

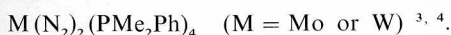
DIAZENIDO, DINITROGEN AND RELATED COMPLEXES

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ABSTRACT. — This paper presents a qualitative molecular orbital picture of the structure and reactivity of diazenido NNR complexes and related molecules including dinitrogen NN, hydrazido NNR₂, imido, NNR₃, nitrido N, as ligands. The primary focus is the geometry of the ligands in six and five-coordinate structures and the reactivity of these molecules to acid attack. Specific questions treated are bending at N' and N'', the charge distribution in the coordinated dinitrogen and diazenido ligands, the difference in photochemical reactivity of mono- and bis-dinitrogen complexes, deformations in square-pyramidal and trigonal-bipyramidal diazenido complexes, comparison of nitrosyl and diazenido ligands, and the electronic structure of hydrazido, imido and nitrido complexes.

Current interest in transition metal complexes containing dinitrogen itself, diazenido and other reduced forms of the dinitrogen ligand stems from their potential as models for the biological process of nitrogen fixation, and as nitrogen-fixing catalysts in their own right^{1, 2}. Stoichiometric protonation of coordinated dinitrogen to ammonia has been achieved for the well defined complexes



Other interesting alkylation⁵ and protonation⁶ reactions have yielded ligands containing reduced nitrogen. Our purpose here is to present a systematic molecular orbital analysis of the electronic structure of some dinitrogen, diazenido, and related complexes to aid in understanding their chemistry and structure.

The discussion that we present will be quite qualitative. It is supported by extended Hückel calculations, with parameters described in the Appendix. This computational method has well-known deficiencies, so that the reader should be aware that any detailed numerical outcomes of the calculations should be viewed with caution. Dinitrogen complexes of transition metals have been subject to a number of other theoretical studies⁷.

The nomenclature of coordinated nitrogenic ligands could be charitably described as "diversified". Throughout this paper we will use the verbal descriptor dinitrogen instead of N₂. Where the symbols N' or N'' appear, they refer to the individual nitrogen atoms respectively adjacent and removed from the metal atom (i. e. M—N'—N''). The NNR ligand will be called "diazenido", NNR₂ "hydrazido", NNR₃ "imido", N "nitrido".

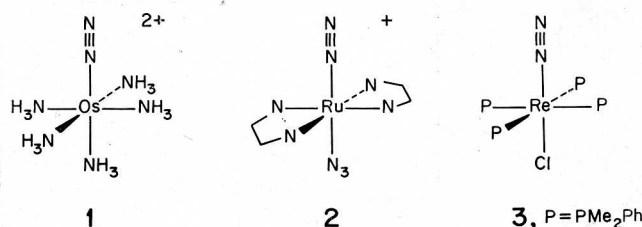
Six-coordinate mono- and bisdinitrogen complexes

Most dinitrogen complexes are six-coordinate, and the structural details of several of these are known from crystallographic studies⁸. Among these are compounds **1**^{8b}, **2**^{8c}, and **3**^{8d}.

All of these complexes have {MNN}⁶ electronic configurations with MNN angles of nearly 180°. Here we have adopted the notation introduced by Enemark and Feltham for nitrosyl complexes⁹. Dinitrogen and diazenido complexes are designated by {MNN}^r and {MNNR}^r respectively

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where *r* is the number of electrons associated with metal *d* orbitals and the π* orbitals of the ligand.



The interaction of N₂ with the square-pyramidal fragment RuCl₃(PH₃)₂⁻ to form the hypothetical RuCl₃(PH₃)₂N₂⁻ complex is shown in Figure 1. There is nothing novel about the molecular orbital scheme given here, but we would like to have the nature of the molecular orbitals well in mind for further discussion. The five-coordinate metal fragment has the typical splitting pattern for square pyramidal complexes¹⁰. The x²-y² orbital which is antibonding to all four ligands of the basal plane lies highest, the antibonding combination of the z² orbital with the axial ligand lies considerably lower, and the three lowest *d* block molecular orbitals are the *xz*, *xy*, and *yz* which are sigma-nonbonding. The small energy differences in the latter three orbitals arise from varying degrees of π bonding with the ligands. The σ and π* orbitals of the dinitrogen ligand shown on the right-hand side of Figure 1 are of proper energy and symmetry to interact significantly with the metal fragment^{10c}.

The mixing of the sigma orbital of dinitrogen with the z² orbital of the square-pyramidal fragment produces bonding and antibonding combinations and results in the typical energy level ordering of an octahedral complex, i. e. with x²-y² and z² (e_g) above the *xy*, *xz*, and *yz* (t_{2g}) orbitals. The π* orbitals of dinitrogen lie between the e_g and t_{2g} sets in our calculations. These π* orbitals interact with the *xz* and *yz* orbitals of an ML₅ fragment to give the bonding and antibonding combinations of Figure 1. The *xy*, *xz*, and *yz* orbitals are nearly of equal energy as shown, but the *xy* orbital is expected to lie above the *xz* and *yz* orbitals as the latter are stabilized by interaction with the π* orbitals of dinitrogen. Our molecular orbital scheme for a dinitrogen complex is thus a typical diagram for an octahedral complex,

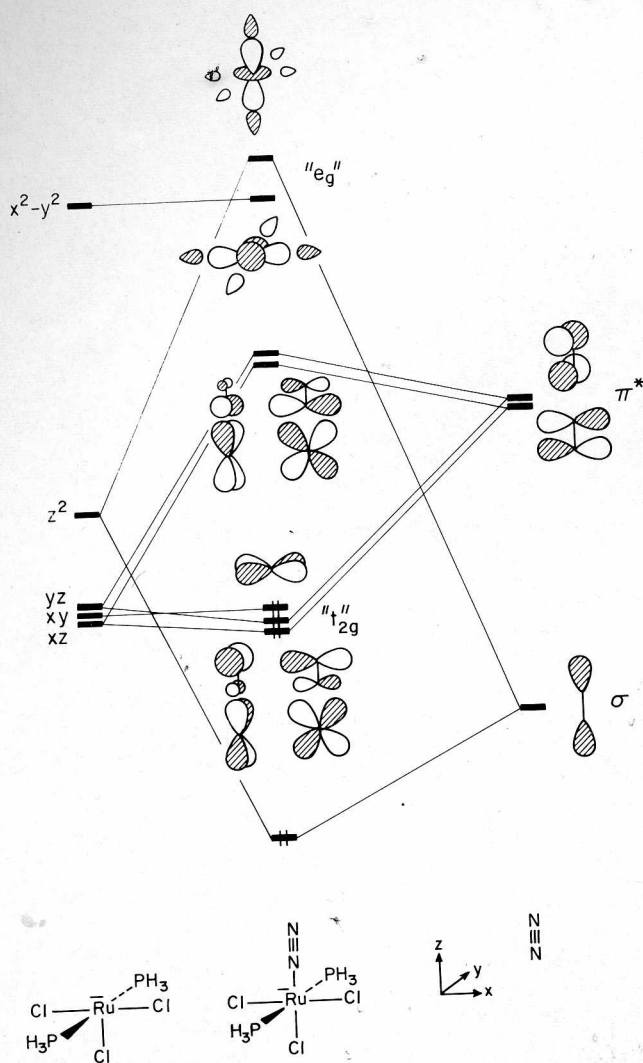


Figure 1. — Orbitals of $\text{RuCl}_3(\text{PH}_3)_2\text{N}_2^-$ constructed from those of a five-coordinate fragment and N_2 .

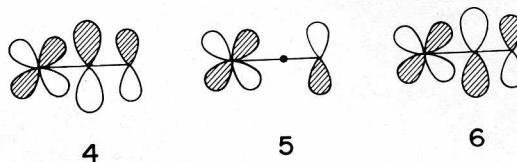
modified by the presence of the antibonding combination of π^* dinitrogen with xz and yz between the t_{2g} and e_g levels. Others have reversed the ordering of the π^* and e_g levels^{7, 11}.

CHARGE DISTRIBUTION IN THE COORDINATED DINITROGEN LIGAND

An important chemical question is the site of protonation of dinitrogen complexes. Should protonation occur at the nitrogen atom bound to the metal atom, at the terminal nitrogen, or at the metal itself? Our calculations indicate that the terminal nitrogen atom is more negative than the bound nitrogen atom. For example, for a model *cis*- $\text{Mo}(\text{PH}_3)_4(\text{N}_2)_2$ the atomic charges on Mo, N' (nitrogen adjacent to metal), and N'' (terminal nitrogen) are +0.15, -0.11, and -0.88 respectively. The charge polarization predicted by our calculations is in agreement with the interpretation of X-ray photoelectron spectra which indicate that N'' is more negative than N' ¹².

The origin of this charge polarization is an interesting one. It may be discussed in a number of ways. The xz and yz orbitals of the metal fragment and the four p orbitals of π symmetry from the dinitrogen ligand form two orthogonal

three orbitals sets. These have a characteristic allylic shape, shown for one plane in 4-6. If the lower two orbitals are occupied by four electrons, a typical pile-up of electron density at the ends results, giving N'' a decidedly more negative charge than N' ¹³. In model calculations on various compounds the charge difference between N' and N'' was

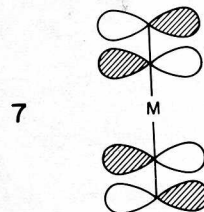


typically ~ 0.75 of an electron. An alternative explanation of the polarization of these orbitals may be obtained by a perturbation theoretic analysis of the mixing of dinitrogen π and π^* into metal xz or yz ^{10c}.

