. Chem. Commun.* 747 (1982).

195. Hussain, W., Leigh, G. J., Mohd-Ali, H., Pickett, C. J., Rankin, D., *J. Chem. Soc. Dalton Trans.* submitted.

196. Huttner, G., Gartzke, W., and Allinger, K., *Angew. Chem. Int. Ed. Engl.* **13,** 822 (1974).

197. Ibers, J. A., and Haymore, B. L., *Inorg. Chem.* **14,** 1369 (1975).

198. Isaeva, S. A., and Nikonova, L. A., *Izv. Akad. Nauk SSSR* 1968 (1977).

199. Ittel, S. D., and Ibers, J. A., *Inorg. Chem.* **12,** 2290 (1973).

200. Ittel, S. D., and Ibers, J. A., *Inorg. Chem.* **14,** 1183 (1975).

201. Ittel, S. D., and Ibers, J. A., *J. Am. Chem. Soc.* **96,** 4804 (1974).

202. Jackson, R., Ruddlesden, J., Thompson, D. J., and Whelan, R., *J. Organomet. Chem.* **125,** 57 (1977).

203. James, T. A., and McCleverty, J. A., *J. Chem. Soc. A* 1068 (1971).

204. Jeffery, J., Lappert, M. F., and Riley, P. I., *J. Organomet. Chem.* **181,** 25 (1979).

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

206. Jones, C. J., Drane, A. S., El Murr, N., Denti, G., McClarence, M. A., McCleverty, J. A., Neaves, B. D., and Reynolds, S. J., *Proc. Int. Conf. Chem. Uses Molybd., 4th* (1982).

207. Jones, T., Hanlon, A. J. L., Einstein, F. W. B., and Sutton, D., *J. Chem. Soc. Chem. Commun.* 1978 (1980).

208. Kaden, L., Loven, B., Schmidt, K., Spring, H., and Wahren, M., *Z. Chem.* **19,** 305 (1979).

209. Kasenally, A. S., personal communication reported in Ref. (*143*).

210. King, R. B., and Bisnette, M. B., *J. Am. Chem. Soc.* **86,** 5694 (1964).

211. Kita, W. D., McCleverty, J. A., Mann, B. E., Seddon, D., Sim, G. A., and Woodhouse, D. J., *J. Chem. Soc. Chem. Commun.* 132 (1974).

212. Klein, H. F., Hammer, R., Wenniger, J., Friedrich, P., and Huttner, G., *Z. Naturforsch.* **33b,** 1267 (1978).

213. Klein, H. F., and Nixon, J. F., *J. Chem. Soc. Chem. Commun.* 42 (1971).

214. Kobeleva, S. J., and Denisov, N. T., *Kinet. Katal.* **18,** 794 (1977).

215. Kosower, E. M., *Acc. Chem. Res.* **4,** 193 (1971).

216. Krogsrud, S., Toniolo, L., Croatto, V., and Ibers, J. A., *J. Am. Chem. Soc.* **99,** 5277 (1977).

217. Kulakovskaya, S. I., Tsarev, V. N., Efimov, O. N., and Shilov, A. E., *Kinet. Katal.* **18,** 1045 (1977).

218. Laing, K. R., Robinson, S. D., and Uttley, M. F., *J. Chem. Soc. Dalton Trans.* 2713 (1973).

219. Lalor, F. J., and Pauson, P. L., *J. Organomet. Chem.* **25,** C51 (1970).

220. Lau, C.-K., Chang, B.-H., Grubbs, R. H., and Brubaker, C. H., *J. Organomet. Chem.* **214**, 325 (1981).

221. Lappert, M. F., Power, P. P., Sanger, A. R., Srivastava, R. C., "Metal and Metalloid Amides." Harwood, Chichester, 1980.

