smaller than that by nitrogen or oxygen donors.

The *g* values of Cu(II) complexes with sulfur donors are relatively small under the square-planar symmetry. The stabilization of SOMO achieved by the distortion of the copper environment results in the large *g* values in spite of the small contribution of a d orbital in SOMO. The existence of the Cu–S bond in the distorted ligand field is the origin of the small $A_{\parallel}$ value.

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Registry No. $Cu(NH_3)_6^{2+}$, 14946-73-7; $Cu(P2A-H)_2$, 15170-36-2; $Cu(MNT)_2^{2-}$, 19562-26-6; $Cu(14\text{-ane-}S_4)^{2+}$, 57673-86-6.

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Theoretical Study on Dinitrogen Complexes. Change of the Electronic Structure of the N_2 Moiety due to Protonation

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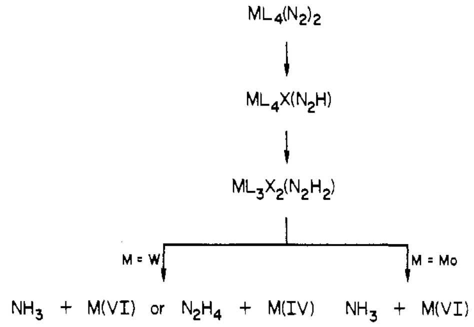
This paper concerns the effect of protonation to dinitrogen complexes. It is ascertained that protonation causes a remarkable rearrangement of the electron distribution of N_2 complexes. The d_π orbital as HOMO is one of the most characteristic features of the Cr complex. This orbital relates to the charge transfer from the N_2 moiety to the hydrogen 1s orbital as well as to the large protonation energy. The d_π–π^* type polarization is also effective in forming the N–H bond. The change of atomic bond population of the Cr–N and N–N bonds due to protonation is consistent with the experimental results that the M–N bond is strengthened and the N–N bond is weakened by protonation.

Introduction

Since the first dinitrogen complex (N_2 complex) was synthesized,[1] one of its main purposes for chemists has been to reduce the nitrogen molecule under mild conditions by use of transition-metal complexes. It is, however, difficult to reduce them to NH_3 and N_2H_4 because the N–N bond is not largely weakened by coordination.[2] In 1972, Chatt et al. succeeded in reducing N_2 complexes to protonated ones, $M(dppe)_2X_2N_2H_2$ (M = Mo or W, dppe = $PPh_2CH_2CH_2PPh_2$, and X = Cl or Br).[3] Subsequently, similar complexes, $ML_2(N_2H_n)$ (L = dppe, etc., n = 1 or 2; hereafter, they are represented by N_2H and N_2H_2 complexes, respectively),[4,5] were synthesized by using different ligands and reaction conditions. Moreover, Chatt et al. found that NH_3 was given by the treatment of $ML_4(N_2)_2$ (M = Mo or W, L = $PMePh_2$ or PMe_2Ph) with H_2SO_4 in alcoholic solution.[6] They also found that W complexes produce both NH_3 and N_2H_4 with high yields. They proposed two different mechanisms for the reactions:



Using HCl as acid, Takahashi et al.[7] obtained N_2H_4 as well as NH_3 from Mo dinitrogn complexes. In both cases, N_2H and N_2H_2 complexes were considered as important intermediates for the formation of the reduction products.

Crystallographic analysis of these protonated complexes showed that the MNN fragment was almost linear and hydrogen atoms were attached to the terminal nitrogen (N_T).[8] They usually have a longer N–N bond by ca. 0.2 Å and a shorter M–N bond by ca. 0.2 Å than those of parent dinitrogen complexes. These results suggest that the nature of the N_2 complex is largely changed by protonation. Therefore, it is very interesting to investigate the change of the electronic structure in the N_2 moiety because it will influence the reaction mechanism. It is known that this trend is well described by molecular orbital (MO) calculations. Dubois et al.[9] discussed the stable conformation of the N_2H fragment by use of extended Hückel calculations. However, they did not discuss

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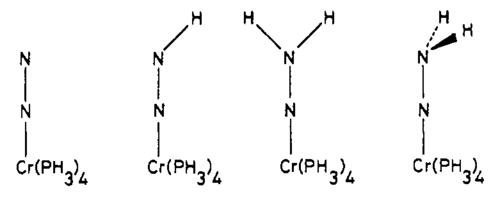

1 2 3 4

Figure 1. Geometries of model complexes calculated. The $Cr(PH_3)_4$ moiety has C_4 symmetry.

the relation between protonation and the reduction mechanism. A more sophisticated method should be used in order to describe the nature of transition-metal complexes more accurately and to discuss the reduction mechanism.

