

constants, though, show little difference.

Relative to $K(M-S)$ values that were obtained in normal-coordinate analyses of other metal-sulfur complexes²¹ such as dithioacetylacetonates,^{12a} monothioacetylacetonates,^{12c} and dithienes,¹¹ results that were obtained herein for dithioimidodiphosphinates represent the lowest $K(M-S)$ values. Both the tetrahedral geometry (as opposed to square planar)

and the nature of the ligand (not a thiolate sulfur donor) probably contribute to the low metal-ligand bond strengths. Some intensification of Cu(I)-S Raman bands in the 200-300-cm⁻¹ region for Cu^IL₃ and Cu^IL₃⁺ clusters in comparison to Raman band intensities in the same region for bis chelates such as Mn^{II}L₂ might be surmised to arise from weak Cu...Cu bonding interactions.

Registry No. Mn^{II}L₂, 40362-04-7; Co^{II}L₂, 31747-72-5; Co^{II}L₂, 31747-71-4; Cu^IL₃⁺, 65404-72-0.

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Bonding in Ni(PH₃)₂(C₂H₄) and Ni(PH₃)₂(C₂H₂). An ab Initio SCF-MO Study

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Ab initio MO calculations were carried out on Ni(PH₃)₂(C₂H₄) and Ni(PH₃)₂(C₂H₂). C-C bond lengths and bending angles of complexed ethylene and acetylene were determined. The binding energy was found to be larger in the acetylene complex than in the ethylene complex. The relative magnitude of σ donation and π back-donation was revealed through an analysis of binding energy and electron distribution. The influence of other ligands on the Ni-C₂H₄ bonding was discussed by comparing PH₃ with NH₃ as ligands.

Introduction

The Dewar-Chat-Duncanson bonding model² has been the basis for qualitative understanding of chemical and physical properties of metal-olefin complexes. A number of semi-empirical and ab initio MO calculations have been performed for a more quantitative description of the bonding.³ However, most of these prior studies have discussed the relative importance of σ donation and π back-donation solely on the basis of the electron population on the metal atom and olefin. In the present work, we will attempt to reveal how σ donation and π back-donation contribute to the metal-olefin bond, through an analysis of the binding energy, as well as the electron distribution. We apply the scheme of energy decomposition analysis (EDA),⁴ developed for studying intermolecular interactions. EDA enables us to understand the origin of bonding in terms of various meaningful interactions: electrostatic (Coulombic), exchange-repulsion, polarization, charge-transfer, and others. Though EDA and similar methods⁵ have been widely applied to various types of intermolecular complexes,^{4a} only a few applications have been made for transition-metal complexes.⁶ Sakaki et al. have recently

studied the bonding nature and stereochemistry of metal-carbon dioxide complexes by EDA with the ab initio SCF-MO method.⁷ Ziegler and Rauk have carried out a similar analysis with a Hartree-Fock-Slater method for transition-metal ethylene and carbonyl complexes.⁸

In this paper, after giving the definition of energy components relevant to the σ donation and π back-donation, we will study the nature of bonding between Ni(PH₃)₂ and C₂H₄ in detail. The influence of other ligands on the Ni-C₂H₄ bonding will also be discussed. A comparison will be made between Ni-C₂H₄ and -C₂H₂ bonding.

Computational Procedures

We have assumed that the complexes Ni(PH₃)₂(C₂H₄), Ni(PH₃)₂(C₂H₂), and Ni(NH₃)₂(C₂H₄) are singlets in their ground states, as was also assumed in previous studies.²¹ As will be discussed later, with the stabilizing PH₃ ligands the electron configuration of these complexes is close to d¹⁰, which would favor a singlet state. All calculations were performed with use of the closed-shell restricted Hartree-Fock (RHF) method.