222. Lazarus, M. S., and Sham, T. K., *J. Am. Chem. Soc.* **101**, 7022 (1979).

223. Le Ny G., Shilov, A. E., Shilova, A. K., and Tchoubar, B., *Nouv. J. Chim.* **1**, 397 (1977).

224. Lehn, J. M., and Mumsch, B., *Theor. Chim. Acta* **12**, 91 (1968).

225. Leigh, G. J., Murrell, J. N., Bremser, W., and Proctor, W. G., *J. Chem. Soc. Chem. Commun.* 1661 (1970).

226. Leigh, G. J., and Pickett, C. J., *J. Chem. Soc. Dalton Trans.* 1797 (1977).

227. Lembke, R. R., Ferrante, R. F., and Wettner, W., *J. Am. Chem. Soc.* **99**, 416 (1977).

228. Lemenovskii, D. A., Baukora, T. V., Perevalova, E. G., and Nesmeyanov, A. N. *Izvt. Akad. Nauk SSSR* 2404 (1976).

229. Liebett, W., and Dehnicke, K., *Z. Naturforsch.* **34b**, 7 (1979).

230. Liese, W., and Dehnicke, K., *Z. Naturforsch.* **33b**, 1061 (1978).

230a. Lowe, D. J., Thorneley, R. N. F., and Smith, B. E., "Metalloproteins" (P. M. Harrison, ed.), Vol. 1. Macmillan, New York, 1983, in press.

231. Luneva, N. P., Moravsky, A. P., and Shilov, A. E., *Nouv. J. Chim.* **6**, 245 (1982).

232. Luneva, N. P., Nikonova, L. A., and Shilov, A. E., *Kinet. Katal.* **21**, 1041 (1980).

233. Luneva, N. P., Nikonova, L. A., and Shilov, A. E., *Kinet. Katal.* **18**, 254 (1977).

234. Lygina, I. A., *Zhur. Fiz. Khim.* **52**, 425 (1978).

235. Maatta, E. A., and Wentworth, R. A. D., *Inorg. Chem.* **18**, 2409 (1979).

236. Mahmoud, K. A., Naraganassway, N., and Rest, A. J., *J. Chem. Soc. Dalton Trans.* 2199 (1981).

237. Manriquez, J. M., McAlister, D. R., Rosenberg, E., Shiller, A. M., Williamson, K. L., Chan, S. I., and Bercaw, J. E., *J. Am. Chem. Soc.* **100**, 3078 (1978).

238. Manriquez, J. M., Sanner, R. D., Marsh, R. E., and Bercaw, J. E., *J. Am. Chem. Soc.* **98**, 3042 (1976).

239. Masters, A. F., Mertis, K., Gibson, J. F., and Wilkinson, G., *Nouv. J. Chim.* **1**, 389 (1977).

240. Matsubara, T., Bergkamp, M., and Ford, P. C., *Inorg. Chem.* **17**, 1604 (1978).

241. McArdle, J. V., Schultz, A. J., Corden, B. J., and Eisenberg, R., *Inorg. Chem.* **12**, 1676 (1973).

242. McCleverty, J. A., Rae, A. E., Wolochowicz, I., Bailey, N. A., and Smith, J. M. A., *J. Chem. Soc. Dalton Trans.* 71 (1983).

243. McCleverty, J. A., Seddon, D., and Whiteley, R. N., *J. Chem. Soc. Dalton Trans.* 839 (1975).

244. McCleverty, J. A., and Whiteley, R. N., *J. Chem. Soc. Chem. Commun.* 1159 (1971).

245. McKenna, C. E., *J. Am. Chem. Soc.* **98**, 4657 (1976).

246. McKenna, C. E., *Nature (London)* **280**, 609, 611 (1971).

247. Minzoni, F., Pelizzi, C., and Predieri, G., *J. Organomet. Chem.* **231**, C6 (1982).

248. Miura, Y., and Yamamoto, A., *Chem. Lett.* 937 (1978).

249. Monacelli, T., Mattagno, G., Gattegno, D., and Mattese, M., *Inorg. Chem.* **9**, 686 (1970).

250. Morris, D. F. C., and Ritter, T. J., *J. Chem. Soc. Dalton Trans.* 216 (1980) and refs. therein.

251. Mortenson, L. E., and Thorneley, R. N. F., *Annu. Rev. Biochem.* **48**, 387 (1979).

252. Moorehead, E. L., Weathers, B. J., Ufkes, E. A., Robinson, P. R., and Schrauzer, G. N., *J. Am. Chem. Soc.* **99**, 6089 (1977).