The site of protonation need not necessarily be determined by the charge distribution, but could be set by the composition of the highest occupied orbitals. These are xy and the xz , yz pair shown in Figure 1. The latter are analogous to 5, which for emphasis was drawn with comparable contributions of metal and N_2 orbitals. In fact the xz , yz pair is localized more on the metal. For example for the monodinitrogen complex $\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4$ the preferred site of protonation is at the metal¹⁴, at least under conditions of thermodynamic control. The problem of choice of protonation site is a complex one and is not well resolved by our calculations.

DIFFERENCES BETWEEN MONO- AND BISDINITROGEN COMPLEXES

Among the most intensively studied dinitrogen complexes are the bisdinitrogen complexes of tungsten and molybdenum. The replacement of a phosphine or halide with a second dinitrogen ligand has some interesting consequences. Figure 2 shows the essential part of the molecular orbital schemes for the model complexes *trans*- $\text{Mo}(\text{PH}_3)_4\text{Cl}(\text{N}_2)^-$, *trans*- $\text{Mo}(\text{PH}_3)_4(\text{N}_2)_2$, and *cis*- $\text{Mo}(\text{PH}_3)_4(\text{N}_2)_2$. A low energy e_u set of orbitals is present in the *bis* complex *trans*- $\text{Mo}(\text{PH}_3)_4(\text{N}_2)_2$ that has no counterpart in *trans*- $\text{Mo}(\text{PH}_3)_4\text{Cl}(\text{N}_2)^-$. One member of this e_u set is redrawn below, 7. It is an in-phase combination of the acceptor



orbitals of the two N_2 groups. The only metal orbitals that can mix with this set are x , y and that mixing is minor and stabilizing. In the *cis* complex the lower symmetry complicates the interactions, but nonetheless there is a low-lying unoccupied orbital, primarily based on the dinitrogen groups.

We think that this low-lying e_u set may be responsible for the interesting photochemical reactions exhibited by *trans*- $\text{W}(\text{diphos})_2(\text{N}_2)_2$ ¹⁵ and *trans*- $\text{Mo}(\text{diphos})_2(\text{N}_2)_2$ ^{sc, d, e}.

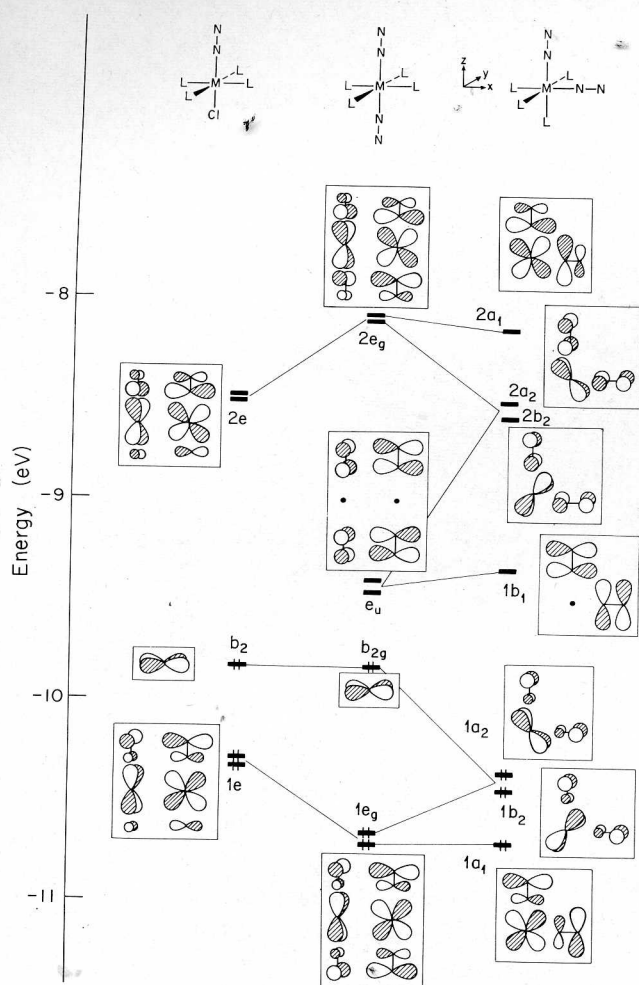
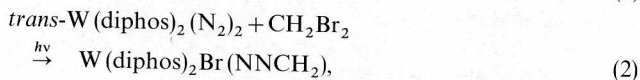
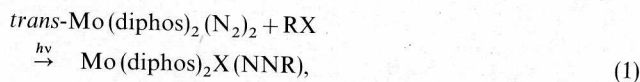


Figure 2. — Orbitals of a mono-dinitrogen complex (left), a *trans* bis-dinitrogen complex (middle), and its *cis* isomer (right). The connecting lines show approximate correlations.

For instance these complexes react under visible and ultraviolet irradiation to produce alkyldiazenido complexes^{s,c,d,e}, equation (1), or diazomethane complexes¹⁵, equation (2).



The promotion of an electron from the xy orbital to π^* (e_u) increases the electron density on the dinitrogen ligands at the expense of the charge on the metal¹⁶. The lowest energy metal to π^* transition in *cis*- and *trans*-bisdinitrogen complexes does not populate a metal-ligand antibonding orbital as for *trans*-[Mo(PH₃)₄(N₂)Cl]⁻. Because this excited state of bisdinitrogen complexes is not metal-ligand antibonding, such complexes should have a relatively better opportunity to undergo reactions at the dinitrogen ligand rather than the ligand dissociation expected for the analogous monodinitrogen complexes. Enhancement of ligand reactivity upon photochemical excitation has been discussed by others as well^{19, 20}.

It should be mentioned that recent work on the alkylation reaction indicates that some of the reactions do not require

photochemical activation, and that they proceed by predissociation of dinitrogen, coordination of alkyl halide, generation of a carbon-centered free radical from the coordinated alkyl halide, and attack of the radical on the remaining coordinated dinitrogen^{15c}.

COMPARISON OF *cis*- AND *trans*-BISDINITROGEN COMPLEXES

Our understanding of other chemical properties of *cis*- and *trans*-bisdinitrogen complexes can be aided by a careful examination of the changes which the b_{2g} and $1e_g$ orbitals of the *trans* complex (center of Figure 2) undergo when it is transformed into the *cis* complex (right-hand side of Figure 2). The $1a_2$ orbital of the *cis* complex is higher in energy than the corresponding $1e_g$ orbital of the *trans* complex due to poorer overlap of the metal orbital with the two π^* orbitals of the dinitrogen ligands. The b_{2g} or xy orbital of the *trans*-bisdinitrogen complex is nonbonding with respect to the π^* orbitals of the two dinitrogen ligands. In the lower symmetry of the *cis*-bisdinitrogen complex this metal orbital interacts with the π^* orbitals of the two dinitrogen ligands to form a bonding molecular orbital, $1b_2$, of much lower energy. If two electrons are placed in the b_{2g} orbital of the *trans* complex, they may reside only on the metal atom; however, if two electrons are placed in the b_2 orbital of the *cis* complex, the electrons will distribute themselves on both the metal and the dinitrogen ligand. This results in a higher electron density on the dinitrogen ligands of the *cis*-bisdinitrogen complex. Our calculations give the charge distributions shown in Table I.

Table I. — Calculated Charge Distribution in a Model Mo(PH₃)₄(N₂)₂.

	<i>trans</i>	<i>cis</i>
Mo	-0.59	+0.15
N'	+0.05	-0.11
N''	-0.67	-0.88

Because of the greater electron density on the dinitrogen ligand in *cis* complexes, we might expect them to be more easily protonated than *trans* complexes.

Although the electrochemistry of bisdinitrogen complexes has been only briefly studied¹⁷, that of the electronically similar dicarbonyl complexes, Cr(CO)₂(diphos)₂, Mo(CO)₂(diphos)₂, and W(CO)₂(diphos)₂ is well defined¹⁸. We can see from Figure 2 that the oxidation of a *trans*-bisdinitrogen complex would involve the removal of an electron from a b_{2g} orbital which is higher in energy than the corresponding $1b_2$ orbital of the *cis* complex. In agreement, the *trans*-dicarbonyl complexes are more easily oxidized than the *cis* complexes¹⁸.

Another interesting feature of the electrochemistry of the dicarbonyl complexes is that the oxidation of a *trans* complex always leads to a *trans* cation and the oxidation of a *cis* complex will also generally lead to the formation of a *trans* cation. For example oxidation of *trans*-Cr(CO)₂(diphos)₂ gives *trans*-Cr(CO)₂(diphos)₂⁺ and *cis*-Cr(CO)₂(diphos)₂ gives *trans*-Cr(CO)₂(diphos)₂⁺^{18a}. It is apparent from Figure 2 that the *trans* isomer gains more in stability than the *cis* upon ionization, so that predominance of the *trans* cation is to be expected, provided that a pathway exists for facile interconversion of the two forms. A ligand field rationalization

of the experimental trends in *cis* and *trans* dicarbonyl oxidations has been presented by Wimmer, Snow, and Bond^{18a}.