The present paper is a theoretical study on the electronic structures of dinitrogen complexes and their protonated derivatives by use of an ab initio method. Cr complexes, employed for the sake of the simplicity of calculations, are good model compounds for Mo(0) and W(0) complexes since they all have d^6 configurations. Moreover, it has been ascertained that a nitrogenase with Cr or W instead of Mo at the active site shows similar activity.[10] The bonding nature of M–N and N–N bonds of protonated complexes is discussed in comparison with that of the original dinitrogen complex. Configuration analyses have been performed in order to understand the change of electron distribution more quantitatively.[11] The protonation energies of N_2 and N_2H complexes are discussed on the basis of the energy decomposition technique.[12]

Method of Calculations

LCAO–MO–SCF calculations are carried out with the GAUSSIAN-76 program[13] and subroutines of the IMSPAK program.[14] The Gaussian basis set of Cr (12s6p4d) given by Roos et al.[15] is contracted to [5s2p2d], and p-type orbitals ($\zeta = 0.25$) are added in order to represent 4p orbitals. STO-3G minimal basis sets including the program are used for ligand atoms.

Geometries of model complexes, which have five ligands for the simplicity of calculations, are shown in Figure 1, where the metal fragment, $Cr(PH_3)_4$, has the C_4 symmetry. Two nitrogen atoms are on the z axis, and lengths of Cr–N (1.774 Å) and N–N (1.162 Å) bonds, which are optimized in the Cr dinitrogen complexes, are taken to be the same in all complexes. Those of Cr–P and N–H bonds are 2.53 and 1.05 Å, respectively. The NNH angle is fixed at 120.0°. Moreover, $Cr(PH_3)_4ClN_2H$ and $Cr(PH_3)_4ClN_2H_2^+$ complexes (Cr–Cl = 2.4 Å) are also calculated in order to estimate the effect of the trans ligand.

Results and Discussion

N_2 Complex. In our previous paper,[16] it was concluded that the π back-donation mainly contributed to the weakening of the N–N bond and the σ donation played a major role in the formation of the M–N bond. The same trend is obtained for the complex. Table I summarizes the total energies (TE), total atomic charge (TAC), atomic bond populations (ABP), and atomic orbital bond populations (AOBP) calculated for N_2, N_2H, and N_2H_2 complexes. The d_σ AOBP in the table is the sum of those such as d_{z^2}–$2s2p_z$ and $4s4p_z$–$2s2p_z$. The d_π AOBP is that of d_{xz}–$2p_x$ or d_{yz}–$2p_y$, where d, 4s4p orbitals are AO's of the central metal. The 2s and 2p orbitals are those of the

Table I. Total Energies, ABP, AOBP, and TAC Calculated for Model Complexes[a]

	$Cr(PH_3)_4N_2$	$Cr(PH_3)_4N_2H$	$Cr(PH_3)_4N_2H_2$
TE	−2509.90447	−2503.46499	−2503.81212
TAC Cr	24.048	23.490 (23.497)	23.330 (23.404)
N	7.103	7.267 (7.310)	7.135 (7.153)
N	7.222	7.210 (7.247)	7.179 (7.202)
H		0.858 (0.913)	0.700 (0.730)
ABP Cr–N	0.147	0.245 (0.239)	0.185 (0.173)
N–N	0.550	0.475 (0.465)	0.481 (0.469)
N–H		0.289 (0.277)	0.338 (0.340)
AOBP d_σ	0.117	0.207 (0.211)	0.170 (0.131)
$d_{\pi x}$	0.043	0.072 (0.061)	0.042 (0.035)
$d_{\pi y}$	0.043	0.010 (0.012)	0.021 (0.029)
σ	0.234	0.325 (0.285)	0.299 (0.317)
π_x	0.164	0.006 (−0.009)	−0.002 (0.011)
π_y	0.164	0.168 (0.191)	0.194 (0.157)

[a] Abbreviations used in this table: TE, total energy (in au); TAC, total atomic charge; ABP, atomic bond population; AOBP, atomic orbital bond population.