Basis Set and Geometry. Ab initio SCF-MO calculations were carried out with use of the IMSPACK program system.⁹ The basis sets used were the 4-31G set^{10a} for ligand atoms and the [4s3p2d] contracted set for nickel atoms. The [4s3p2d] set was contracted from the (11s7p5d) primitive Gaussian set, which was modified from (12s6p4d)^{10b} by deleting the two most diffuse s-type functions and adding an s-type, a p-type, and a d-type function with the exponents 0.2, 0.25, and 0.2, respectively. The 3s-type functions arising from the totally symmetric linear combination of d-type functions were removed from the basis set. The basis set used here was found to give reasonable binding energies and geometries.¹¹

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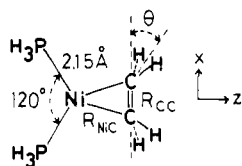


Figure 1. Geometric parameters. Bond lengths are in angstroms and angles are in degrees. For Ni(PH₃)₂(C₂H₂) θ refers to the H-C-C angles.

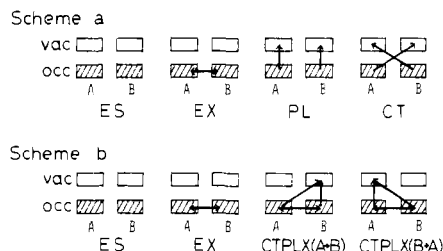


Figure 2. Modes of orbital mixing and components of interaction. Scheme a is useful for weakly interacting systems and scheme b is for strongly interacting systems.

The geometry of the fragmental part Ni(PH₃)₂ was constructed with use of the experimental geometry of free PH₃,¹² the Ni-P bond distance of 2.15 Å, the experimental value in Ni(PPh₃)₂(C₂H₄),¹³ and the assumed P-Ni-P angle of 120°. Since the purpose of this series of study is to examine and compare the nature of binding of small molecules, we adopted the above standardized geometry for Ni(PH₃)₂ and did not change it throughout. In order to examine the change of basicity of the NiX₂ fragment, we also carried out calculations for imaginary nickel(0) ammine complexes. The geometry of Ni(NH₃)₂ was assumed to have the experimental geometry for NH₃, the Ni-N bond distance of 2.15 Å, a standard value for Ni(II) complexes,¹² and the N-Ni-N angle of 120°.

A C_{2v} symmetry was assumed for all the complexes. The definitions of geometrical parameters are shown in Figure 1. The C-H bond lengths of ethylene and acetylene were fixed at the experimental values for a free molecule.¹² Geometry optimizations were performed for the Ni-C and C-C bond distances (R_{NiC} and R_{CC}) and the out-of-plane bending angle (θ) of ethylene and acetylene. The three geometrical parameters were varied independently, and the energy minima were obtained by a parabolic fit for each parameter.

Scheme of Energy Decomposition Analysis.⁴ The binding energy, BE, can be written as

$$BE = DEF + INT$$

where DEF is the destabilization energy due to the geometrical deformation of A and B upon complexation. INT is the interaction energy between deformed A and B. The scheme of EDA, shown in Scheme a of Figure 2, classifies components of the electronic interaction on the basis of modes of orbital mixing. The charge-transfer interaction from A to B, for instance, is defined as the interaction between occupied orbitals of A and vacant orbitals of B. INT includes the electrostatic (ES), polarization (PL), exchange-repulsion (EX), and charge-transfer (CT) interaction energies and the coupling energy of the above components (MIX). The conceptual components of interaction have been proved to be useful in describing bonding in weakly interacting systems such as hydrogen bonds and electron donor-acceptor com-

Table I. Calculated and Experimental Geometric Parameters^d

	R_{NiC} , Å	R_{CC} , Å	θ , deg
Computed ^a			
Ni(PH ₃) ₂ (C ₂ H ₄)	1.95	1.42	26
Ni(NH ₃) ₂ (C ₂ H ₄)	1.94	1.43	32
Ni(PH ₃) ₂ (C ₂ H ₂)	1.89	1.28	40
Experimental ^b			
Ni(PPh ₃) ₂ (C ₂ H ₄)	1.99 ^c	1.431	
NiPR' ₂ (CH ₂) ₂ PR'' ₂ (C ₂ R ₄)	1.98 ^c	1.42	26
Ni(CNR'') ₂ (C ₂ Ph ₂)	1.90	1.28	31

