

Theoretical Study on the Bonding Nature of Transition-Metal Complexes of Molecular Nitrogen

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The bonding nature of diazomethane, diazirine, and dinitrogen complexes is studied with molecular orbital calculations and is discussed by the mode of the orbital interaction. It is ascertained that the end-on coordination of the dinitrogen ligand is more favorable than the side-on one. For the end-on coordination, it is suggested that " σ donation" is more important for the formation of the metal-nitrogen bond than " π back-donation", which mainly contributes to the weakening of the nitrogen-nitrogen bond.

Introduction

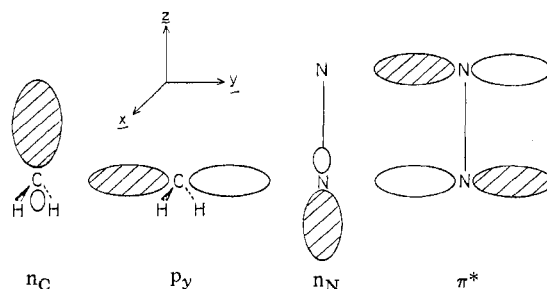
Nitrogen fixation has been one of the current topics in recent organometallic chemistry. After the synthesis of the dinitrogen complex $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{X}_2$, ($\text{X} = \text{Br}^-$, I^- , BF_4^- , PF_6^-) by Allen and Senoff,¹ a large number of dinitrogen complexes of transition metals (Fe, Co, Ni, Mo, etc.) have been synthesized and investigated. Most of them had the structure not of the side-on but of the end-on coordination, and the N-N bond of the dinitrogen ligand (N_2) was not so largely weakened in the complex, irrespective of the strong-bond formation between a metal and a dinitrogen ligand.²

The stable conformations of these dinitrogen complexes were discussed by Hoffmann et al. by use of a correlation diagram which they proposed.³ They demonstrated that the end-on coordination is more advantageous than the side-on one in some dinitrogen complexes. Recently, Vaillard⁴ carried out ab initio calculations for the dinitrogen complexes of the metals Fe, Co, Ni, and Ti and showed that the end-on coordination is more favorable than the side-on one. He also discussed the bonding nature in the end-on coordination, pointing out that the weakening of the N-N bond cannot be explained on the basis of the π back-donation only and the hybridization of the σ orbital in the N_2 ligand is important for the bonding.

In regard to the bonding nature of the dinitrogen complex, there are two kinds of important interactions between the metal (M) and N_2 (Figure 1). One is the π back-donation from the occupied d orbitals of M to the unoccupied π^* of N_2 , and the other is the σ donation from the lone pair of the latter to the unoccupied orbitals of the former. The energy gap between the occupied orbitals of M and π^* of N_2 is small, and hence this interaction is favored. On the other hand, the lone-pair orbital of N_2 is considered to lie too low to interact with the unoccupied d and sp orbitals of M. Therefore, the π back-donation has been attributed to the main origin of the metal-nitrogen bond, and the σ donation has not been considered to contribute to it so much.² It seems, however, to be insufficient to inspect the magnitude of the orbital interaction only by the energy gap, since this interaction depends on the overlapping of the molecular orbitals (MO's) as well as the energy gap. It is interesting and necessary to analyze the contribution of each interaction in order to understand the bonding nature of dinitrogen complexes. In the present paper, the general aspect of the bonding nature of the N-N and M-N bonds in the dinitrogen complex is studied by the mode of the

orbital interaction between the MO's of N_2 and those of M.

Before the investigation of the dinitrogen complexes, it seems quite suggestive to examine the bonding nature of the model compounds such as diazomethane and its geometrical isomer diazirine⁵ because these compounds show some similarities to the bonding properties of dinitrogen complexes. For example, the force constant of the weak bond between CH_2 and N_2 in diazomethane⁶ is found to be very close to that of the Ru-N₂ bond in $\text{Ru}(\text{NH}_3)_5(\text{N}_2)^{2+}$. Moreover, diazomethane is formed by the direct reaction of carbene (CH_2) and N_2 ,⁷ just as dinitrogen complexes are formed by the direct reaction of metal complexes and N_2 . In the former reaction, two electrons are regarded as being promoted from the lone-pair orbital, n_{C} , to



p_y in CH_2 .⁸ Therefore, the orbital interactions in the model compounds are considered to be very similar to those of dinitrogen complexes; i.e., the charge transfer (CT) interaction from p_y to π^* in diazomethane corresponds to the π back-donation from the occupied d orbitals of M to the unoccupied π^* of N_2 in the end-on complex. The CT interaction from the lone-pair orbital of N_2 , n_{N} , to n_{C} corresponds to the σ donation from n_{N} to the d_{z^2} and sp orbitals of M (Figure 1a). The orbital interactions in diazirine also correspond to those in the side-on complex. Therefore, diazomethane and diazirine seem to be good model compounds for understanding the essence of the bonding nature of the N-N and M-N bonds in the end-on and side-on complexes, respectively.