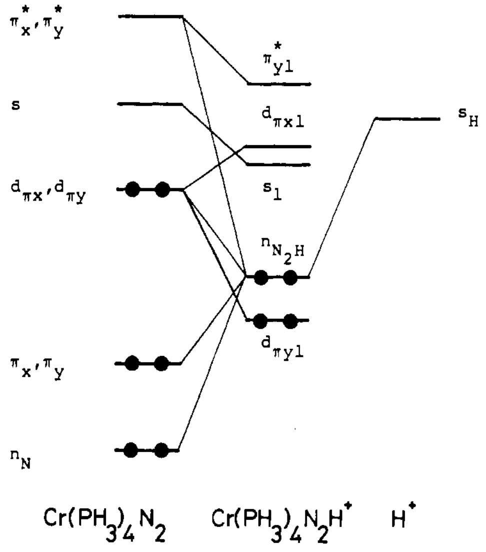

Figure 2. MO diagram of $Cr(PH_3)_4N_2$.

nitrogen atom attached to the central metal, N_A. The former is the contribution of the σ donation to the Cr–N bond strength and the latter is that of the π back-donation. The d_σ AOBP (0.117) is larger than that of d_π (0.086), which means that the former is more effective in the Cr–N bond formation than the latter. For the N–N bond, AOBP of the σ bond (0.234) increases, whereas that of the π bond (0.164) decreases in comparison with those in the nitrogen molecule (AOBP's of σ and π are 0.195 and 0.212, respectively). The TAC's of the N_2 complex are 24.048, 7.103, and 7.222 for Cr, N_A, and N_T,respectively. This indicates that the N_2 ligand is overall negatively charged, consistent with results of XPS, dipole moment, and other measurements.[2c]

The position and direction of the first protonation to the N_2 ligand is largely influenced by specific MO's of the N_2 complex. As a proton electrophilically attacks the N_2 ligand, either HOMO or the lone-pair orbital, n_N, are involved. In the present case, the HOMO of **1** is not n_N but d_π as shown in Figure 2, and these orbitals are shown in Figure 3. The n_N itself lies under d_π by 0.34 au. Moreover, the orbital spreads out along the z axis while the $d_{\pi x}$ HOMO has a large p_x coefficient of N_T. Therefore, the protonation along the CrNN axis seems to be difficult. It is then suggested that the first proton attacks the N_2 ligand not along the Z axis but from the slanting direction.[17] Indeed, the NNC angle in Mo-

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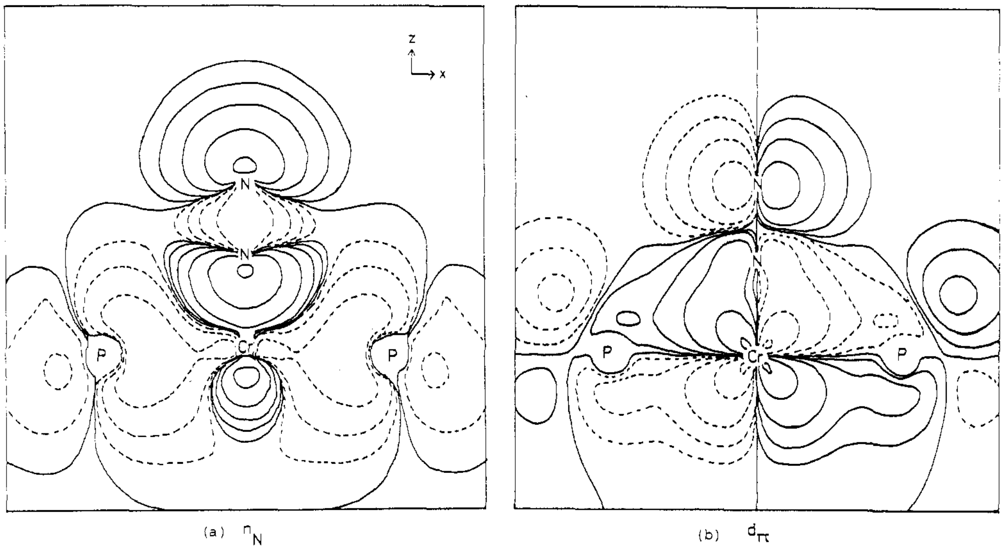