^a The C_{2v} point group symmetry was assumed for all the complexes. ^b R = CH₃, R' = (o-C₆H₁₁), and R'' = (t-C₄H₉). The values are taken from ref 13. Other experimental data for similar complexes are also found in ref 13. ^c The average of two Ni-C bond lengths. ^d The calculated C-C bond lengths of free ethylene and acetylene are 1.32 and 1.19 Å, respectively. The experimental values are 1.337 and 1.204 Å.

plexes. However, in strongly interacting systems such as transition-metal complexes the coupling interaction (MIX) becomes more ambiguous. In this case, the modes of orbital interaction shown in scheme b of Figure 2 seem to be more appropriate in describing bonding, especially in analyzing the σ donation and the π back-donation.¹⁴ The component CTPLX(A \rightarrow B), for instance, involves the charge-transfer from A to B and the polarization of B under the presence of electrostatic and exchange-repulsion interactions. Ziegler and Rauk also have defined the donative and back-donative interaction by this mode of orbital mixing.⁸ INT in scheme b is decomposed into four components and the remainder (R):

$$INT = ES + EX + CTPLX(A \rightarrow B) + CTPLX(B \rightarrow A) + R$$

The numerical procedure for computing components of binding energy and charge distributions is similar to that found in ref 3b.

We regard the complex NiX₂L (X = PH₃ or NH₃ and L = C₂H₄ or C₂H₂) as an interacting system between NiX₂ and L, and EDA is applied to the interaction. The binding energy is calculated as the difference between the total energy of NiX₂L and the sum of the total energies of NiX₂ and a free ligand molecule L. The spin multiplicity of the fragment NiX₂ was assumed to be a singlet. The binding energy defined here does not necessarily correspond to the observed binding energy when the fragment has the ground state different from that assumed in the complex. In such a case, the state of the fragment used in EDA should be considered as a "promoted state" and the "promotion energy" should be subtracted from BE for a real binding energy.

In the following sections, the donative FCTPLX and the back-donative BCTPLX interaction refer to CTPLX(L \rightarrow NiX₂) and CTPLX(NiX₂ \rightarrow L), respectively.

Bonding of Ni-C₂H₄

The electron configuration of Ni(0) in Ni(PH₃)₂(C₂H₄) is formally considered as d¹⁰. The calculation shows a substantial decrease of electron population in d orbitals due to delocalization to C₂H₄ but little increase in s and p orbitals (Table III). Therefore, the electron configuration in the complex may be considered as being d¹⁰ rather than s¹d⁹, which was obtained for the coordinatively highly unsaturated NiC₂H₄ adduct from the GVB¹⁵ and MCSCF¹⁶ calculations.

Geometry. The optimized values of geometrical parameters for Ni(PH₃)₂(C₂H₄), which is a model complex for Ni(PPh₃)₂(C₂H₄), are given in Table I, along with available experimental data. The increase in the C-C bond length of ethylene was calculated to be 0.1 Å, in good agreement with experimental values. No bending angle of unsubstituted ethylene has been determined experimentally. Our calculation suggests that the coordinated ethylene is bent back by 26°.

- The interaction energy between Ni(PH₃)₂ and planar C₂H₄ was calculated with a small ([4s3p2d] and STO-3G), a medium ([4s3p2d] and 4-31G), and a large ([6s4p3d] and 4-31G) basis set. The interaction energies were obtained to be -46, -28, and -25 kcal/mol for the small, medium, and large sets, respectively. The small set gave too large a binding energy, probably due to the superposition error. The medium set overestimated only -13 kcal/mol compared to the large set. The optimized geometrical parameters with the small set were 1.39 Å and 25° for R_{CC} and θ , respectively. R_{CC} is a little shorter than 1.42 Å, and θ is nearly equal to 26° of the medium set. Accordingly, we decided to use the medium basis in the present work.
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Table II. Calculated Binding Energies and Components (kcal/mol)^a

	Ni(PH ₃) ₂ - (C ₂ H ₄) ^b	Ni(NH ₃) ₂ - (C ₂ H ₄)	Ni(PH ₃) ₂ - (C ₂ H ₂)
BE	-30 (-19)	-64	-37
	Components		
DEF	15 (9)	29	40
INT	-45 (-28)	-93	-77
ES	-132 (-120)	-141	-148
EX	168 (157)	179	189
FCTPLX	-16 (-13)	-21	-24
BCTPLX	-54 (-44)	-84	-75
R	-11 (-20)	-26	-19

^a A minus sign shows stabilization. BE = DEF + INT and INT = ES + EX + FCTPLX + BCTPLX + R. ^b The energies at $\theta = 0^\circ$ are given in parentheses.