The first part of this paper will be devoted to the discussion of the interaction between CH_2 and N_2 by the mode of the orbital interaction. In the second part, the M-N and N-N bonding nature will be discussed by comparing the calculated

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- (8) The ground state of the carbene (1A_1) has an occupied n_{C} orbital. It is necessary, however, to promote two electrons from n_{C} to p_y in the reaction of CH_2 and N_2 . This assumption is confirmed by the state correlation diagram of this reaction.

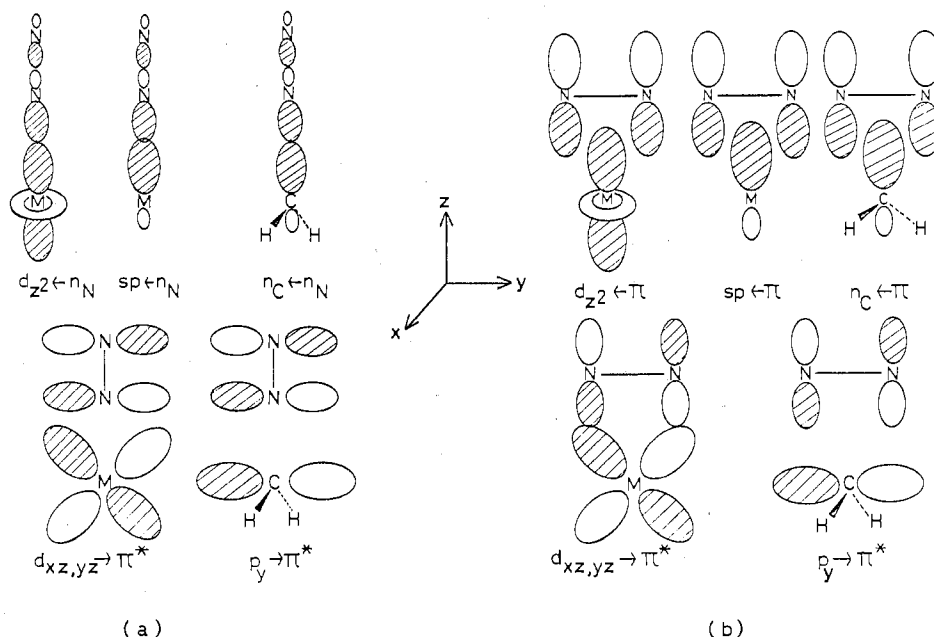


Figure 1. Schematic representation of orbital interactions in dinitrogen complexes and model compounds.

results of dinitrogen complexes with those of the model compounds. These considerations of the bonding nature will be applied to the explanation of the observed IR frequencies of some dinitrogen complexes.

Method of Calculation

The model compounds diazomethane and diazirine⁹ are calculated by the STO-3G minimal basis set. The MO's of these model compounds are transformed into the localized MO's (LMO) in order to represent the nature of the lone-pair orbital explicitly and expanded by the LMO's of N_2 and CH_2 . The bond strength is discussed in terms of the atomic bond population (ABP).

The transition-metal complexes $Ru(NH_3)_5(N_2)^{2+}$, $CoH(PH_3)_3(N_2)$, and $[(PH_3)_2Ni]_2(N_2)$ were determined by the CNDO-type semi-empirical method.¹⁰ For metals, the ionization potentials are estimated by using the data of Di Sipio et al.,¹¹ and the values of one-center Coulomb repulsion integrals are also taken from the same paper. For ligands, these parameters are taken from Hinze's work.¹² The double- ζ -type wave functions of Richardson¹³ are used for the Ni and Co complexes. The wave function of Ru defined by Hoffmann et al.³ is used here. For the ligands, overlap integrals are calculated with single Slater-type orbitals by Clementi and Raimondi.¹⁴ The E_{AB} values which are defined as the energy contribution of the A-B bond to the total energy¹⁵ are used for the measure of the bond strength. The E_{AB} value

$$E_{AB} = \sum_r^A \sum_s^B (2P_{rs}H_{rs} - 0.5P_{rs}^2\gamma_{rs}) + \sum_r^A \sum_s^B (P_{rr} - N_r)(P_{ss} - N_s)\gamma_{rs}$$

has two components which are considered to be the covalent (the first term) and the electrostatic (ES, the second term) interactions. The covalent component of E_{AB} is divided into each type interaction¹⁶ such as $E_{d_{xz,yz} \rightarrow \pi^*}$, $E_{sp \rightarrow n_C}$, and so on.