253. Murrell, J. N., Derzi, A. H., Leigh, G. J., and Guest, M. F., *J. Chem. Soc. Dalton Trans.* 1425 (1980).

254. Nefedov, V. I., Lenenko, V. S., Shur, V. B., Volpin, M. E., Salyn, J. E., and Porai-Koshits, M. A., *Inorg. Chim. Acta* **7,** 499 (1978).

255. Nesmeyanov, A. N., Chapovskii, Y. A., Ustynink, N. A., and Makarova, L. G., *Izv. Akad. Nauk SSSR Ser. Khim.* 449 (1968).

256. Niblev, J. W., and Bondybey, V. E., *J. Chem. Phys.* **60,** 1307 (1974).

257. Nikoleva, G. W., Efimov, O. N., Brikenshtein, K. M. A., and Shilov, A. E., *React. Kinet. Catal. Lett.* **6,** 349 (1977).

257a. Nikonova, L. A., Rummel, S., Shilov, A. E., and Wahren, M., *Nouv. J. Chem.* **4,** 427 (1980).

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

259. Nishihara, H., Saito, T., and Sasaki, Y., *Chem. Lett.* 451 (1981).

260. Nugent, W. A., and Haymore, B. L., *Coord. Chem. Rev.* **31,** 123 (1980).

261. Oh-Kita, M., Midorikawa, H., Aika, K. I., and Ozaki, A., *J. Catal.* **70,** 384 (1981).

262. Ohya, A., Urabe, K., Aika, K., and Ozaki, A., *J. Catal.* **58,** 313 (1979).

263. Okawa, T., Ohishi, T., and Tamaru, K., *Z. Phys. Chem. (Frankfurt)* **107,** 239 (1977).

263a. Oosawa, Y., *J. Chem. Soc. Chem. Commun.* 221 (1982).

264. Otsuka, S., Yoshida, T., and Tatsumo, Y., *J. Chem. Soc. Chem. Commun.* 67 (1971).

265. Otsuka, S., Yoshida, T., and Tatsumo, Y., *J. Am. Chem. Soc.* **93,** 6462 (1971).

266. Panov, G. I., Boreskov, G. K., Kharitonov, A. S., and Moroz, E. M., *React. Kinet. Catal. Lett.* **16,** 247 (1981).

267. Parshall, G. W., *J. Am. Chem. Soc.* **87,** 2133 (1965).

268. Parshall, G. W., *J. Am. Chem. Soc.* **89,** 1822 (1967).

269. Pelikan, P., Haring, M., Ceppan, M., Breza, M., Liska, M., and Nagy, L. T., *J. Mol. Catal.* **5,** 349 (1979).

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

271. Pez, G. P., and Kwan, S. C., *J. Am. Chem. Soc.* **98,** 8072 (1976).

272. Pez, G. P., and Kwan, S. C., *J. Am. Chem. Soc.* **98,** 8079 (1976).

273. Pickett, C. J., and Leigh, G. J., *J. Chem. Soc. Commun.* 1033 (1981).

274. Pickett, C. J., Tolhurst, J. E., Copenhaver, A., George, T. A., and Lester, R. K., *J. Chem. Soc. Chem. Commun.* 1071 (1982).

275. Pickett, C. J., and D. R. Stanley, "Inorganic Reactions and Methods" (J. J. Zuckerman, ed.). Verlag Chemie, Weinheim, in press.