The magnitude of the bending angle is comparable with experimental values for the (tetracyanoethylene)nickel complex.

Binding Energy and Its Components. The calculated binding energy and its components are shown in Table II. The experimental estimate of binding energy of 33 kcal/mol for Ni(PR₃)₂(C₂H₄) (R = *o*-tolyl)¹⁷ may be compared with the computed value of 30 kcal/mol for Ni(PH₃)₂(C₂H₄).

The distortion of the ethylene molecule from equilibrium costs 15 kcal/mol (DEF), 9 kcal/mol for stretching the C-C bond length and 6 kcal/mol for bending CH₂ groups, while the electronic interaction stabilizes the complex by 45 kcal/mol (INT). The Coulombic interaction (ES) between Ni(PH₃)₂ and C₂H₄ gives a large stabilization energy as expected from a simple point-charge interaction model between Ni^{δ+} and C^{δ-}-C^{δ-}. The donative interaction (FCTPLX) contributes to the binding energy by -16 kcal/mol. The back-donative interaction (BCTPLX) carries an attractive energy of -54 kcal/mol, which is about 3 times larger than the donative interaction energy. Thus the back-donative interaction, whose main mode is the π back-donation, is found to be the dominant contributor to the bonding from the energetic point of view. The result, the first of this kind in the *ab initio* method, is in accordance with common intuitive understanding of bonding between a low-valent transition-metal atom and an olefin.¹⁸

Electron Distribution and Its Components. The density difference maps are shown in Figure 3. ρ_T is the difference between the electron density of Ni(PH₃)₂(C₂H₄) and the superposition of Ni(PH₃)₂ and C₂H₄ densities and represents the change in density distribution due to complex formation. ρ_{EX} , ρ_{FCTPLX} , and ρ_{BCTPLX} are the corresponding components of ρ_T . Mulliken population for the fragments and complexes, its change, and the component analysis are given in Tables III, IV, and V, respectively. The mulliken population is known to be strongly basis set dependent, and caution is necessary in discussing electron distributions based on it. For the systems studied here, however, we find that the change of Mulliken population due to the interaction reflects well the trend actual change in the electron density map. Therefore we will use it for convenience in the following discussions.

EX decreases the electron density in the intermolecular region, on the line connecting Ni and the bisector of the C-C bond (Figure 3 and Table V).¹⁹ The donative interaction causes the density to decrease on C₂H₄ and at the vicinity of the Ni nucleus, accompanied by an increase in density in the Ni-C bonding region. An analysis indicates that the delo-

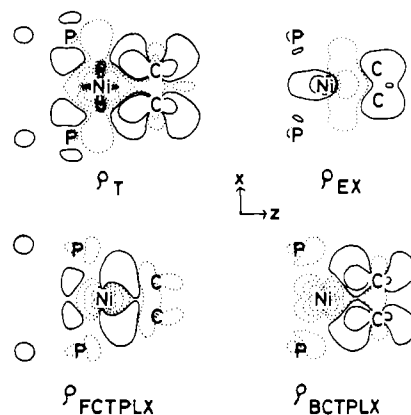
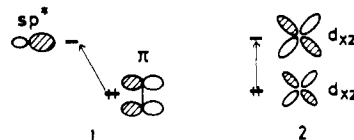
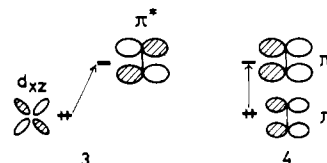


Figure 3. Difference density maps of Ni(PH₃)₂(C₂H₄). Solid lines show an increase in density and dotted lines a decrease. The contours are ± 0.05 , ± 0.01 , and $\pm 0.001 e/a_0^3$.