Table I. Atomic Bond Populations (ABP) and Their Differences before and after the C-N Bond Formation of the Model Compounds

	N_2	diazomethane	diazirine
N-N Bond			
π	0.424	-0.117	-0.198
σ	0.195	0.058	0.002
total	0.619	-0.059	-0.196
C-N Bond			
π		0.129	0.180 ^a
σ		0.313	0.180
total		0.442	0.360

^a This value is the sum of the ABP's of two C-N bonds.

Table II. Molecular Orbital Populations of Diazomethane and Diazirine

	diazomethane	Δ_{end-on}	diazirine	$\Delta_{side-on}$
CH_2 n_C	0.610	0.610	0.663	0.663
p_y	1.380	-0.620	1.020	-0.980
N_2 n_N	1.400	-0.600	1.952	-0.048
π^*	0.634	0.634	0.826	0.826
π	1.985	-0.015	1.413	-0.587

Although dinitrogen complexes have tertiary phosphines as ligands, we employed the PH_3 group for simplicity. However, this replacement would not give rise to the essential difference on the M-N and N-N bonding nature. Bond lengths and bond angles of dinitrogen complexes were taken from X-ray studies.¹⁷

Result and Discussion

Bonding Nature of Diazomethane. The ABP of the N-N bond in the free N_2 and those of the C-N bonds in diazomethane and diazirine are given in Table I. The differences in these values between the free N_2 molecule and the N_2 in the model compounds, $\Delta = ABP(CH_2N_2) - ABP(N_2)$, are also displayed in Table I.

The difference population of the N-N bond, Δ , gives the negative value for diazomethane (-0.059), indicating the weakening of this bond through the C-N bond formation. The

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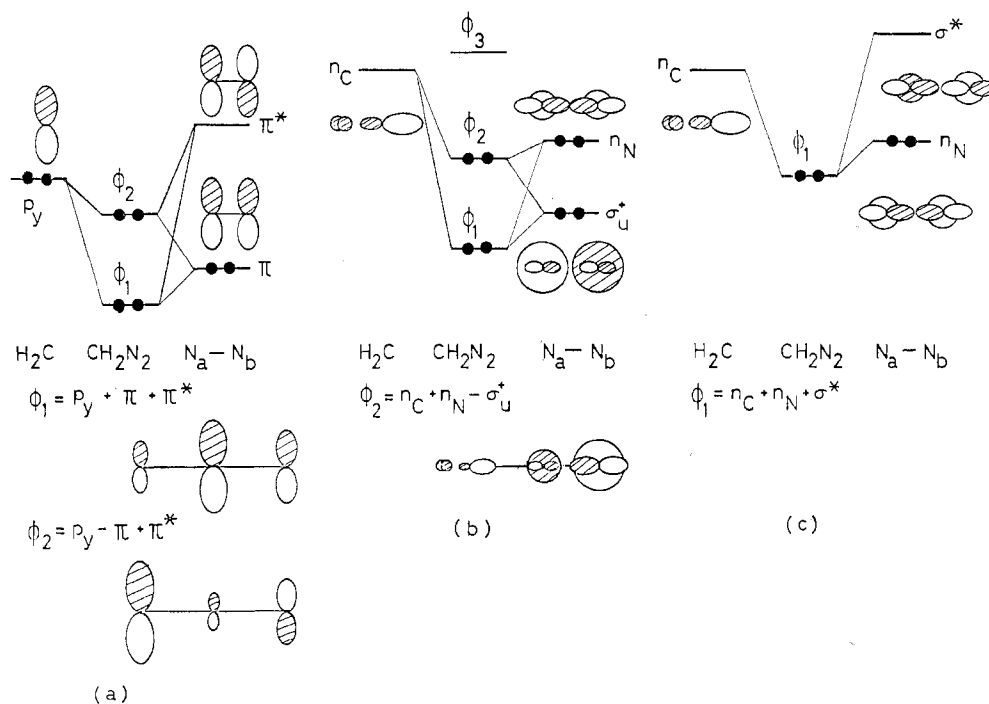


Figure 2. Schematic representation of the orbital interaction causing the σ and π back-donations in diazomethane.

σ ABP increases slightly (0.058), and the π ABP largely decreases (-0.117). The decrease of the ABP of this bond is primarily attributed to that of the π -type population. The electron densities (the molecular orbital populations) and the change of these values in some MO's before and after the C-N bond formation are listed in Table II. The change of the electron densities in n_N and π^* is considerably large ($n_N -0.600$, $\pi^* 0.634$). The decrease of the density in the former orbital is caused by the σ donation, and the increase of that in the latter is due to the π back-donation. It implies that the π back-donation is important to weakening of the N-N bond.