(a) n_N (b) d_π

Figure 3. MO's related to the direction of the first protonation: (a) n_N and (b) d_π. The N_2 complex has two d_π orbitals, $d_{\pi x}$ and $d_{\pi y}$, which are in the *xz* and *yz* planes, respectively. Dashed and solid lines indicate negative and positive signs of the wave functions, respectively.

$(dppe)_2(N_2C_6H_{11})$ is 142.8°.[8b]

N_2H Complex. It is known that one N_2 ligand in $M(dppe)_2(N_2)_2$ is replaced with a halogen ligand to form protonated complexes, $M(dppe)_2X(N_2H)$ or $M(dppe)_2X(N_2H_2)^+$.[2c] Therefore, it is necessary, at this point, to estimate the effect of the trans ligand for the change of the electronic structure in the N_2H and N_2H_2 moieties of these complexes. Values in parentheses of Table I are those calculated for complexes with a chlorine atom as the trans ligand. The d-electron configuration of the N_2 complex is calculated to be the d^6 one, which is consistent with that expected by the ligand field theory. The table shows that the difference between values of complexes with and without the ligand are within ~0.1. Moreover, in both cases, the d_{xz} orbital largely loses its electron density by protonation in the *xz* plane.[18] It is considered that the trans ligand does not have a large influence on the electron distribution in N_2H and N_2H_2 moieties. The ability of the Cl ligand to transfer electrons to the central metal plays a role in the third or fourth protonation. However, it seems to be possible to discuss the bonding nature of the CrN_2H_n fragment on the basis of results without including the effect of the trans ligand. Therefore, for the discussion about the change of the electron distribution and further calculations, the trans ligand is omitted for the simplicity of calculations.

Several changes in the bonding nature of the N_2 moiety are caused by protonation. Table I shows that the ABP of the N–N bond decreases (from 0.550 to 0.475) and, in contrast, that of the Cr–N bond increased (from 0.147 to 0.245). In the N–N bond, AOBP's of σ and π_y in **2** are larger than those of **1**. On the other hand, that of π_x in the former is very small in comparison with that in the latter. This means that the π bond in the *xz* plane disappears due to protonation. The increase in the AOBP by the formation of the N–H bond is accompanied by the weakening of the N–N bond. This is mainly attributed to the large decrease of the π-type AOBP in the plane. In the Cr–N bond, AOBP's of d_σ and $d_{\pi x}$ increase while $d_{\pi y}$ decreases. The increase in the former two terms is, however, larger than the decrease of the latter. The bond is thus strengthened by protonation.[19] These results mean that the N–N bond is lengthened and the M–N one is shortened. Such a trend is actually found in the crystallographic data. For example, bond lengths in $Mo(dppe)_2(N_2)_2$ are 2.014 and 1.118 Å, respectively.[20] Those of $MoF(dppe)_2N_2H$ are 1.76 and 1.33 Å, respectively.

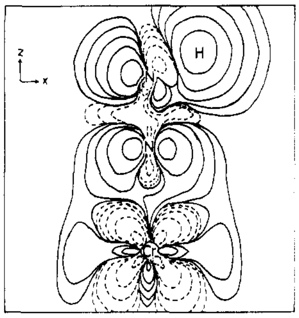

Figure 4. Difference density map between N_2 and N_2H complexes. Dashed or solid lines indicate the decrease or increase, respectively, of the electron density due to protonation.