calization of the ethylene π orbital over the Ni sp^* vacant orbital, **1**, is the major cause for this density change. The



orbital mixing in **2** also contributes to the electron redistribution. This mixing of the occupied d_{xz} -type MO with a vacant MO of the same symmetry is nothing but the expansion of the radius of the nickel d_{xz} orbital upon C₂H₄ complexation, caused by the repulsion due to the electron delocalized from C₂H₄ in mixing **1**. The mixing in **2** pushes the electron distribution around the Ni atom outward and also increases the Ni-C overlap population. The back-donative interaction causes two characteristic changes in the electron distribution. One is the charge transfer from Ni(PH₃)₂ to C₂H₄ and the accumulation of electrons in the Ni-C bonding region. The amount of transferred charge is about 5 times larger than that of reverse charge transfer (Table V). The contribution to the Ni-C overlap population is also 2.5 times larger than that of the donative interaction. The main origin of the change in electron distribution is understandable in terms of the orbital mixing in **3**. The other change is the density decrease along the line



of the C-C bond (Figure 3). The orbital mixing in **4**, the expansion of the π orbital similar to **2**, helps to reduce the electron repulsion in ethylene. Diffusion of the electron distribution through **4** accompanies a decrease in electron density at the C-C bond, as the π orbital of bent ethylene contains a small portion of the C-C σ orbital. The remainder term (R), though not important energetically, causes similar changes in Mulliken population as the back-donative interaction. The shrinkage of the nonbonding $d_{x^2-y^2}$ orbital (perpendicular to the plane of Figure 3) seen in ρ_T is apparently due to R. This change may be explained as the additional polarization following the decrease of electrons on Ni through the back-donative interaction.

We have reillustrated the contribution of donative and back-donative interaction to the Ni(PH₃)₂-C₂H₄ bonding through the component analysis of electron distribution. The C-C bond weakening of the coordinated ethylene may have

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Table III. Mulliken Populations on Ni and Ligands

	Ni(PH ₃) ₂	Ni(NH ₃) ₂	Ni(PH ₃) ₂ (C ₂ H ₄) ^a	Ni(NH ₃) ₂ (C ₂ H ₄)	Ni(PH ₃) ₂ (C ₂ H ₂)
Ni	27.75	27.89	27.48 (27.54)	27.13	27.44
s	6.03	6.06	6.06 (6.05)	6.09	6.08
p	12.00	11.99	12.15 (12.12)	12.12	12.23
d	9.71	9.84	9.26 (9.36)	8.92	9.14
d _{xz}	1.93	1.95	1.43 (1.53)	1.01	1.23
PH ₃ or NH ₃	18.13	10.06	18.02 (18.04)	10.01	17.98
C ₂ H ₄ or C ₂ H ₂			16.49 (16.38)	16.85	14.59

^a The values for $\theta = 0^\circ$ are given in parentheses.

Table IV. Change in Gross and Overlap Populations^a

	Ni(PH ₃) ₂ - (C ₂ H ₄) ^b	Ni(NH ₃) ₂ - (C ₂ H ₄)	Ni(PH ₃) ₂ - (C ₂ H ₂)
Gross			
Ni	-0.27 (-0.21)	-0.76	-0.30
s	0.03 (0.02)	0.03	0.05
p	0.15 (0.12)	0.13	0.23
d	-0.45 (-0.35)	-0.92	-0.57
d _{xz}	-0.50 (-0.40)	-0.65	-0.93
PH ₃ or NH ₃	-0.11 (-0.09)	-0.05	-0.14
C ₂ H ₄ or C ₂ H ₂	0.49 (0.38)	0.85	0.59
Overlap			
Ni-P or Ni-N	0.08 (0.06)	0.08	0.11
Ni-C	0.05 (0.02)	0.08	0.08
C-C	-0.13 (-0.11)	-0.22	-0.11

^a The difference between the population of the complex and the sum of populations of fragments. ^b The values for $\theta = 0^\circ$ are given in parentheses.