The change of the N-N bond strength is explained in terms of the orbital interaction. The schematic representation of the orbital interaction is shown in Figure 2. The CT interaction from p_y of CH_2 to π^* of N_2 contributes to the weakening of the N-N bond because of the antibonding nature of π^* (Figure 2a). For the CT interaction from n_N to n_C , two types of orbital interactions are considered; one is the interaction which contributes to the strengthening of the σ -bond nature because of the mixing of n_N with σ_u^+ through n_C as shown in Figure 2b. The interaction of n_C with n_N and σ_u^+ gives ϕ_1 , ϕ_2 , and ϕ_3 MO's, and the orbital mixing of n_N and σ_u^+ is considered to be the largest in ϕ_2 .¹⁸ In this orbital, n_N and n_C overlap in an in-phase manner, whereas σ_u^+ and n_C overlap in an out-of-phase fashion. Consequently, the interaction between the 2s AO of the N_a atom and the $2p_z$ AO of the N_b atom in ϕ_2 contributes to strengthening of the N-N bond. This trend is clearly shown in the change of the atomic orbital bond population (AOBP; $0.055 \rightarrow 0.138$). The other is the polarization from σ to σ^* through n_C as shown in Figure 2c. This interaction weakens the N-N bond because of the antibonding nature of σ^* . In the case of diazomethane, the former interaction is more important than the latter, since the ABP of the σ -bond nature increases.

The C-N ABP of the π -bond nature is smaller than that of the σ -bond nature (0.313 (σ) $>$ 0.129 (π)). From this trend of the ABP, the σ donation is more important to the formation of the C-N bond than the π back-donation. However, the

decrement of the p_y density due to the π back-donation (-0.620) is larger than that of the n_N density due to the σ donation (-0.600). It means that the π back-donation gives charge transfer without the effective contribution to the C-N bond formation, whereas the σ donation mainly contributes to the C-N bond formation. This is probably attributed to the fact that the overlapping between p_y and π^* is smaller than that between n_N and n_C .

Bonding Nature of Diazirine. As Table I shows, the N-N bond of diazirine is largely weakened in comparison with that of diazomethane. The origin of its weakening is of course the decrease of the π -bond nature. The π^* density of N_2 in diazirine (0.826) is larger than that in diazomethane (0.634). This is easily explained in terms of the concept of the orbital interaction. Since the overlapping between p_y of CH_2 and π^* of N_2 in diazirine is larger than that in diazomethane, the CT interaction from p_y to π^* in the former is stronger than that in the latter. The π density of the N_2 ligand of diazirine (1.413) is smaller than that of diazomethane (1.985), because in the case of the latter the CT interaction from π of N_2 to n_C of CH_2 is negligibly small due to the nodal property. The electron densities of π and π^* show that the π nature of the N-N bond in diazirine is more weakened than that in diazomethane. Therefore, the N-N bond of diazirine is more weakened than that of diazomethane. In the case of diazomethane, only the π back-donation leads to the weakening of the N-N bond, whereas in the case of diazirine the π back-donation and CT interaction from π of N_2 to n_C of CH_2 contribute to it. These CT interactions also contribute to the formation of the C-N bond of diazirine.

Configuration Analysis. In order to understand the bonding nature of these compounds more quantitatively, we carried out the method of configuration analysis.¹⁹ The results of the model compounds using the LMO's of the N_2 and CH_2 fragments are shown in eq 1 and 2 for diazomethane and diazirine, respectively. ϕ_0 stands for the adiabatically inter-

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$$\phi_{\text{CH}_2\text{N}=\text{N}} = 0.304\phi_0 + 0.273\phi_{n_N \rightarrow n_C} + 0.120\phi_{2(n_N \rightarrow n_C)} - 0.123\phi_{p_y \rightarrow \pi^*} + 0.070\phi_{2(p_y \rightarrow \pi^*)} + \dots \quad (1)$$

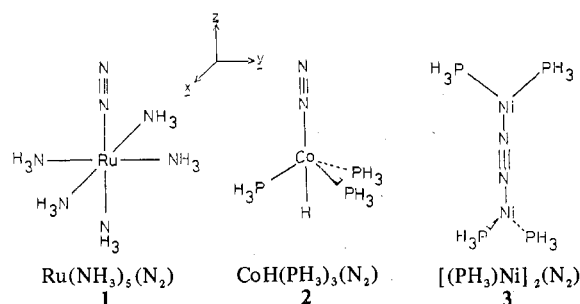
$$\phi_{\text{CH}_2\text{N}=\text{N}} = 0.233\phi_0 - 0.200\phi_{\pi \rightarrow n_C} + 0.066\phi_{2(\pi \rightarrow n_C)} - 0.268\phi_{p_y \rightarrow \pi^*} + 0.142\phi_{2(p_y \rightarrow \pi^*)} + \dots \quad (2)$$

acting configuration, $\phi_{i \rightarrow j}$ indicates the configuration in which one electron is transferred from MO i to MO j , and $\phi_{2(i \rightarrow j)}$ also indicates the configuration of two-electron transfer. It should be noted that in the present calculation the CH_2 fragment is assumed to have the doubly occupied p_y and the unoccupied n_C .⁸