It should be noted that a large amount of electron density on H (0.858) is transferred from the N_2 moiety. Such a large density on the hydrogen atom contributes to the formation of the N–H bond. In fact, the ABP between N_T and H (0.289) is close to that in NH_3 (0.321), and the stabilization energy of the protonation is larger than those of N_2 or NH_3 as discussed later. It is, therefore, considered that there exists a strong N–H bond in the complex in comparison with that formed by protonation to other nitrogen donors. In any case, the formation of the bond results in the rearrangement of the electron density in the N_2 moiety. This trend is well described by the difference density map between N_2 and N_2H complexes as shown in Figure 4. There are two regions where electron density decreases: in d_{xz} of Cr and around the N_2 ligand. On the other hand, that around H^+ attached to N_T increases, and a lone-pair orbital grows up in the opposite site of the proton. The electron density in d_{xz} of Cr or the lone-pair orbital of the N_2 ligand is transferred to H^+ in the formation of the lone-pair orbital at N_T. The π–π^* type polarization is also expected by the decrease of the π-electron density in the N_2 ligand. So that the change of the electron density caused by protonation might be analyzed in more detail, the configuration analysis has been performed for the N_2H complex by dividing

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(18) The trend obtained for the N_2H complex with five ligands is unchanged from that where the ligands are omitted. Therefore, the results of the simple calculations are qualitatively reliable.

(19) The change of ABP between the metal and ligand atoms does not always show that of the bond strength between them. In the case of the complexes calculated here, the trend of ABP is consistent with the fact that the M–N bond length is shortened by protonation.

(20) Uchida, Y.; Hidai, M.; Kodama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2883.

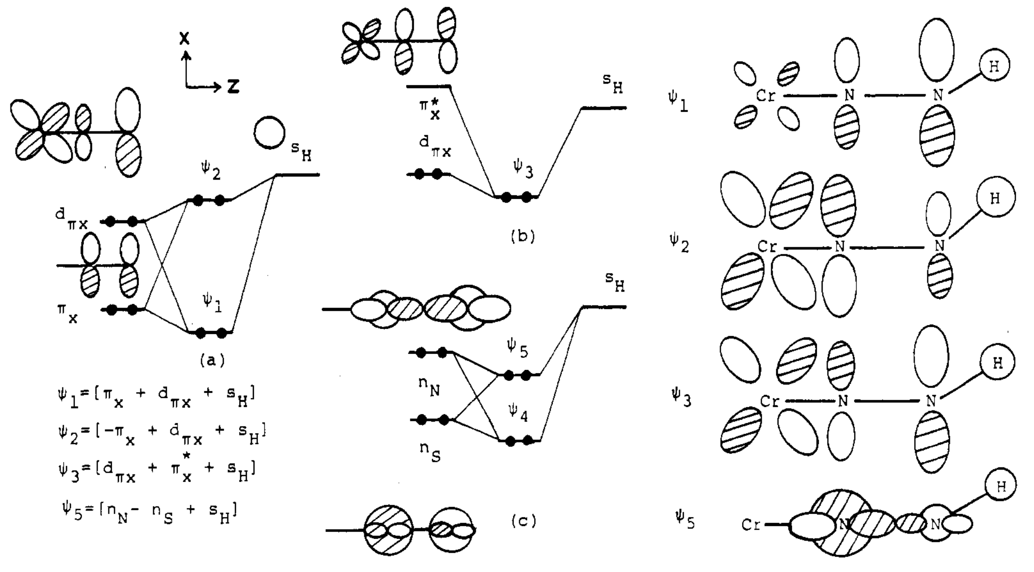

Figure 5. Schematic representation of orbital interactions between the N_2 moiety and H^+.

it into two parts, H^+ and the N_2 moiety. The results of configuration analysis are represented in eq 1[21]

$$\Phi_{N_2H} = 0.118\Phi_0 - 0.236\Phi_{d_{\pi x}-\pi^*_x} + 0.221\Phi_{d_{\pi x}-s_H} + 0.198\Phi_{d_{\pi x}-s_H, d_{\pi x}-\pi^*_x} + 0.146\Phi_{2(d_{\pi x}-\pi^*_x)} + 0.126\Phi_{2(d_{\pi x}-s_H)} \quad (1)$$

where

$$d_{\pi x_1} = 0.762 d_{\pi x} + 0.566\pi^*_x + ... \quad (2)$$

$$n_{N_2H} = 0.606 d_{\pi x} - 0.508\pi^*_x - 0.349 s_H - 0.260 n_N - 0.220\pi_x + ... \quad (3)$$