Comparison of NN, NO⁺, and NNR⁺ ligands

The ligands NN, NO⁺, and NNR⁺ are isoelectronic. The analogy between NO⁺ and NNR⁺ is frequently used both in synthesis and in discussions of molecular structure^{1,2}. In our calculations we have used NNH⁺ to simulate the behavior of both aryl- and alkyl-diazenido ligands. Figure 3

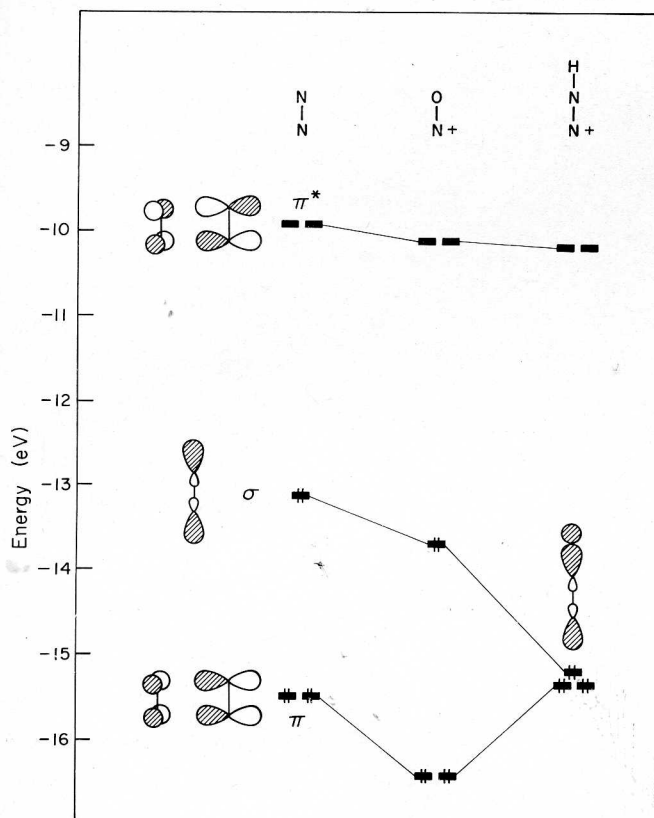


Figure 3. — The frontier orbitals of NN, NO⁺ and NNH⁺.

shows the relative energies of the valence orbitals of NN, NO⁺, and NNH⁺ for bond distances typically found in transition metal complexes. The molecular orbitals are filled through the σ level. The σ orbital of NNH⁺ is much lower than for NO⁺ and NN as a result of the $1s$ orbital of hydrogen interacting in a bonding fashion with the σ orbital of NN. The π^* orbitals of NN, NO⁺, and NNH⁺ are of roughly comparable energy from our calculations. However, the energy of the π^* orbitals is sensitive to the N-N and N-O bond distances, and the extent of polarization of π and π^* orbitals for heteronuclear diatomics makes the assessment of comparative donor and acceptor properties of these ligands in metal complexes extremely difficult.

The primary feature we would like to examine is how the triatomic NNH⁺ differs from the diatomics NN and NO⁺. NNH⁺ has an additional structural feature; it may bend at the central atom, N'. In fact the diazenido ligand has always been observed to bend at N' in transition metal complexes. The effect of bending NNH⁺ on the π^* , σ , π orbitals is shown in Figure 4. Upon bending, the hydrogen $1s$ orbital interacts

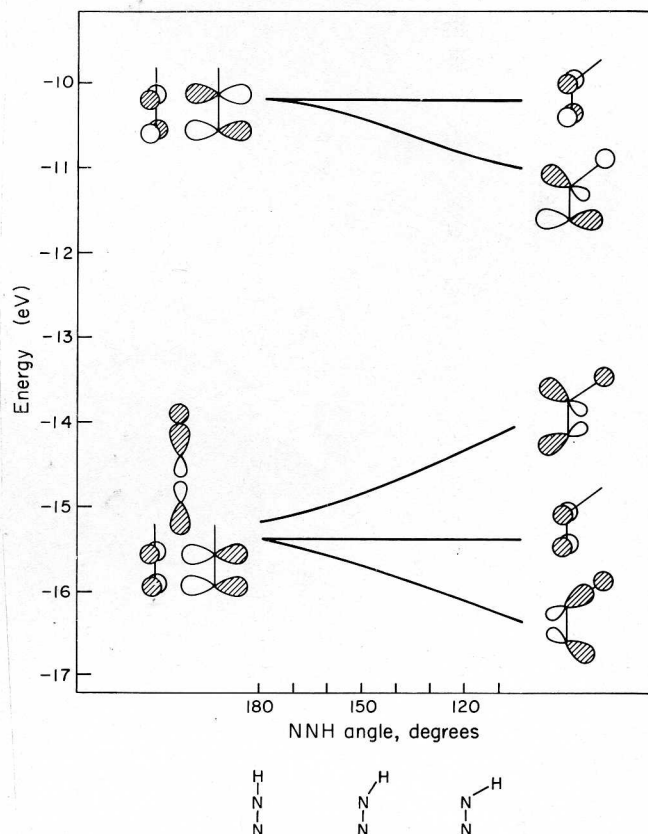
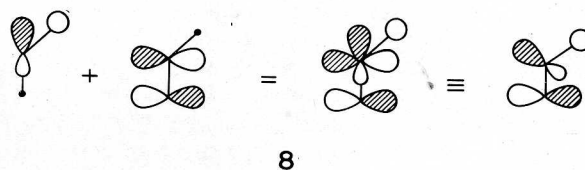


Figure 4. — Evolution of NNH orbitals as a function of bending angle.

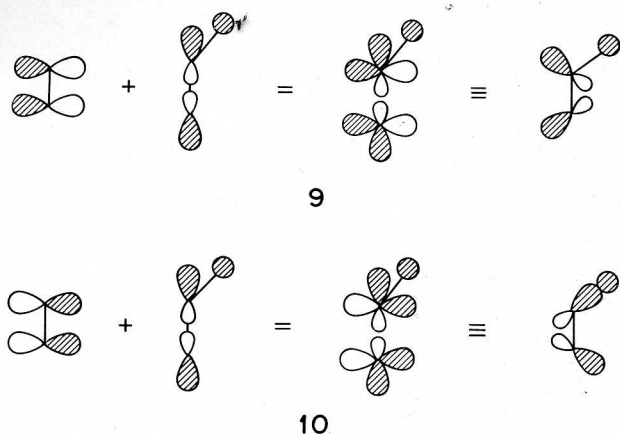
in a bonding fashion with both π_x and π_x^* orbitals, lowering their energies. The decrease in the bonding interaction between the hydrogen $1s$ orbital and the σ orbital of dinitrogen causes the σ orbital of NNH⁺ to rise in energy with bending. Bending at N' thus produces a ligand of greater π acceptor and σ donor ability. Both the donor and acceptor properties of NNH⁺ are a function of the NNH angle. This angle may be used to probe the π donor ability of metal complexes.

In addition to the changes in the acceptor and donor ability of the valence orbitals of NNH⁺, the lower symmetry of bent NNH⁺ allows the σ , π_{xz} , π_{xz}^* orbitals to mix with each other to change the shapes of the molecular orbitals. The results of mixing σ and π systems are shown on the right-hand side of Figure 4. The geometry of the π_{xz}^* orbital is affected only slightly by mixing in a small amount of a higher σ orbital which is primarily antibonding between N' and hydrogen, as shown in 8. As noted above, the hydrogen $1s$ orbital mixes in-phase with the π^* orbital stabilizing it.



The σ and π_x orbitals lie very close to each other and therefore mix strongly upon bending. The higher orbital which results, 9, is that orbital which will play a crucial role in determining the geometry of metal complexes as it is closer

in energy to the metal d orbitals than the low energy combination, **10**. In summary, bending the diazenido ligand produces



a stronger π acceptor orbital in the plane of the bending and a σ donor orbital pointing in a direction *trans* to the hydrogen atom.

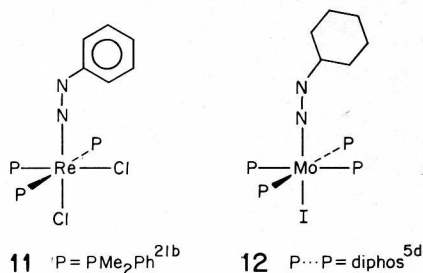
Six-coordinate diazenido complexes

Six-coordinate diazenido complexes with $\{MNNR\}^6$ and $\{MNNR\}^8$ electronic configurations are known. Examples

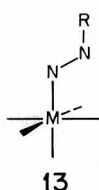
are $RuCl_3(PPh_3)_2(NNPh)$ ¹⁹ and

$RuCl(CO)_2(PPh_3)_2(NNPh)$ ^{20a}

respectively, X-ray structural determinations have been carried out on a number of six-coordinate $\{MNNR\}^6$ complexes²¹, two of which are shown in **11** and **12**. All have a nearly linear MNN arrangement while the NNR groups



are bent, with angles ranging from 118 to 142°. By analogy with nitrosyl complexes $\{MNNR\}^8$ compounds would be expected to be bent at both N' and N'' , **13**, and indeed the first structural determination of a molecule in this class, $IrCl_2(o-N_2C_6H_4NO_2)(CO)(PPh_3)_2$, has been reported recently^{20b}. The molecular orbitals which result from the



interaction of a linear NNH^+ fragment with a model $RuCl_3(PH_3)_2^-$ are shown on the left-hand side of Figure 5. They are nearly identical with those of $RuCl_3(PH_3)_2(N_2)^-$ shown in Figure 1. For an $\{MNNR\}^6$ complex the molecular orbitals are filled through the xy orbital.