Table V. Charge Decomposition Analysis for Ni(PH₃)₂(C₂H₄)^a

	EX	FCTPLX	BCTPLX	R
Gross				
Ni	-0.01	0.05	-0.27	-0.04
s	0	0	0	0.03
p	0.01	0.09	0	0.05
d	-0.01	-0.04	-0.27	-0.13
d _{xz}	-0.00	-0.03	-0.26	-0.29
PH ₃	0.01	0	-0.04	-0.08
C ₂ H ₄	0	-0.06	0.34	0.21
Overlap				
Ni-P	0	-0.02	0.03	0.07
Ni-C	-0.08	0.02	0.05	0.06
C-C	0.02	-0.02	-0.07	-0.07

^a The change in Mulliken population (Table IV) is decomposed into its components. These components correspond to the component difference densities of Figure 3.

been realized through the exchange polarization as well as the delocalization of π electrons. We have shown that the back-donative interaction plays the major role on bonding between Ni(PH₃)₂ and C₂H₄, as shown for the electron distribution here and for the binding energy in the preceding section.

Distortion of Coordinated Ethylene. The coordinated ethylene was shown to have a stretched C-C bond and a bending angle θ of 26°. The factors favoring the bent-back structure are examined by the component analysis. Figure 4 gives potential energy curves as functions of θ . The INT stabilization energy increases almost linearly as θ increases. The energy components at $\theta = 0^\circ$ are given in parentheses in Table II. The ES stabilization energy is larger at 26° than at 0°; the net charge on carbon atoms in free ethylene varies little with bending of the CH₂ groups, and a simple point-charge interaction model does not explain the increase in ES at 26°. A bending of the CH₂ groups brings about a deformation of the π orbital toward Ni through mixing with the 2s orbital. Then, the center of π -electron distribution reaches

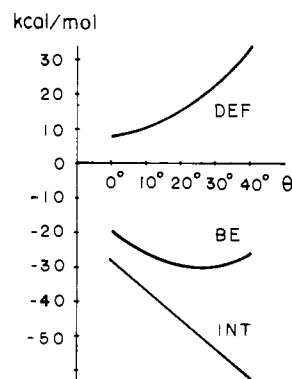


Figure 4. Potential energy curves of Ni(PH₃)₂(C₂H₄) as a function of θ .

closer to the nickel atom, resulting in a stronger ES interaction; the increase in EX repulsion also reflects this π -orbital deformation. A delocalization interaction energy is known to depend on the overlap and the energy difference between interacting orbitals. The π^* -orbital energy of the ethylene molecule lowers as θ increases, while the π energy level stays nearly constant.²⁰ A little larger stabilization energy of the donative interaction at 26° than at 0° may be due to an increase in overlap between the π and sp^* orbitals. Upon deformation the back-donative interaction gains the largest increase in stabilization energy. This may be caused by the diminished energy gap between the π^* and d_{xz} orbitals. From the component analysis we may conclude that the bent-back structure of ethylene in the complex is mainly favored through the back-donative interaction, compensating enough for the increased deformation energy.

Influence of Other Ligands on the Ni-C₂H₄ Bonding. The calculation was carried out on an imaginary amine complex, Ni(NH₃)₂(C₂H₄). It should be noted that neither Ni(NH₃)₂(C₂H₄) nor any similar complex has been isolated. The calculation is to examine how the change of basicity of Ni, caused by the change of ligands, affects the nature of the metal-olefin bond.

The optimized Ni-C and C-C bond lengths and the bending angle of ethylene are shown in Table I. The computed values of geometric parameters are not very different from the corresponding values of Ni(PH₃)₂(C₂H₄) except for the bending angle.

The binding of energy for this imaginary Ni(NH₃)₂-C₂H₄ was found to be -64 kcal/mol, which is nearly twice as large as that of the phosphine complex (Table II). This does not mean that Ni(NH₃)₂(C₂H₄) is more stable than Ni(PH₃)₂(C₂H₄), but rather it means that the C₂H₄-Ni interaction is strengthened, as is expected, by an increase of the basicity of Ni.