Equation 2 shows that $d_{\pi x_1}$, an unoccupied MO in 2, is mainly constructed with $d_{\pi x}$ and π^*_x. On the other hand, n_{N_2H}, which is an occupied MO, is constructed with several orbitals such as $d_{\pi x}$, π^*_x, s_H (1s orbital of the proton), n_N, and π_x. It is expected that $d_{\pi x}$ largely releases its electron density to π^*_x and s_H. In fact, the MO density of the orbital decreases from 2.00 to 0.82. Those of π^*_x and s_H increase from 0.00 to 0.64 and 0.86, respectively. There is a fairly large amount of the electron density on s_H because of the acceptance of the density from n_N as well as $d_{\pi x}$. These results indicate that the $d_{\pi x}$–π^*_x type polarization and $d_{\pi x}$–s_H, n_N–s_H type charge-transfer (CT) interactions facilitate the N–H bond formation. The MO density in $d_{\pi y}$ decreases (from 2.00 to 1.86) whereas that of π^*_y increases (from 0.00 to 0.12). It is, therefore, considered that the $d_{\pi y}$–π^*_y type polarization also occurs due to protonation.

From results of MO calculations, three types of orbital interactions are considered, as represented in Figure 5. Figure 5a shows the orbital mixing of π_x, $d_{\pi x}$, and s_H. According to the orbital-mixing rule,[22] their interactions give ψ_1 and ψ_2 (the highest orbital is neglected in the figure). The mixing of $d_{\pi x}$ and s_H is the largest in ψ_2, and they overlap in an in-phase manner, whereas $d_{\pi x}$ and π_x overlap in an out-of-phase fashion. Consequently, the interaction between d_{xz} of Cr and $2p_x$ of N_T is strengthened, tending to make the Cr–N bond strong. The increase of the ABP of the bond is mainly attributed to this type of orbital mixing. On the other hand, the interaction between s_H and π_x in ψ_1 and ψ_2 weakens the N–N bond because of the decrease of the bonding π electron. The interaction between $d_{\pi x}$ and π^*_x in ψ_3 (Figure 5b) is also expected on the basis of the increase of the MO density in the latter orbital. The strong effect of these orbital interactions is enough to get rid of π-type AOBP. In fact, those of N_2 and N_2H complexes are 0.164 and 0.006, respectively. The interaction between n_N, n_S and s_H gives ψ_4 and ψ_5 (Figure 5c). The antibonding nature between 2s orbitals of N_A and N_T is diluted by this type of interaction. Indeed, AOBP of the σ bond of the N_2 ligand increases from 0.234 to 0.325 by protonation. A similar trend was discussed for the change of the N–N bond strength in diazomethane and dinitrogen complexes.[16] The weakening of the π bond is dominant over the reinforcement of the σ bond due to the last orbital interaction. Therefore, the N–N bond length in N_2 complexes is shorter than that in N_2H ones, as experimentally observed.[2]

N_2H_2 Complex. Two types of the geometry, 3 and 4, are considered for the N_2H_2 complex because the X-ray crystallographic analysis has shown that the MNN moiety is almost linear.[2c] Cr, N_A, N_T, and two hydrogen atoms are in the *xz* plane in 3 whereas the H_2 moiety lies out of the plane in 4. N_T of 3 has an sp^2 configuration and that of 4 is sp^3. The total energy of the former (−2503.812 12 au) is lower by 0.034 14 au than that of the latter.[23] The AOBP of π_y in 4 (0.006) is much smaller than that of 3 (0.194), which indicates that the π bond in the *yz* plane disappears due to the bending of the NH_2 plane. The nuclear repulsion energy of 4 (962.220 10 au) is smaller by 0.512 25 au than that of 3. Therefore, the instability of geometry 4 is mainly attributed to the destabilization of the π bond in the *yz* plane.