276. Pombeiro, A. J. L., Pickett, C. J., Richards, R. L., and Sangakoya, S. A., *J. Organomet. Chem.* **202,** C15 (1980).

277. Rest, A. J., Sodeau, J. R., and Taylor, D. J., *J. Chem. Soc. Dalton Trans.* 651 (1978).

278. Roberts, D. R., Geoffroy, G. L., and Bradley, M. G., *J. Organomet. Chem.* **198,** C75 (1980).

279. Robinson, P. R., Moorehead, E. L., Weathers, B. J., Ufkes, E. A., Vickrey, T. M., and Schrauzer, G. N., *J. Am. Chem. Soc.* **99,** 3657 (1977).

280. Rocklage, S. M., and Schrock, R. R., *J. Am. Chem. Soc.* **102,** 7808 (1980).

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

282. Rocklage, S. M., Turner, H. W., Felleman, J. D., and Schrock, R. R., *Organometallics* **1,** 703 (1982).

283. Sato, M., Tatsumi, T., Kodama, T., Hidai, M., Uchida, T., and Uchida, Y., *J. Am. Chem. Soc.* **100,** 4447 (1978).

284. Schmidt, F. K., Nindakova, L. O., Krasnopolskaya, S. M., Devyatkova, N. G., Dimitrieva, R. V., and Ratovskii, D. V., *Kinet. Katal.* **19,** 111 (1978).

285. Schrauzer, G. N., "New Trends in the Chemistry of Nitrogen Fixation" (J. Chatt, L.

M. da Câmara Pina, and R. L. Richards, eds.), Academic Press, New York, 1980, Ch. 4, and references therein.

286. Schrauzer, G. N., *Angew. Chem. Int. Ed. Engl.* **14,** 514 (1975) and references therein.

287. Schrauzer, G. N., and Guth, T., *J. Am. Chem. Soc.* **99,** 7189 (1977).

288. Schrauzer, G. N., Hughes, L. A., Palmer, M. R., Strampach, N., and Gate, R. W., *Z. Naturforsch.* **33b,** 1439 (1980).