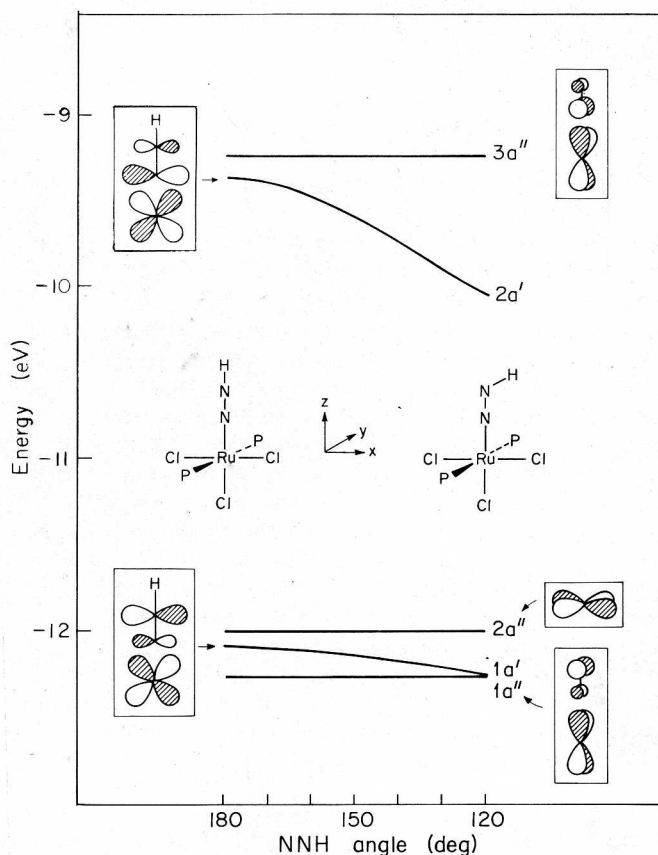
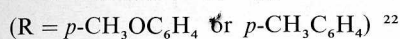
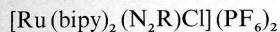


Figure 5. — Orbitals of $RuCl_3(PH_3)_2(NNH)$ as a function of bending at N'' .

BENDING AT N''

Figure 5 shows the effect of bending at N'' on the valence orbitals of $RuCl_3(PH_3)_2(NNH)$. From Figure 4 we recall that bending the diazenido fragment has a large stabilizing effect on the π^* orbital in the plane of the bending. Because of this, the molecular orbitals which should be affected most strongly by the bending of the NNH ligand at N'' are those populated MO's having π^* NNR character. As the NNH angle decreases from 180 to 120°, the energy of both the $1a'$ and $2a'$ orbitals drop since both have π^* NNH components in them. The energy of $2a'$ drops much more rapidly than $1a'$ as it has a much larger fraction of π^* NNH character. As the admixture of the π^* NNH orbital is increased in the populated $1a'$ orbital, the NNH angle should become progressively smaller. The amount of NNH π^* mixing in $1a'$ may be increased by raising the energy of the xz orbital of the metal fragment, which in turn can be accomplished by increasing the basicity of the metal complex. Good σ donating ligands, low oxidation states, and negative charge should favor a small NNR angle. For the neutral low valent complex, $MoHB(pz)_3(CO)_2(N_2Ph)$, an angle of 121° is observed^{21a} while $RuCl_3(PPh_3)_2(p-N_2PhMe)$ has an NNR angle of

136-137°^{21c,e}. The complexes of

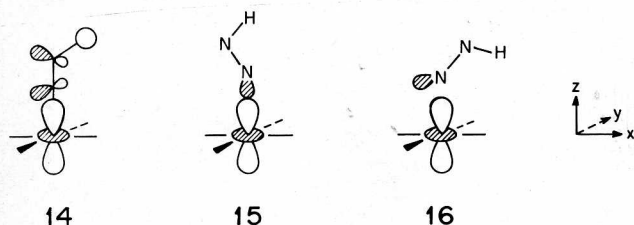


by virtue of their large positive charge and high oxidation states should have large NNR angles.

BENDING AT N'

Another interesting structural feature in diazenido and nitrosyl complexes is the ability of these ligands to bend at the nitrogen bound to the metal. For a diazenido complex this produces the doubly bent structure **13**. This property has been discussed extensively for nitrosyls^{9, 10b, c, 23}, and the same general arguments are applicable to diazenido complexes.

Our interest is to explore those structural features of diazenido complexes which result from the perturbation introduced by the substituent group at N', that is we want to know how a bent NNR group will differ from NO. If we examine the orbitals on the right-hand side of Figure 5, we see that bending at N' in the *xz* plane should destabilize the bonding combination of *xz* with π_{xz}^* , $1a'$ and stabilize the antibonding combination, $2a'$. The computed behavior of these orbitals upon bending at N' is shown in Figure 6. In general the pattern which we expected is followed with molecular orbital $1a'$ destabilized by bending and $2a'$ stabilized. However, there is considerable asymmetry observed in the *xz*- π_{xz}^* antibonding orbital, $2a'$. This asymmetry is the result of mixing in a small amount of the antibonding combination of z^2 - σ NNH, **14**. It was noted in the discussion of the effects of bending the diazenido ligand that a σ orbital



was directed *trans* to the hydrogen. This orbital will interact most strongly with the z^2 orbital in geometry **15** which points the σ orbital of NNH directly at the z^2 orbital. The mixing of the antibonding molecular orbital of σ NNH and z^2 , **15**, into the *xz*- π_{xz}^* antibonding combination results in the $2a'$ orbital having a higher energy for a *trans* geometry **15** than a *cis* geometry **16**.

Now consider what happens when the molecular orbitals of Figure 6 are filled through the $2a''$ orbital to give an $\{\text{MNNR}\}^6$ complex. The three occupied orbitals are obviously not ones which strongly influence the geometry of the complex. The orbital which controls the geometry in the $\{\text{MNNR}\}^6$ case is the bonding counterpart of **15** which is more stable for **14** than **16**. Our calculations give an MNN angle of 172° for an NNR angle of 120°. As a strictly linear NNR ligand would give an MNN angle of 180°, the MNN angle should approach 180° as the NNR angle goes to 180°. The crystallographically observed angles are shown in Table II. Variations in extent of π bonding complicate matters in seeking such a correlation.

For an $\{\text{MNNR}\}^8$ complex four of the orbitals shown in Figure 6 are populated. The last two electrons enter into

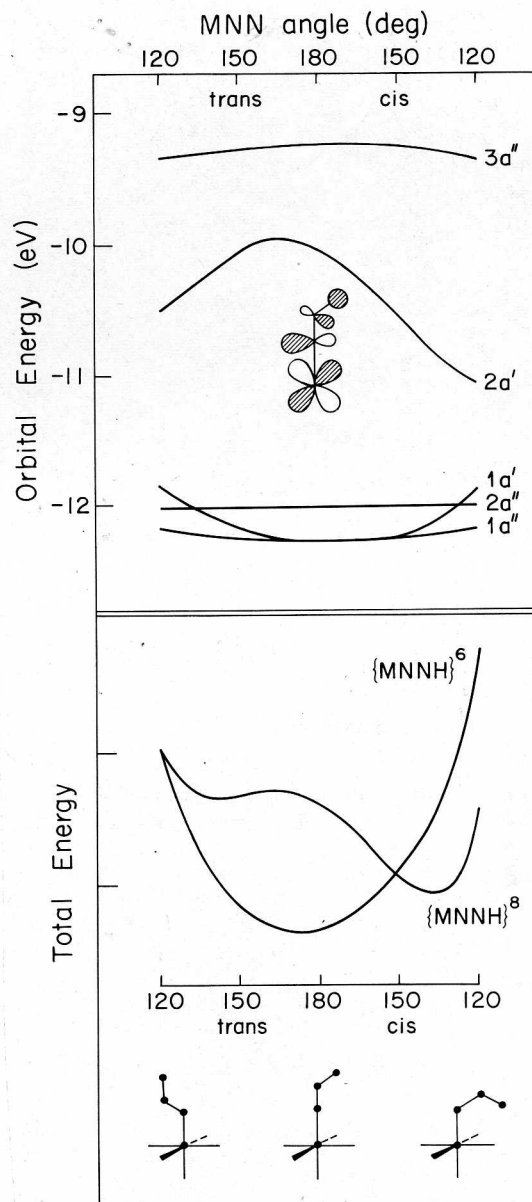


Figure 6. — Orbital energies (top) and total energy (bottom) for $\text{RuCl}_3(\text{PH}_3)_2(\text{NNH})$ bending at N'. The scale markings on the total energy graph are 1 eV apart. The two configurations are arbitrarily referred to the same energy zero at 120°.

Table II. — Angles in Diazenido Structures.

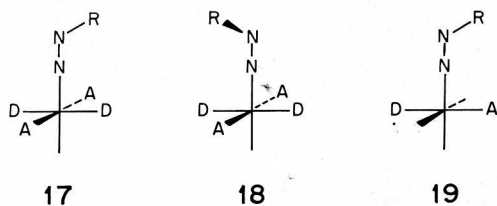
Compound	MNN Angle (°)	NNR Angle (°)	Ref.
$\text{ReCl}_2(\text{PMe}_2\text{Ph})_3(\text{N}_2\text{Ph})$	172	118	21 b
$\text{RuCl}_3(\text{PPh}_3)_2(\text{N}_2\text{PhCH}_3)$	172	137	21 c,e
$\text{MoI}(\text{diphos})_2(\text{N}_2\text{C}_6\text{H}_{11})$	176	142	21 e

the $2a'$ orbital which is antibonding between the *xz* metal orbital and the π_x^* ligand orbital. It is clear that an $\{\text{MNNR}\}^8$ complex should be doubly bent.