The result of the configuration analysis of the complex is represented in eq 4, where it is divided into H^+ and the N_2H

$$\Phi_{N_2H_2} = 0.441\Phi_0 - 0.126\Phi_{n_{N2H}-d_{\pi x1}} + 0.072\Phi_{d_{\pi y1}-\pi^*_{y1}} + 0.322\Phi_{n_{N2H}-s_H} + 0.105\Phi_{2(n_{N2H}-s_H)} + ... \quad (4)$$

moiety. Only the MO density in n_{N_2H} significantly decreases by protonation (from 2.00 to 1.054). These results show that

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[21] Φ_0 stands for the adiabatically interacting configuration. Φ_{i-j} indicates the configuration in which one electron is transferred from MO i to MO j, and $\Phi_{2(i-j)}$ and $\Phi_{i-j,k-l}$ also indicate configurations of two-electron transfer.

[22] Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 405.

[23] Such large stabilization energies by protonation are not given in solution. The energy including the solvation effect should be defined as the protonation energy. For example, the difference between total energies of H_2O and H_3O^+ is added to protonation energies for the reaction in aqueous solution. This is estimated to be 227.6 kcal/mol for those with the assumed geometries (H_2O r_{OH} = 0.96 Å, HOH = 105.0°; H_3O^+ r_{OH} = 0.96 Å, C_{3h} symmetry). Stabilization energies including solvation effect are −111.8, 32.9, 123.6, and −10.2 kcal/mol for N_2, NH_4^+, and the N_2 and N_2H complexes, respectively. Moreover, solvation of the complexes must be considered for the correct estimation of protonation energies.

Table II. Decomposition of Protonation Energies (kcal/mol) of N_2, NH_3, $Cr(PH_3)_4N$, and $Cr(PH_3)_4N_2H^+$

	ΔE_{total}	ΔE_{ES}	ΔE_{CT}	ΔE_{PL}	ΔE_{MIX}
N_2	115.9	10.6	72.2	27.3	5.8
NH_3	260.6	105.8	115.2	16.8	22.8
$Cr(PH_3)_4N_2$	351.3	50.5	158.2	70.0[a]	
$Cr(PH_3)_4N_2H$	217.5	56.7	126.7	46.0	−11.9

[a] Estimated value.[27]

the CT interaction from the orbital to s_H is mainly involved in the formation of the second N–H bond. The $d_{\pi y}$–π^*_y type polarization also occurs by protonation.

Analysis of the Protonation Energy. The stabilization energy of protonation is expected largely to influence the reduction of the nitrogen molecule as a ligand. It is, therefore, interesting to analyze protonation energies by use of the energy decomposition technique, and results are listed in Table II. The protonation energies to N_2 and N_2H complexes are calculated to be 351.3 and 217.5 kcal/mol, respectively.[23] They are much larger than that of the nitrogen molecule (115.9 kcal/mol), which does not form a protonated species in usual solvents. On the other hand, they are similar to or even larger than that of NH_3 (260.6 kcal/mol), which forms NH_4^+ in aqueous solution. All protonation energies are divided into several types of energies,[24] the electrostatic (ES), charge-transfer (CT), and polarization (PL) energies listed in the table. The contribution of CT is the largest, and the other components are small in N_2. The contribution of ES and CT is much larger than the contribution of PL and MIX in NH_3. The difference of the stabilization energies between N_2 and NH_3 is mainly attributed to that of ES. In the case of the N_2 complex, the stabilization energy due to the CT interaction is the most important of all contributions and larger than those of NH_3 and N_2. As mentioned above, the $d_{\pi x}$–s_H and n_N–s_H type CT interactions facilitate the N–H bond formation on the basis of the results of configuration analysis and the large electron density on H^+ in N_2H complex in comparison with those in N_2H^+ (0.467) and NH_4^+ (0.648). Therefore, the large stabilization due to the CT interaction is consistent with these results. The contribution of ES is almost half of that estimated for NH_3. The most characteristic feature of the complex is the contribution of the polarization interaction to the total stabilization energy. This interaction does not contribute to the N–H bond formation in N_2H^+ and NH_4^+ because these compounds do not have easily polarizable MO's. Therefore, CT, ES, and PL interactions are all related to the large protonation energy of the N_2 complex.