Equation 1 shows that the CT interaction from n_N to n_C (σ donation) as well as that from p_y to π^* (π back-donation) is important to the diazomethane formation. The coefficients of the configuration representing the σ donation, $\phi_{n_N \rightarrow n_C}$ and $\phi_{2(n_N \rightarrow n_C)}$, are larger than those representing the π back-donation, $\phi_{p_y \rightarrow \pi^*}$ and $\phi_{2(p_y \rightarrow \pi^*)}$. The configuration analysis together with the results of ABP demonstrates that the σ donation plays a more important role in the C-N bond formation of diazomethane than the π back-donation. The π back-donation seems to contribute to mainly weakening of the N-N bond.

In the case of diazirine, the coefficients of eq 2 show that both the CT from π to n_C and the π back-donation are important to the formation of this molecule. These two interactions contribute to weakening of the N-N bond, because of the decrease of the electron density in the bonding π orbital and the increase of that in the antibonding π^* orbital. Therefore, the N-N bond in diazirine would be more weakened than that in diazomethane.

Dinitrogen Complexes of Transition Metals. $\text{Ru}(\text{NH}_3)_5(\text{N}_2)^{2+}$ (**1**) has a square-bipyramidal structure. The structures of dinitrogen complexes $\text{CoH}(\text{PH}_3)_3(\text{N}_2)$ (**2**) and $[(\text{PH}_3)_2\text{Ni}]_2(\text{N}_2)$ (**3**) are shown. Ru, Co, and Ni complexes are



formally characterized as the complexes with d^6 , d^8 , and d^{10} configurations, respectively. The calculated MO levels of the fragments²⁰ $\text{Ru}(\text{NH}_3)_5^{2+}$ and $\text{CoH}(\text{PH}_3)_3$ are shown in Figure 3. The LUMO of the Ru fragment is found to be d_{z^2} , and its HOMO is found to be not $d_{xz,yz}$ but the lone-pair orbitals of the NH_3 ligands in the equatorial plane. The order of the energy levels of the d orbitals is in agreement with that expected by the ligand field theory. The LUMO of the Co fragment is composed of d_{z^2} , $4p_z$ AO's of M and the $1s$ AO of the hydride ligand (s_H). The LUMO's of these metal fragments indicate the ability to accept electrons from the N_2 ligand to d_{z^2} of M in an end-on manner. On the other hand, in the Ni complex of d^{10} configuration its d_{z^2} is an occupied MO. The σ donation is limited to that from the N_2 ligand to sp orbitals of M.

Calculated E_{AB} 's indicating the strength of the bond A-B are given in Table III. The absolute values of the E_{NN} 's are in the order $\text{N}_2 > \text{Co}(\text{N}_2)$, $\text{Ru}(\text{N}_2) > \text{Ni}(\text{N}_2)$, being consistent

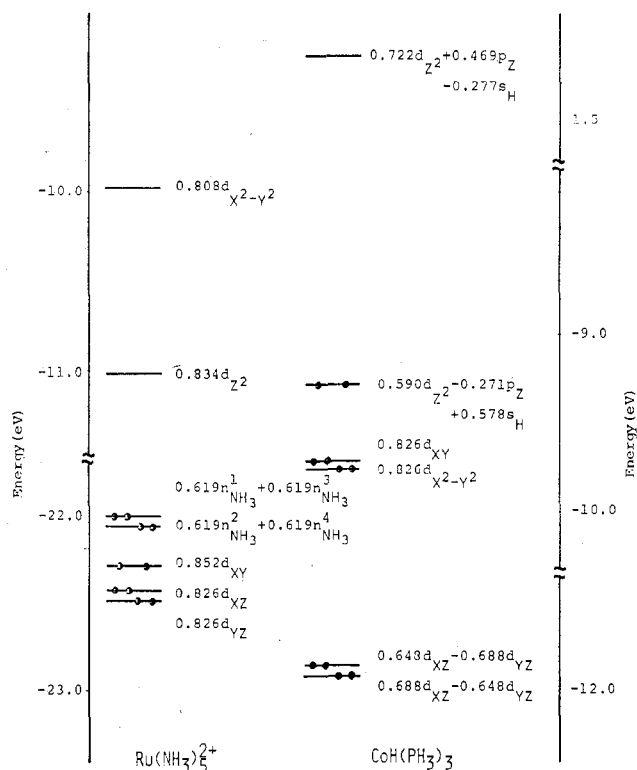


Figure 3. Upper portions of the MO energy diagram of the fragments $\text{Ru}(\text{NH}_3)_5^{2+}$ and $\text{CoH}(\text{PH}_3)_3$. $n_{\text{NH}_3}^i$ ($i = 1-4$) indicates the lone-pair orbital of the NH_3 ligand in the equatorial plane.