Another feature evident from Figure 6 is that bending at N' should favor a *cis* geometry. This *cis* preference is caused by the asymmetry of the $2a'$ orbital which has its origin in the unsymmetrical interaction of the z^2 orbital with the *trans* directed orbital of bent NNH. The only $\{MNNR\}^8$ complex whose structure is known is *trans* bent 20b . If the R group is bulky, a *cis* geometry may be precluded. There do exist cyclic six-coordinate structures in which a *cis* doubly bent arrangement is enforced by the ring constraint 24 .

ORIENTATION OF THE DIAZENIDO LIGAND

The above discussion has shown that bending at N'' is expected, whereas bending at N' depends on the electron count and the ligand set. If the metal fragment is unsymmetrically substituted by donors and acceptors, an interesting further conformational question may be raised—the preferred orientation of the diazenido ligand plane relative to the metal moiety. The interplay of inversion at N'' , bending at N' , and rotation around the $M-N'$ bond is assuredly complex, and has not been studied by us. However, by means of an analysis closely patterned on our previous considerations for the nitrosyls 10b the following conclusions concerning equilibrium geometries may be obtained: the NNH ligand should lie in the plane containing the better π donor ligands, i. e. **17** is preferred to **18**. If the diazenido group is given a choice of orienting the R group toward a π donor or acceptor, it should be directed toward the π acceptor, as in **19**.

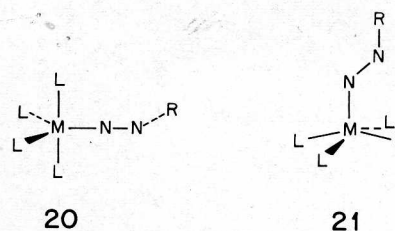


CHARGE DISTRIBUTION FOR THE DIAZENIDO LIGAND

The charge distribution for a singly bent $\{MNNR\}^6$ molecule shows a much higher electron density at N'' than at N' . For the doubly bent $\{MNNR\}^8$ complexes there are large increases in charge on both nitrogen atoms, but particularly on the nitrogen attached to the metal. Depending on the model compound chosen for the calculations, N' may be either more or less negative than N'' for an $\{MNNR\}^8$ complex. Protonation of $\{MNNR\}^6$ complexes occurs at N'' 25 and of $\{MNNR\}^8$ complexes at N' $^{20, 26a}$, but as was mentioned above this need not reflect the charge distribution in these complexes if the protonation is frontier-controlled. A recent X-ray photoelectron study of diazenido complexes supports our charge distribution conclusions 27 .

Five-coordinate diazenido complexes

Five-coordinate diazenido complexes, analogous to five-coordinate nitrosyl complexes, exhibit both square pyramidal and trigonal bipyramidal geometries. For a trigonal bipyramidal $\{MNNR\}^8$ complex, the diazenido ligand occupies an equatorial site and is singly bent, **20** 26 . The doubly bent diazenido ligand of a square pyramidal $\{MNNR\}^8$ complex occupies the axial position, **21** 28 . Again what we would like to examine are those features unique to the diazenido complexes.



SQUARE PYRAMIDAL COMPLEXES

The major difference between a square pyramidal complex and an octahedral one is the presence of the $2a'$ molecular orbital of Figure 7. This orbital arises from the $z^2-\sigma$ NNH antibonding interaction. In an octahedral complex this orbital is much higher in energy due to the other antibonding interaction of the z^2 orbital with the σ orbital of the sixth

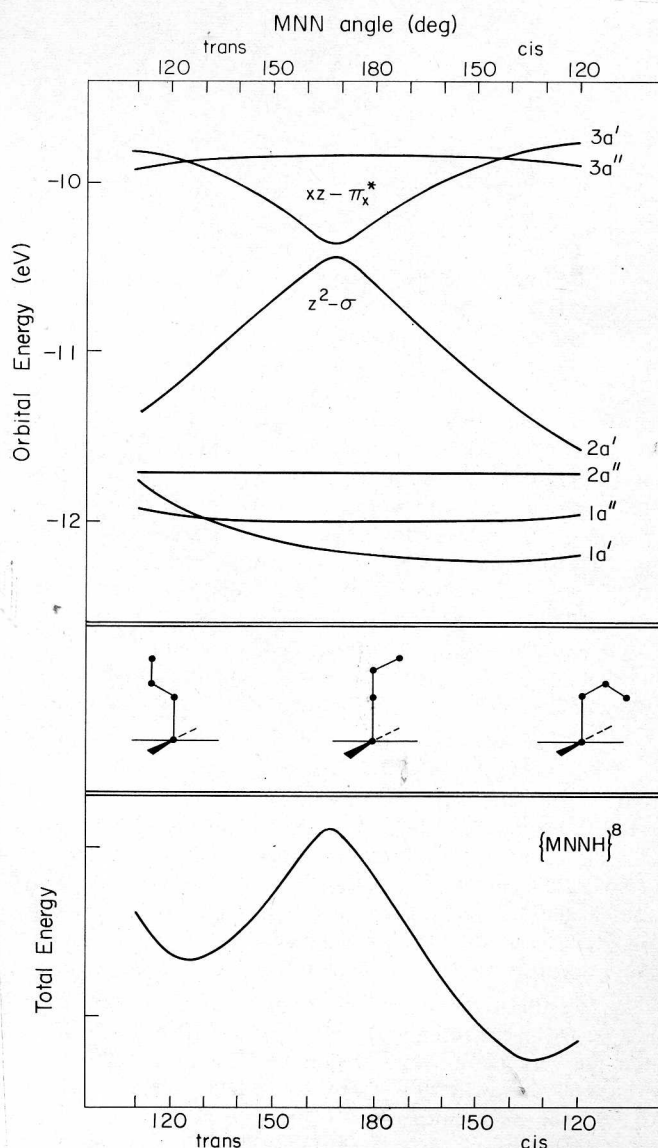
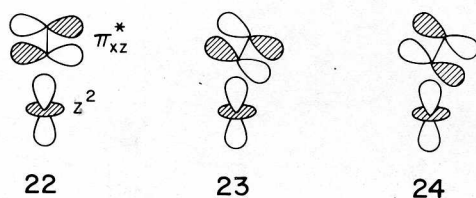


Figure 7. — Orbital energies (top) and total energy (bottom) for a model $\text{IrCl}_4(\text{NNH})_2^-$ bending at N' . The scale markings on the total energy graph are 1 eV apart.

ligand. The presence of this low-lying z^2 - σ NNH antibonding orbital of the same symmetry as the xz - π^* antibonding orbital results in a strong mixing of the two.

The energy of the molecular orbitals as a function of the MNN angle is shown in Figure 7. As expected, the three a' orbitals which are orthogonal to the plane of the bending are only slightly affected. The greatest change in energy occurs for the $2a'$ and $3a'$ molecular orbitals. To understand the behavior of these two orbitals upon bending we must first realize that part of the behavior of these orbitals is due to the xz - π^* antibonding interaction just as for an octahedral complex (Fig. 6), and secondly that there is the interaction of z^2 with π_{xz}^* and σ NNR. As the xz - π^* interactions have been discussed for octahedral complexes, we will focus on the z^2 - π^* and z^2 - σ interactions.

The z^2 and π_{xz}^* orbitals are nearly degenerate, accidentally so, at MNN 180° . Both orbitals are drawn in **22**. It might



seem that these orbitals should not interact. In fact they do so, albeit in a minor way, because the actual symmetry of the molecule is low. Both transform as a' . As the MNN angle changes from 180° , z^2 and π_{xz}^* interact more obviously to form bonding, **23**, and antibonding, **24**, combinations. This interaction would lead us to expect two symmetrical curves for these two orbitals centered about an MNN angle of 180° with the antibonding combination rising in energy with bending and the bonding combination dropping in energy. Figure 7 does show roughly this behavior. However, superimposed upon this is a mixing of the antibonding combination of σ NNR with z^2 . As discussed above for six-coordinate complexes, this interaction is greatest for a *trans* geometry. The result of combining this z^2 - σ antibonding interaction with the z^2 - π_{xz}^* bonding combination is a curve like that shown in Figure 7 for the $2a'$ orbital.

We thus arrive at the same conclusion for a five-coordinate square pyramidal $\{MNNR\}^8$ complex as we did for a six-coordinate $\{MNNR\}^8$ complex. The NNR ligand will prefer to bend at both N' and N''. In our calculations bending to a *cis* geometry is preferred. The known structures ^{26b, c} are doubly bent in a *trans* fashion, but the *cis* alternative may be unavailable for the relatively bulky R groups studied. We look forward to observation of a *cis* geometry for the case of some sterically undemanding substituent.

In the square-pyramidal five-coordinate complexes there is a low-lying z^2 orbital which mixes with the xz - π_{xz}^* antibonding combination upon bending. This stabilizes the $2a'$ orbital, as shown by **23**. As a result, one would expect somewhat stronger bending for square-pyramidal complexes than for octahedral complexes. This conclusion differs from that reached earlier by us for the corresponding deformation in nitrosyl complexes ^{10b}. This comes out in the calculations and is due to the different positioning of the ML_r , z^2 and NO or NNR π^* orbitals.