289. Schrauzer, G. N., Strampach, N., and Hughes, L. A., *Inorg. Chem.* **21,** 2184 (1982).

290. Schrauzer, G. N., Strampach, N., Palmer, M. R., and Zones, B. I., *Nouv. J. Chim.* **5,** 5 (1981).

291. Sellman, D., *Angew. Chem. Int. Ed. Engl.* **10,** 919 (1971).

292. Sellman, D., *J. Organomet. Chem.* **36,** C27 (1972).

293. Sellman, D., *J. Organomet. Chem.* **44,** C46 (1972).

294. Sellman, D., Brandl, A., and Endell, R., *J. Organomet. Chem.* **97,** 229 (1975).

295. Sellman, D., Brandl, A., and Endell, R., *J. Organomet. Chem.* **49,** C22 (1973).

296. Sellman, D., Brandl, A., and Endell, R., *J. Organomet. Chem.* **111,** 303 (1976).

297. Sellman, D., Brandl, A., and Endell, R., *Angew. Chem. Int. Ed. Engl.* **12,** 199 (1973).

298. Sellman, D., Brandl, A., and Endell, R., *J. Organomet. Chem.* **90,** 309 (1975).

299. Sellman, D., Gerlach, R., and Jodden, K., *J. Organomet. Chem.* **178,** 433 (1979).

300. Sellman, D., and Jodden, K., *Angew. Chem. Int. Ed. Engl.* **16,** 464 (1977).

301. Sellman, D., and Jodden, K., *Angew. Chem.* **89,** 480 (1977).

302. Sellman, D., and Kleinschmidt, E., *Z. Naturforsch.* **32b,** 795 (1977).

303. Sellman, D., and Kleinschmidt, E., *J. Organomet. Chem.* **140,** 211 (1977).

304. Sellman, D., and Maisel, G., *Z. Naturforsch.* 465 (1972).

305. Sellman, D., and Weiss, W., *Angew. Chem. Int. Ed. Engl.* **16,** 880 (1977).

306. Sellman, D., and Weiss, W., *Angew. Chem. Int. Ed. Engl.* **17,** 269 (1978).

307. Sellman, D., and Weiss, W., *J. Organomet. Chem.* **160,** 183 (1978).

308. Sharp, P. R., and Schrock, R. R., *J. Am. Chem. Soc.* **104,** 4291 (1982).

309. Shilov, A. E., personal communication.

310. Shilov, A. E., *Usp. Khim.* **43,** 378 (1974).

311. Shriver, D. F., *Acc. Chem. Res.* **3,** 231 (1970).

312. Shur, V. B., Tikhonova, I. A., Aleksandrov, G. G., Struchkov, Y. T., and Volpin, M. E., *Inorg. Chim. Acta* **44,** L275 (1980).

313. Shur, V. B., Berkovich, E. G., Yunusov, S. M., Mamedov, S. M., Nizker, I. L., and Volpin, M. E., *Izv. Akad. Nauk SSSR* 2841 (1977).

314. Smith, B. E., Lowe, D. J., Postgate, J. R., Richards, R. L., and Thorneley, R. N. F., *Proc. Int. Symp. Nitrogen Fixation, 4th, Aust. Acad. Sci., Canberra, 1981* p. 67.

315. Sobota, P., and Jezowska-Trzebiatowska, B., *J. Organomet. Chem.* **131,** 341 (1977).

316. Subba Rao, N. S., ed., "Recent Advances in Biological Nitrogen Fixation." Arnold, London, 1980.

317. Sutton, D., *Chem. Soc. Rev.* 443 (1975).

318. Summerville, D. A., and Cohen, I. A., *J. Am. Chem. Soc.* **98,** 1747 (1976).

319. Takahashi, T., Mizobe, Y., Sato, M., Uchida, Y., and Hidai, M., *J. Am. Chem. Soc.* **102,** 7461 (1980).

320. Takahashi, T., Mizobe, Y., Sato, M., Uchida, Y., and Hidai, M., *J. Am. Chem. Soc.* **101,** 3405 (1979).

321. Talanty, E. R., Schwartz, A. K., and Simons, G., *J. Am. Chem. Soc.* **97,** 972 (1975) and refs. therein.

322. Tatsumi, T., Tominaga, H., Hidai, M., and Uchida, Y., *Chem. Lett.* 37 (1977).

323. Tatsumi, T., Tominaga, H., Hidai, M., and Uchida, Y., *J. Organomet. Chem.* **199,** 63 (1980).

324. Tatsumi, T., Hidai, M., and Uchida, Y., *Inorg. Chem.* **14,** 2530 (1975).

325. Tevault, D., Strommen, D. P., and Nakamoto, K., *J. Am. Chem. Soc.* **99,** 2997 (1977).

326. Thomas, R. J. W., Laurence, G. S., and Diamantis, A. A., *Inorg. Chim. Acta* **30,** L353 (1978).

327. Thorn, D. L., Tulip, T. H., and Ibers, J. A., *J. Chem. Soc. Dalton Trans.* 2022 (1979).

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

329. Thorneley, R. N. F., and Lowe, D. J., *Isr. J. Bot.* **31,** 61 (1982).

330. Thorneley, R. N. F., and Lowe, D. J., "Current Perspectives in Nitrogen Fixation" (A. H. Gibson and W. E. Newton, eds.), p. 360. Australian Academy Sciences, Canberra, 1981.

331. Toniolo, L., and Eisenberg, R., *J. Chem. Soc. Chem. Commun.* 455 (1971).

332. Trofimenko, S., *Inorg. Chem.* **8,** 2675 (1969).

333. Trofimenko, S., *J. Am. Chem. Soc.* **92,** 5118 (1970).

334. Turner, H. M., Felleman, J. D., Rocklage, S. M., Schrock, R. R., Churchill, M. R., and Wasserman, H. J., *J. Am. Chem. Soc.* **102,** 7809 (1980).