Table III. E_{AB} Values and Their Covalent and Electrostatic Components in Some Dinitrogen Complexes

	Ru(N_2)		Co(N_2)		Ni(N_2)Ni
	N_2	end-on	side-on	end-on	side-on
N-N Bond					
ν_{NN} , cm^{-1}	2312	2105		2105	2028
E_{NN} , eV	-59.64	-57.78	-54.16	-58.97	-54.04
π	-24.48	-23.42	-21.28	-23.56	-22.01
σ	-35.16	-34.74	-33.17	-34.93	-33.35
ES^a	0.00	0.38	-0.57	-0.38	0.14
M-N Bond					
$E_{\text{M-N}_2}$, eV		-15.52	-18.64 ^b	-21.98	-26.35 ^b
$d_{xz,yz}-\pi^*$		-0.56	-1.13	-0.57	-2.04
$d_{z^2}-n_N(\pi)$		-4.28	-3.97	-1.41	-1.32
$sp-n_N(\pi)$		-9.71	-11.09	-14.98	-14.42
$d_{z^2}-\sigma$		0.00	-1.85	0.00	-1.36
$sp-\sigma$		0.00	-6.71	0.00	-15.36
ES^a		-0.68	-1.15	-3.66	-2.06

^a See Method of Calculation. ^b This value is the sum of the E_{AB} 's of two M-N bonds.

with the tendency observed in the experimental results of the IR frequencies of the N-N bond, ν_{NN} .²¹ The π -bonding energies of the E_{NN} 's decrease by 0.92-2.48 eV, being consistent with the trend seen in diazomethane. The σ -type interaction, however, decreases in contrast with the case of the model compound. The difference can be interpreted in terms of the orbital interactions, which are schematically shown in Figure 4. In this case, there are also two types of important interactions as is considered in diazomethane. One is the polarization from σ to σ^* , which makes the N-N bond of the

(20) The MO levels of these fragments are calculated with the use of the same geometries of the parent complexes, i.e., $\text{Ru}(\text{NH}_3)_5(\text{N}_2)^{2+}$ and $\text{CoH}(\text{PH}_3)_3(\text{N}_2)$.

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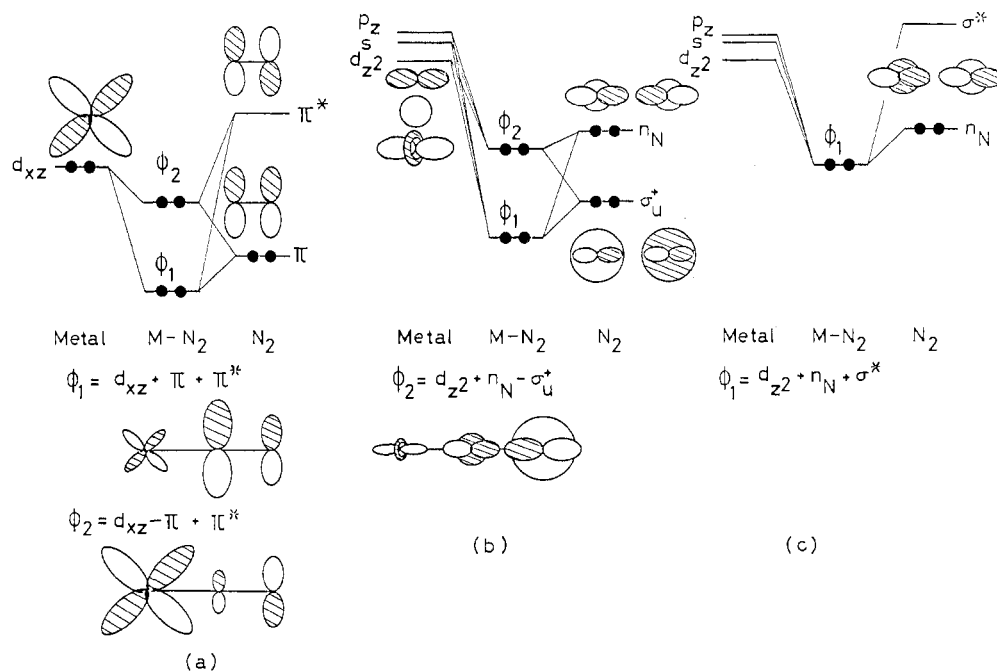


Figure 4. Schematic representation of the σ and π back-donations in the dinitrogen complex.