TRIGONAL BIPYRAMIDAL COMPLEXES

Here our starting point might have been a model $L_4M(NNH)$ system, easily constructed from the interaction of a C_{2v} ML_4 fragment and a linear NNH group. The orbitals so obtained are quite analogous to our previous study of nitrosyls ^{10b}. In order to anticipate a further analysis of an interesting structural deformation in the known $Fe(CO)_2(PPh_3)_2NNPh^+$ structure ^{26b}, let us instead choose the slightly less symmetrical model of $Fe(CO)_2(PH_3)_2NNH^+$. For a linear NNH geometry the orbital ordering is given at left in Figure 8. Once again great similarities are observed between the level scheme for this molecule and the nitrosyl analogue. The two π -type orbitals of the molecule, xz and yz , are differentiated in an obvious manner by the asymmetry between axial phosphines and equatorial carbonyls.

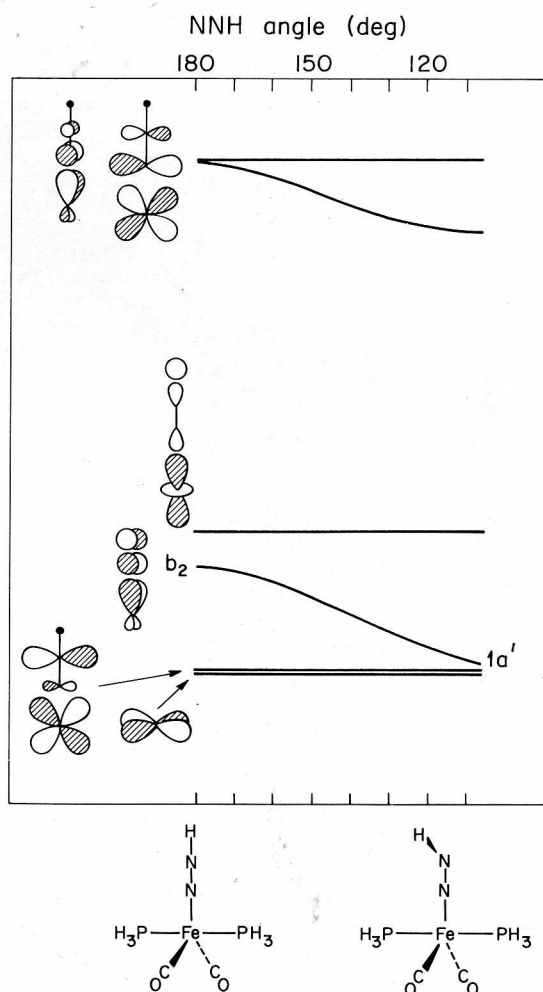
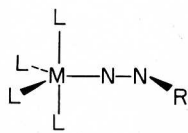
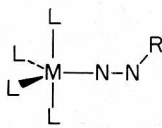


Figure 8. — Orbital energies for a trigonal bipyramidal diazenido complex bending in the equatorial plane.

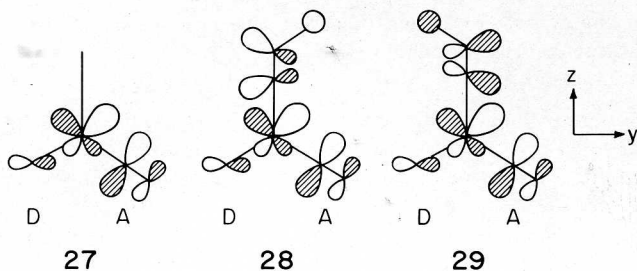
Quite analogous to the nitrosyl case ^{10b}, bending at N' is a deformation that is much less favored in the trigonal bipyramid than in the square pyramid. Our model calculations keep the MNN angle close to 180° for bending either in the axial or the equatorial plane. Figure 8 also shows the evolution of the levels with bending at N''. This bending is strongly favored, for reasons which are much the same as we analyzed for the six-coordinate complex. Indeed, the tendency to bend at N'' is even greater in the trigonal bipyramid.

In previous discussion of five-coordinate complexes it has been pointed out that the best π interactions in a trigonal bipyramidal complex are available in the equatorial plane¹⁰. In principle the singly bent NNR fragment has the option of orienting itself so that the R substituent lies either in the equatorial plane **25** or in the axial plane **26**. For those trigonal

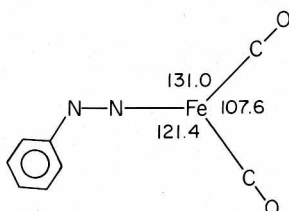
**25****26**

bipyramidal complexes whose structures have been determined^{26b, c, 29}, the diazenido ligand lies in the equatorial plane as in **25**. This orientation is the one which allows the best acceptor orbital, the π^* orbital in the plane of the bent NNR ligand, to interact with the best π donor orbital of the metal, the equatorial yz orbital. The orientational preference is calculated to be fairly large (0.3 eV).

In a trigonal bipyramidal complex with a π acceptor and a π donor in the equatorial plane, the diazenido ligand should direct its substituent toward the π acceptor. The polarization of the yz fragment molecular orbital **27** by the π acceptor and donor substituents causes orientation **28** to be preferred to **29**, since the σ -NNH interaction with yz is a repulsive one. Orientation **28** allows the σ NNR orbital to lie near a nodal plane.

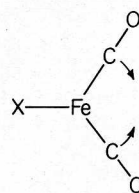
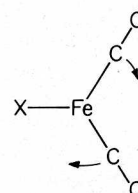
**27****28****29**

In addition to the questions concerning bending at N' and N'' and the orientation of the NNH fragment with respect to the metal fragment, it is also interesting to examine one other structural distortion that is observed for trigonal bipyramidal complexes. The observed angles in the trigonal plane of $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\text{NNPh})^+$ are indicated in structure **30**^{26b}.

**30**

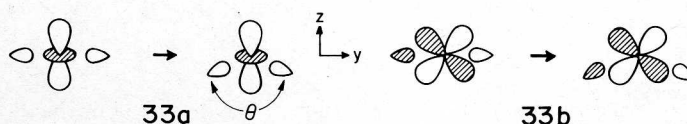
The angular deformations are interesting, in their asymmetry, and in the fact that the smaller N-Fe-C angle is *cis* to the R group of the diazenido ligand. Conceptually the distortion may be decomposed into a closing of the

C-Fe-C angle from 120° , **31**, followed by a rotation of the $\text{Fe}(\text{CO})_2$ fragment, **32**. Let us analyze this two-stage deformation. The first stage is produced by a strong π acceptor

**31****32**

such as the diazenido group. The geometrical parameter under discussion has been nicely used as a probe of the comparative π acceptor strength of nitrosyl, carbonyl and methylisocyanide ligands³⁰. Our analysis follows.

Let us examine what happens to the z^2 and yz orbitals of a C_{2v} metal fragment when the LML angle is varied in the trigonal plane. Moving the ligands together from 180° stabilizes the z^2 orbital, **33a**, and destabilizes the yz , **33b**.

**33a****33b**

In **33a** the ligands move from an antibonding position on the torus of the z^2 orbital to a node. At the same time the σ orbitals of the ligands move from a nonbonding position on the node of the yz orbital to a strongly antibonding position, as shown in **33b**. If a ligand equivalent to the other two equatorial ligands is placed along the z axis, the stabilization of the z^2 orbital and the destabilization of the yz orbital would produce an LML angle of 120° . However, if a π donor is placed along the z axis, then as θ decreases the yz orbital will rise more rapidly than the z^2 orbital drops and an LML angle greater than 120° should result. For a strong π acceptor ligand the yz orbital will not rise as rapidly as the z^2 orbital drops. Therefore a strong π acceptor ligand in an equatorial position of a trigonal bipyramid will cause other equatorial ligands to bend away from it.

The second distortion, the rotation of the $\text{Fe}(\text{CO})_2$ moiety about the PFeP axis in $\text{Fe}(\text{PPh}_3)_2(\text{CO})_2(\text{NNPh})^+$ towards the phenyl group of the phenyldiazenido ligand tends to

**34**

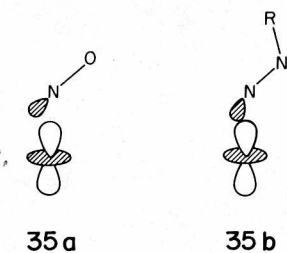
reduce the yz - σ NNR lone pair interaction **34** by placing the σ orbital more nearly on the node of the yz orbital. However, π bonding between the yz and π^* NNR orbital is lost during such a rotation and the computed preference

for the rotation of the carbonyls toward the diazenido substituent is very small (0.01 eV). Nevertheless, we think the observed deformation is a reflection of an electronic bonding effect.

The nitrosyl analogy and RNN^+ vs. RNN^-

As we have mentioned several times and as has been obvious to workers in this field for some time, there is a strong analogy between diazenido and nitrosyl complexes. Given their resemblance, it becomes interesting to pinpoint any differences.

Both $\{MNO\}^8$ and $\{MNNR\}^8$ complexes bend at N' . We would expect the diazenido complex to bend more strongly. In either case the bending is caused by a desire to reduce antibonding between metal z^2 and NO or NNR σ . Compare the two cases at some intermediate but equal MNO or MNN angle, **35a** vs. **35b**.