The protonation energy of the N_2H complex is smaller than that of the N_2 complex because the stabilization energy due to CT is small in comparison with that of the latter. CT mainly occurs from n_{N_2H} to s_H in the former, whereas the latter has two orbitals, $d_{\pi x}$ and n_N, to transfer electron density to s_H.

The third or fourth protonation is needed for the formation of reaction products. Triprotonated complexes $Cr(PH_3)_4NHNH_2^{3+}$ and $Cr(PH_3)_4N_2NH_3^{3+}$[25] ($NHNH_2$ and N_2H_3 complexes) are calculated with assumed geometry. However, the third protonation does not give the stabilization energy in both cases. Therefore, the formation of the third N–H bond is expected to be difficult. Two electrons have already been transferred from $Cr(PH_3)_4$ to the N_2H_2 fragment in the N_2H_2 complex. It is thus considered that the Cr moiety does not have the ability to transfer more than two electrons. It is known that the substitution of phosphine ligands to halogen atoms occurs by way of the reduction of the N_2 ligand in Mo or W complexes. This effect must be considered in further investigating protonation or the reduction mechanism.

According to the preliminary calculations of $CoH(PH_3)_3N_2$[26] and its protonated complex with 4-31G basis sets for N_2 and H^+, the protonation energy (147.2 kcal/mol) is much smaller than that of the Cr complex with similar basis sets (300.5 kcal/mol). The configuration of the central metal largely affects the magnitude of the protonation energy. The former value is similar to that calculated for the nitrogen molecule (the protonation energy when 4-31G basis sets are used is 123.0 kcal/mol). These two species have not been found to give derivatives in usual solvents. On the other hand, Mo and W dinitrogen complexes give both NH_3 and N_2H_4. The d configuration of the metal is the same the Cr dinitrogen complex employed as the model complex. Therefore, the d configuration of the metal largely affects the magnitude of the protonation energy.

Concluding Remarks

(1) The protonation to the dinitrogen ligand causes a remarkable rearrangement of the electron distribution in the N_2 moiety. The electron density in d_{xz} is mainly transferred to s_H. CT from n_N to s_H strengthens the N–N bond. On the other hand, π_x and $d_{\pi x}$–π^*_x type polarizations, which are strong enough to eliminate the π bond, are involved in the weakening of the N–N bond. The latter interaction is dominant over the former one. Therefore, the N–N bond in the protonated complexes is longer than that in the unprotonated forms. The trend of ABP of the M–N bond is consistent with the observation that the bond is shortened by protonation.

(2) The protonation energy of the Cr dinitrogen complex is much larger than those of N_2 and $Co(PH_3)_3HN_2$, which do not form protonated species in usual solvents. Therefore, the large stabilization due to the first and the second protonation to dinitrogen complexes is needed in order to reduce the fairly stable N_2 molecule through complexation with transition metals. It is considered that the large protonation energy comes from the existence of d_π as HOMO, which has the ability to transfer electrons to s_H. Moreover, the complex has orbitals that can be easily polarized. These features of the complex give the large protonation energy calculated.

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(24) Geometries of N_2H^+ and NH_4 are optimized by use of the STO-3G minimal basis set. N_2H^+ is a linear molecule, and N–N, N–H distances obtained are 1.04 and 1.08 Å, respectively. NH_4 has a T_d symmetry, and a N–H distance is calculated to be 1.05 Å.

(25) Geometries of $NHNH_2$ and N_2H_3 complexes are assumed in calculating protonation energies. CrNN, CrNH, and NNH angles are all 120.0° for the former complex. CrNN and NNH angles in the latter complex are 180.0 and 126.5°, respectively. The N–H bond lengths are all 1.05 Å.

(26) Bond lengths and angles of Co complexes are taken from the crystallographic data of $Co(PPh_3)_3HN_2$: Davis, B. R.; Payne, N. C.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2719. The NNH angle and N–H bond length are 180.0° and 1.05 Å, respectively.

(27) The value for the N_2 complex is considered to be much larger that that for the N_2H complex on the basis of the results of configuration analysis and the MO density in π^* in the complex.