Table IV. Observed ν_{NN} Frequencies of Some Dinitrogen Complexes

complex	transition series ^a	no. of d electrons	ν_{NN} , cm^{-1}
$\text{Ru}(\text{NH}_3)_5(\text{N}_2)^{2+}$	2	6	2105
$\text{Os}(\text{NH}_3)_5(\text{N}_2)^{2+}$	3	6	2012
$\text{MnCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$	1	6	2100
$\text{ReCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$	3	6	1980
$\text{Rh}(\text{N}_2)\text{Cl}(\text{PPh}_3)_2$	2	8	2105
$\text{Ir}(\text{N}_2)\text{Cl}(\text{PPh}_3)_2$	3	8	2095
$\text{Os}(\text{NH}_3)_5(\text{N}_2)^{2+}$	3	6	2010
$\text{Os}(\text{NH}_3)_5(\text{N}_2)^{3+}$	3	5	2104
$\text{ReCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$	3	6	1980
$\text{ReCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2^+$	3	5	2060

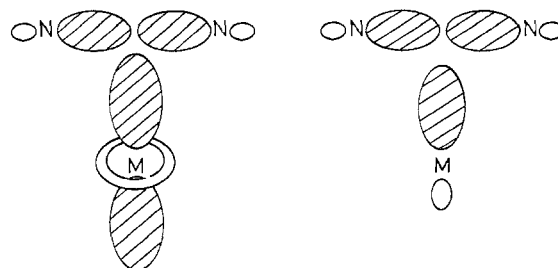
^a See ref 23.

σ nature weak (Figure 4c). The other is the orbital mixing of σ_u^+ with σ through d_{z^2} and sp , which makes this bond stronger (Figure 4b). The decrease of the absolute value of the σ nature indicates that the former interaction is more important than the latter, opposite to the result of diazomethane, whereas the σ donation influences little the N-N bond strength because the destabilization of the σ -type E_{NN} is small. Thus, the π back-donation from $d_{xz,yz}$ to π^* contributes primarily to the weakening of the N-N bond.

In the Ni complex, the decrease of the absolute value of E_{NN} is considerably large in comparison with other end-on-type complexes. This is because the Ni complex has two metal atoms which can donate electrons to π^* .

That the magnitude of $E_{d_{z^2}-n_N}$ is in the order $\text{Ru} > \text{Co} > \text{Ni}$ in the M-N bond is clearly related to the properties of the LUMO of each fragment. As previously mentioned, LUMO's of the Ru and Co fragments are mainly constructed with d_{z^2} and that of the latter one has s_H nature. The hydride ligands prevent the electron in n_N from transferring to the metal. The absolute value of $E_{d_{xz,yz}-\pi^*}$ is smaller than those of $E_{d_{z^2}-n_N}$ and E_{sp-n_N} . This result shows the importance of the σ donation to the formation of M-N bond, being agreement with that of the ABP in diazomethane. Thus, we may come to the conclusion that the σ donation is important to the formation of the M-N bond and the π back-donation plays a minor role in the bond formation.

The absolute values of the E_{NN} 's of the side-on complexes²² considerably decrease in comparison with those of the end-on ones, owing to the interactions of the types $d_{xz,yz}-\pi^*$ and $d_{z^2}, sp-\pi$. Moreover, the interactions between the π orbital of N_2 and the unoccupied d_{z^2} and sp orbitals of M make the N-N bond weaker and the M-N bond stronger as shown in 4.



4

Although the M-N bond is fairly strengthened by these interactions, experimental evidence shows that the side-on coordination is unfavorable. This result may be explained in terms of the followings: the N-N bond of the side-on complex is fairly weakened in comparison with that of the end-on one. For example, in the Ru complex the absolute values of the E_{NN} 's decrease by 1.86 and 5.48 eV for the end-on and the side-on complexes, respectively. On the other hand, those of the E_{MN} 's in the same complexes increase by 15.52 and 18.64 eV, respectively. The total stabilization energies due to the complex formation are 13.66 and 13.16 eV for the end-on and the side-on complexes, respectively. It is, therefore, expected that the end-on complex is more stable than the side-on one. In the side-on complex, the N-N bond is considerably weakened. The destabilization of the N-N bond may overwhelm the stabilization by the formation of the M-N bond. On the contrary, the small weakening of the N-N bond by the end-on coordination is made up for by the gain of the relatively large M-N bonding energy which is mainly caused by the σ donation. The same trend is seen in the Co complex. Thus, the

(22) The geometries of the side-on complexes are assumed. The distance between M and the center of N_2 is same as the M-N distance in the end-on complexes, and the other factors are the same in the geometrical isomers.

end-on coordination is more favorable than the side-on one. Hereafter, the former coordination will be discussed by comparing the theoretical consideration with experimental data.