Because of the *trans* orientation of the σ orbital of the NNR fragment, at a given MNN angle it will have a greater (anti-bonding) overlap with metal z^2 . Accordingly we would expect that the MNNR complex would have to bend more strongly than MNO to accomplish the same amount of reduction in this repulsive interaction. A model calculation gives a 5° difference in bending. Relevant cases for a structural comparison are rare. We know of only one:

$RhLCl(N_2Ph)^+$ vs. $RhLCl(NO)^+$,

L = a tridentate phosphine ^{28b, c}. The $Rh-N-N$ angle is 125° , while $Rh-N-O$ is 131° .

It also may be worthwhile to comment at this point on the formalism which labels the ligands in the $\{MNNR\}^8$ cases as RNN^- rather than RNN^+ . Of course the same thing happens in the nitrosyl case, and in both instances we have bypassed a potential interpretative trouble spot by using the $\{MNNR\}$ notation. But it is interesting to retreat a bit and make the RNN^- assignment in the square pyramidal complexes. This assigns oxidation state III to the metal, d^6 . If this were a good picture of this type of molecule, one would expect a square pyramidal diazenido (or nitrosyl) complex to readily coordinate a sixth ligand, as is true for complexes such as $RhP_3Cl(CH_3)^+$, which will coordinate very weak donors ³¹.

The five-coordinate MNNR and MNO complexes do not show a strong tendency to pick up a sixth ligand. The reason for this may be easily seen in our molecular orbital analysis. A typical $d^6 ML_5$ fragment has a low-lying acceptor orbital ready to coordinate a sixth ligand. An $\{MNNR\}^8$ complex also has an axial acceptor orbital, $3a'$ in Figure 7, but it possesses as well a high-lying axial donor orbital, $2a'$. This orbital will raise the barrier to addition of a sixth ligand.

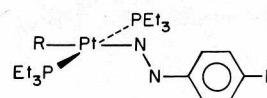
Another way in which this effect can show up is through a large *trans* influence of the nitrosyl or diazenido group,

weakening the bond opposite. This is seen in the single six-coordinate $\{MNNR\}^8$ structure available ^{20b}: Ir-Cl (*trans*) 2.48 Å vs. Ir-Cl (*cis*) 2.37 Å.

Though we are jumping a bit ahead of our order of discussion, it might be added here that when the five-coordinate doubly bent diazenido ligand is protonated at N' an acceptor orbital is formed *trans* to the diazene, $-N(H)NR$, ligand. Such six-coordinate diazene complexes should coordinate even weak donor ligands.

FOUR-COORDINATE DIAZENIDO COMPLEXES

For four-coordinate diazenido complexes only the square planar doubly bent geometry of two derivatives of the general type **36** has been confirmed crystallographically ³². We have

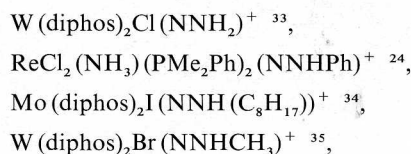


36 R = Cl, CPh

modeled this complex with $PtCl(PH_3)_2(NNH)$. The molecular orbitals are very similar to those of an octahedral complex, and we shall not repeat the arguments here. Instead we shall move on and examine briefly some of the remaining intermediates which may play a role in the reduction of octahedral dinitrogen complexes by successive protonation.

Complexes derived from the successive protonation of octahedral dinitrogen complexes

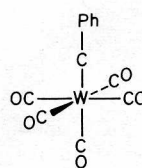
Figure 9 shows the molecular orbitals of four species possibly involved in the sequential protonation of dinitrogen to ammonia, namely octahedral hydrazido and imido complexes and six- and five-coordinate nitrido complexes. The model compounds used for our calculations are shown at the bottom of Figure 9. All of these types of molecules or their analogues have been fully characterized experimentally. For example, crystal structures are known for the hydrazido complexes



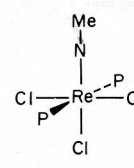
and



The complex $RuCl_3(PH_3)_2(NNH_3)^{2+}$ has analogues in carbyne **37** ³⁸ and imido complexes **38** ³⁹. There are also a number



37



38

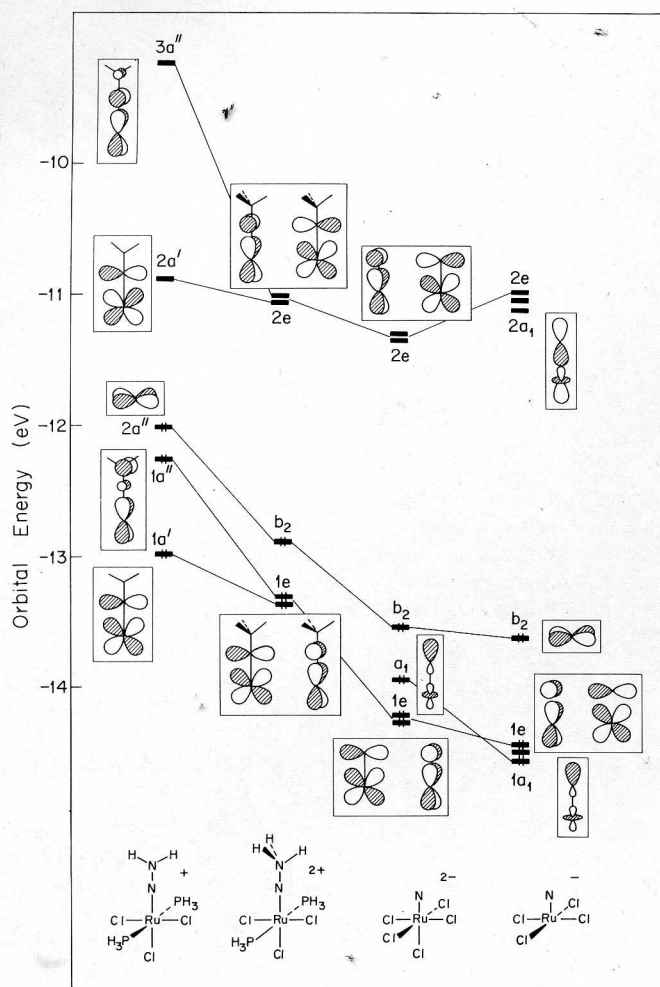
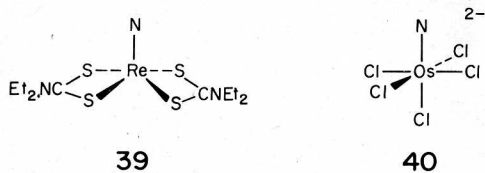


Figure 9. — The evolution of the frontier orbitals along a nitrogen reduction pathway. See text for explanation.

of well characterized five-⁴⁰ and six-coordinate⁴¹ nitrido complexes, for example **39**^{40c} and **40**.

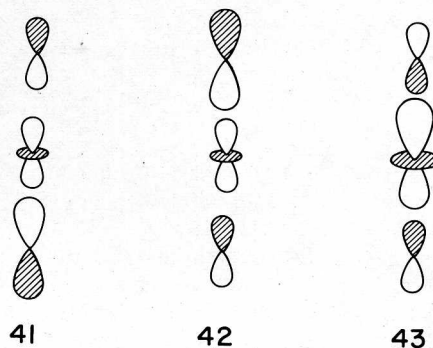
Let us proceed to analyze how one molecular orbital diagram derives from another in Figure 9 and then return



to consider briefly some of the properties of these species. Protonation of a singly bent $\{MNNR\}$ ⁶ complex (see right-hand side of Figure 5 for the molecular orbitals of such a complex) should lead to the formation of a diazenido complex. The orbitals of the latter are shown at extreme left of Figure 9. The two a' orbitals have dropped sharply in energy relative to the a'' orbitals as the hydrogen forms a strong σ bond with N'' , leaving essentially a nitrogen p orbital on N' to interact with the metal xz orbital. Protonation of the diazenido complex to form the $MNNH_3$ moiety, which is analogous to the methyl imido complex, $ReCl_3(PPh_2Et)_2NCH_3$ ^{39a, c},

restores a higher local symmetry with the xz and yz planes becoming nearly equivalent. Thus we see the two $\pi a''$ orbitals of the diazenido complex dropping in energy. These orbitals together with the a' orbitals of the diazenido complex form the two e sets of the imido complex. These orbitals are metal xz -nitrogen x and metal yz -nitrogen y bonding and antibonding combinations.

In the next stage of a hypothetical reaction ammonia is separated from the imido complex. This would leave behind a six-coordinate nitrido complex $RuCl_3(PH_3)_2N^{2+}$. To make a correspondence to the known $OsCl_5N^{2-}$ we exchange two chlorides for phosphine groups. This gets us to $RuCl_5N$, which is still two electrons short of the known Os complex. These two electrons find a place in a new orbital that appears in the scheme, a_1 in Figure 9. The a_1 orbital is descended from the nonbonding combination, **42**, of the three σ orbitals which result from mixing of z^2 with Cl and N z , **41-43**. In these complexes the a_1 orbital is localized almost entirely on the nitrogen atom and makes that center nucleophilic.