335. Urabe, K., Shiratori, K., and Ozaki, A., *J. Catal.* **56,** 71 (1978).

336. Urabe, K., Shiratori, K., and Ozaki, A., *J. Catal.* **55,** 71 (1978).

337. Van der Weij, F. W., Scholtens, H., and Teuben, J. H., *J. Organomet. Chem.* **127,** 299 (1977).

338. Van der Weij, F. W., and Teuben, J. H., *J. Organomet. Chem.* **120,** 223 (1976).

339. Van Gaal, H. L. M., and Van den Bekerom, F. L. A., *J. Organomet. Chem.* **134,** 237 (1977).

340. Veillard, H., *Nouv. J. Chem.* **2,** 215 (1978).

341. Vidyarthi, S. K., Willis, C., and Back, R. A., *J. Phys. Chem.* **80,** 559 (1976).

342. Veith, M., *Angew. Chem. Int. Ed. Engl.* **15,** 387 (1976).

343. Volpin, M. E., Denisov, N. T., Efimov, O. N., Kobeleva, S. I., Kulakovskaya, S. I., Novikov, Y. N., and Postnikov, V. A., *Zhur. Fiz. Khim.* **51,** 487 (1977).

344. Volpin, M. E., and Shur, V. B., *J. Organomet. Chem.* **200,** 319 (1980).

345. Wagniere, G., *Theor. Chim. Acta* **31,** 269 (1973).

346. Weathers, B. J., Grate, J. H., and Schrauzer, G. N., *J. Am. Chem. Soc.* **101,** 917 (1979).

347. Weathers, B. J., Grate, J. H., Strampach, N. A., and Schrauzer, G. N., *J. Am. Chem. Soc.* **101,** 925 (1979).

348. Wiberg, N., Fischer, G., and Bachhuber, H., *Angew. Chem. Int. Ed. Engl.* **16,** 780 (1977) and references therein.

348a. Wiberg, N., Haring, H. W., and Schubert, U., *Z. Naturforsch.* **33b,** 1365 (1978).

349. Wiberg, N., Haring, H. W., and Schieda, O., *Angew. Chem. Int. Ed. Engl.* **15,** 386 (1976).

350. Wiedenhammer, K., Herrman, W. A., and Ziegler, M. L., *Z. Anorg. Chem.* **457,** 183 (1979).

351. Willis, C., and Back, R. A., *Can. J. Chem.* **51,** 3605 (1973).

352. Willis, C., Back, R. A., and Purdon, J. G., *Int. J. Chem. Kinet.* **9,** 787 (1977).

353. Willis, C., Back, R. A., Purdon, J. G., and Parsons, J. M., *J. Am. Chem. Soc.* **99,** 4451 (1977).

354. Wurminghausen, T., and Sellman, D., *J. Organomet. Chem.* **199,** 77 (1980).

355. Yamabe, T., Hori, K., and Fukui, K., *Inorg. Chem.* **21,** 2046 (1982).

356. Yamabe, T., Hori, K., Minato, T., and Fukui, K., *Inorg. Chem.* **19,** 2154 (1980).

357. Yoshida, T., Okana, T., Thorn, D. L., Tulip, T. H., Otsuka, S., and Ibers, J. A., *J. Organomet. Chem.* **181,** 183 (1979).

358. Ziegler, T., and Rauk, A., *Inorg. Chem.* **18,** 1755 (1979).

359. Zones, S. I., Palmer, M. R., Palmer, J. G., Doemeny, J. M., and Schrauzer, G. N., *J. Am. Chem. Soc.* **100,** 2113 (1978).

360. Zones, S. I., Vickrey, T. M., Palmer, J. G., and Schrauzer, G. N., *J. Am. Chem. Soc.* **98,** 7289 (1976).