Comparison with Experimental Results

As a result of the present considerations, it is found that both the σ donation and the π back-donation contribute to the formation of the M-N bond, and the former is more important than the latter. Furthermore, the weakening of the N-N bond due to the formation of the dinitrogen complex is found to be ascribable to the π back-donation. Therefore, it is considered that the observed ν_{NN} values are primarily related not to the strength of the M-N bond but to the magnitude of the π back-donation.

The magnitude of the π back-donation is clearly related to the energy levels of the d orbitals of the central metal atom. Since these values are, in general, parallel to the transition series $3d < 4d < 5d$, the N-N frequencies, which may be expected by the strength of the π back-donation, are parallel to the transition series.²³ Experimental results reported so far are summarized in Table IV, in which complexes are coordinated with the same ligands but are changed by the central atoms of the same group of the different transition series. In the $\text{M}(\text{NH}_3)_5(\text{N}_2)^{2+}$ -type complexes²¹ (M = Ru, Os), the ν_{NN} 's decrease in the order Ru (4d) > Os (5d), and other pairs of the dinitrogen complexes indicate the same trend, being consistent with the present prediction. Moreover, the Os(III) complex is a weaker electron donor than the Os(II) complex. The former has a strong N-N bond in comparison with the latter. The same result is seen in the Re complexes.

While the N-N bond strength has the parallel relationship with the transition series, the M-N bond strength is not so simple, because this is affected by the contribution from the π back-donation as well as the σ donation even though the bond itself is formed mainly by the σ donation. For example, the M-N bond in $\text{Os}(\text{NH}_3)_5(\text{N}_2)^{2+}$ is stronger than that in the Ru analogue.²⁴ It may be attributed to the larger π

back-donation of the Os complex. On the other hand, a complex, $\text{Fe}(\text{Et}_2\text{PC}_2\text{H}_4\text{PET}_2)_2\text{H}(\text{N}_2)$, has been synthesized, but the Ru and Os analogues have not been done yet.² It is considered that there is not σ donation enough to form the stable Os or Ru complex, probably because of the higher energy levels of the unoccupied d_z or sp orbitals of metals owing to the electron transfer from $\text{Et}_2\text{PC}_2\text{H}_4\text{PET}_2$ ligands.

Concluding Remarks

In the present work, the dinitrogen complexes of transition metals are investigated in terms of the MO calculations and the mode of orbital interactions. The calculated results, in the light of experimental data reported so far, suggest the following.

(1) Both the σ donation and the π back-donation are related to the formation of the metal-nitrogen bond in dinitrogen complexes. The former interaction is more important to it than the latter one. The π back-donation contributes to the weakening of the N-N bond.

(2) The N-N bond of the side-on complex is appreciably weakened because of the electron donation from the bonding π orbital and σ orbital of the N_2 ligand to the unoccupied MO's of the metal. Moreover, there is the electron acceptance from the occupied MO's of the latter to the antibonding π^* of the former. Therefore, the end-on coordination is considered to be more advantageous than the side-on one. The weak N-N bond in the side-on complex indicates that the N_2 ligand in this type complex is fairly activated. It may be suggested that the reduction of the coordinated nitrogen molecule proceeds through this activated form.²⁵

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(23) The first transition series is that of metals which have 3d valence orbitals. The second and third ones are those of metals with 4d and 5d valence orbitals, respectively.

(24) The IR absorption band near 500 cm^{-1} is assigned to the M-N stretching frequency in $\text{M}(\text{NH}_3)_5(\text{N}_2)^{2+}$ even though it may couple with other metal-ligand stretching modes. Moreover, the dissociation energy of the M-N bond in the Os complex is larger than that in the Ru one. These facts show that the M-N bond in the former is stronger than that of the latter.

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Group 6 Transition-Metal Complexes of Two Macrocycles Containing Tertiary-Phosphino and -Amino Ligating Sites¹

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Group 6 transition-metal carbonyl complexes of the macrocyclic ligands *cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (**1**, 11- P_2NPh) and *cis*-2,10-diphenyl-6-methyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (**2**, 11- P_2NMe) have been synthesized from the metal hexacarbonyls and the macrocycles by thermolysis. Ligand **1** gives only the tetracarbonyl, whereas **2** yields the *fac*-triacarbonyl via the corresponding tetracarbonyl species. The complexes have been characterized by using ^1H , ^{13}C , and ^{31}P NMR, as well as IR spectroscopy.

The synthesis and chemistry of phosphine complexes of the group 6 transition-metal carbonyls have received considerable

attention over the years, as indicated by several reviews.² We recently described the synthesis and structure of a number of