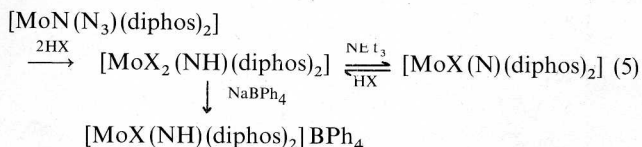
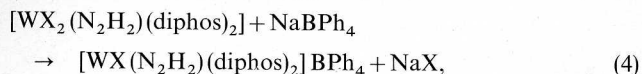
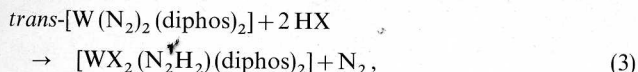


The final molecular orbital scheme in Figure 9 is for $RuCl_4N^-$, the species that would result from the removal of a chloride ligand *trans* to the nitrido ligand in $RuCl_5N^{2-}$. For this complex we note the presence of metal z^2 -nitrogen z bonding and antibonding orbitals. The bonding orbital, $1a_1$, for $RuCl_4N^-$ is somewhat lower in energy than the nonbonding orbital of $RuCl_5N^{2-}$ and has much more metal character. The antibonding combination, $2a_1$, is a relatively low energy orbital and is approximately 50% nitrogen z . Now that we have examined their molecular orbital diagrams⁴², we would like to briefly consider some of the properties and interrelation of the diazenido, diazenido, imido, and nitrido complexes.

One feature which becomes apparent when one compares the molecular orbitals of a dinitrogen complex (Fig. 1) with those of its protonated derivatives (Fig. 9) is the increase in bonding between the metal and N' . For a dinitrogen complex the only metal-ligand π bonding is the xz - and yz - π^* bonding combination, and this orbital as noted earlier is nearly nonbonding between the metal and the dinitrogen ligand. A diazenido complex has one strong metal- N' π bond and the imido and nitrido complexes have two strong π bonds in addition to the σ bond for the orbital populations shown in Figure 9. This change in bonding is reflected in the metal to nitrogen bond lengths. The M-N bond length in $Os(NH_3)_5N_2^{2+}$ ^{8b} is 1.85 Å while that for $OsCl_5N^{2-}$ is 1.61 Å⁴¹.

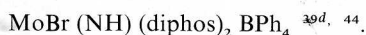
Another interesting phenomenon exhibited by diazenido, diazenido, imido, and nitrido complexes is their ability to form seven-coordinate complexes either by oxidative addition to be MNN or MN moiety or simply by coordina-

tion of a seventh ligand ^{6, 39d, 43}. For example, equations (3), (4), and (5):

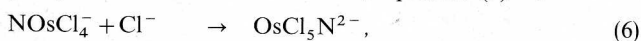


From our qualitative molecular orbital diagrams it can be seen that coordination of a seventh ligand in the xy plane would result in the promotion of electrons from the xy orbital to the xz - x or yz - y antibonding orbital. The occupation of this antibonding orbital should cause bending at N'. Such a promotion would also cause a considerable shift in electron density from the metal to N'. Alternatively, promotion of electrons to the xz - x antibonding orbital would enhance the likelihood of seven coordination if sterically possible. It should be noted that crystallographic substantiation of seven coordinate structures for these complexes is still not available and our considerations here are speculative.

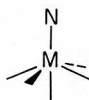
Feeding eight electrons into the molecular orbital scheme of Figure 9 of a six-coordinate nitrido complex (a d^2 configuration) should result in considerable electron density on the nitrido ligand. Consistent with this is the observed protonation of $\text{MoN}(\text{N}_3)(\text{diphos})_2$ which, following treatment with NaBPh_4 [equation (5)], gives



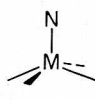
A five-coordinate nitrido complex having a d^2 configuration is filled through the b_2 orbital. This complex has a low-lying acceptor orbital of a_1 symmetry which is approximately 50% metal and 50% nitrogen z . This orbital may act as an acceptor either by coordination of a donor ligand at the metal to form a six-coordinate complex such as $\text{OsCl}_5\text{N}^{2-}$ or by reaction at nitrogen with a base such as triphenylphosphine to form a P-N bond, equation (7) ⁴⁵:



ML_4N and ML_5N complexes generally exhibit a bending of the equatorial ligands away from the nitride ligand as shown in **44** and **45**, i. e. the NML angle is normally greater

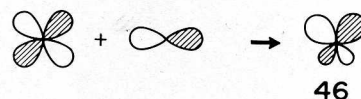


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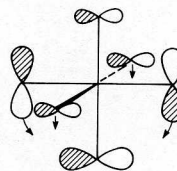
45

than 90° ^{40, 41}. For example, OsCl_4N^- and $\text{OsCl}_5\text{N}^{2-}$ have NML angles of 104.5° and ca. 96° respectively ^{40b, 41}. For both the five- and six-coordinate complexes this distortion is caused by the stabilization of an e set of orbitals upon increasing the NML angle. This e set is the bonding combination of xz and yz with x and y of nitrogen. The bending back of the ligands in the basal plane results in a mixing of the metal x and y orbitals with the xz and yz orbitals as shown in **46** to produce a hybrid which overlaps the p orbitals of nitrogen better ⁴². This distortion is opposed by

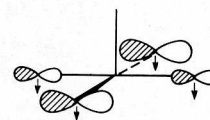


46

another set of e orbitals of lower energy, one component of which is shown by **47** and **48** for six- and five-coordinate nitrido complexes respectively. Orbital **47** is much more



47



48

strongly destabilized by bending than is **48**. The bending for six-coordinate complexes will be less than for five-coordinate complexes due to the stronger nonbonding repulsions of **47** compared to **48** ⁴⁶. For $\text{RuCl}_5\text{N}^{2-}$ and RuCl_4N^- we calculate NRuCl angles of 93° and 103° respectively.

For a five-coordinate nitrido complex the distortion of the four basal ligands away from the nitrogen atom produces a stabilization of the $2a_1$ orbital of Figure 9. This is a result of the four basal ligands which are σ antibonding with z^2 moving off its torus and toward a node. Thus the deformation should make the nitrogen a better electrophile.

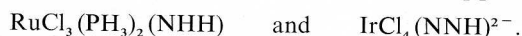
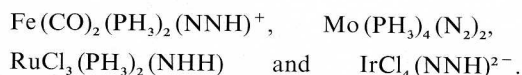
In general we have not done as complete a study of these later stages of nitrogen reduction as is merited by the importance of these reactions. We plan to return to this problem again, and probe as well the general question of the electrophilicity or nucleophilicity of a nitrido or oxido ligand and the mode of transfer of N or O to an organic substrate.

Acknowledgment

We are grateful to the members of our research group for their interest and discussion, and to J. Chatt, J. A. Ibers and T. A. George for telling us of work in progress in their groups. We also wish to thank E. Kronman for the typing and J. Jorgensen for the drawing. Our research was generously supported by the National Science Foundation through grant CHE-7606099.

Appendix

The calculations performed were of the extended Hückel type ⁴⁷ with a weighted H_{ij} formula ⁴⁸. The parameters are listed in Table III. The main group element parameters are standard ones, taken from earlier work, except for P. The metal and phosphorus H_{ii} were obtained from quadratic charge iteration on



The result was a different set of PH_{ii} 's for each compound. The variation was slight, within 0.5 eV of the values listed in Table III.

The transition metal d orbitals were taken as a linear combination of two Slater orbitals, with exponents from the literature ^{49, 50}. The metal s and p orbitals were single Slater-type functions ⁵¹.

The following geometries were used in the charge iteration, with subsequent deformations specified in the text.

Table III. — Extended Hückel Parameters.

Orbital	H_{ii} (eV)	Exponents ^a	
		ξ_1	ξ_2
H 1s	-13.60	1.300	
C	2s	-21.40	1.625
	2p	-11.40	1.625
N	2s	-26.00	1.950
	2p	-13.40	1.950
O	2s	-32.30	2.275
	2p	-14.80	2.275
Cl	3s	-30.00	2.033
	3p	-15.00	2.033
P	3s	-22.0 ^b	1.600
	3p	-13.0 ^b	1.600
Fe	4s	- 8.75	1.675
	4p	- 5.03	1.100
	3d	-12.04	5.350 (0.5505)
Mo	5s	- 7.86	1.960
	5p	- 4.82	1.920
	4d	- 9.81	4.540 (0.5899)
Ru	5s	- 8.51	2.080
	5p	- 5.09	2.040
	4d	-12.29	5.380 (0.5343)
Ir	6s	-11.36	2.500
	6p	- 4.50	2.200
	5d	-12.1	5.796 (0.6698)

^a Two Slater exponents are listed for the *d* functions, each followed in parentheses by its coefficient in the double-zeta expansion.

^b Average value, see text.

Fe(CO)₂(PH₃)₂(NNH)⁺: Fe-N 1.70 Å, Fe-P 2.26, Fe-C 1.79, C-O 1.14, N-N 1.20, N-H 0.99, NNH angle 124°.

Mo(PH₃)₄(N₂)₂: Mo-N 2.00, N-N 1.10, Mo-P 2.50, all angles at metal 90°.

RuCl₃(PH₃)₂(NNH): Ru-N 1.80, Ru-P 2.42, Ru-Cl 2.40, N-N 1.14, all angles at metal 90°.

IrCl₄(NNH)₂²⁻: Ir-Cl 2.40, Ir-N 1.98, N-N 1.17, ClIrCl angle 168°. All phosphines were idealized to a tetrahedral fragment with P-H 1.42 Å.

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