The energy components given in Table II show that the stabilization energy due to the back-donative interaction is

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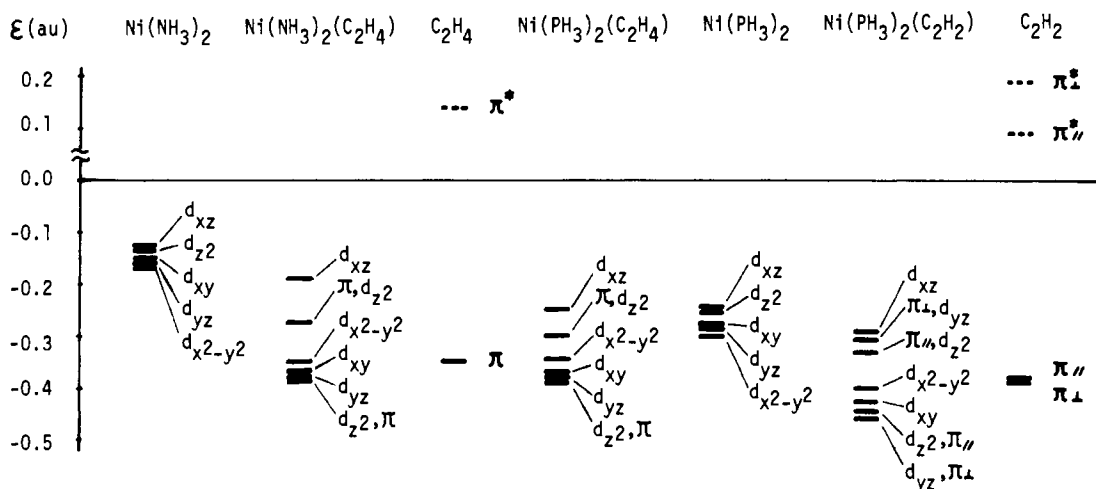


Figure 5. Orbital energy levels. The geometries of the ethylene and acetylene molecules used were the same as those in $\text{Ni}(\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4))$ and $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$, respectively. The symbol \parallel refers to being in the molecular plane and \perp to being perpendicular to the molecular plane.

greatly increased in $\text{Ni}(\text{NH}_3)_2(\text{C}_2\text{H}_4)$. This is explained by the fact that the orbital energy gap between d_{xz} and π^* is much smaller here than in $\text{Ni}(\text{PH}_3)_2$ and C_2H_4 (Figure 5). The d_{xz} orbital energy is increased by a nonbonding interaction with the lone-pair orbital of NH_3 . The lack of electron-accepting ability of NH_3 , compared to the case of PH_3 , may destabilize the d electrons since the larger electron population on Ni (Table III) in the $\text{Ni}(\text{NH}_3)_2$ fragment gives the stronger Coulombic repulsion on the d electrons. On the other hand, the π^* orbital of ethylene is lowered more because of a larger bending angle in this complex.

Changes in Mulliken population are shown in Table IV. It is seen that the nickel atom in this complex loses more electrons to ethylene than does $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$. The large decrease in the d_{xz} density reflects the stronger back-donative interaction. Characteristic changes accompanying donative and back-donative interaction are similar to these pointed out for $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$.

Comparison with Previous Work. Ab initio MO calculations on $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ and $\text{Ni}(\text{NH}_3)_2(\text{C}_2\text{H}_4)$ have been published by Åkermark et al.²¹ They have computed the C-C bond lengths of ethylene to be 1.410 and 1.455 Å for the phosphine and the ammine complexes, respectively. Our result of 1.42 Å for $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ agrees well with their value, but 1.43 Å for $\text{Ni}(\text{NH}_3)_2(\text{C}_2\text{H}_4)$ is somewhat shorter than theirs. The discrepancy may be attributable to the use of a different basis set and a different geometry for the other part of the complex. The binding energies obtained by Åkermark et al. were 36 and 54 kcal/mol for the phosphine and the ammine complexes, respectively. These values may be compared with our results of 30 and 64 kcal/mol, but one should note that they have not optimized the geometry except for the C-C bond length. They have not carried out the EDA analysis either.

Comparison of the Bonding of $\text{Ni}-\text{C}_2\text{H}_2$ with $\text{Ni}-\text{C}_2\text{H}_4$

The calculated geometric parameters of $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$ are shown in Table I. The optimized values are compared with the corresponding experimental values of $\text{Ni}(\text{CN}-t\text{-C}_4\text{H}_9)_2(\text{C}_2\text{Ph}_2)$. The acetylene C-C bond length is stretched in the complex by 0.09 Å, the same magnitude as that of ethylene in $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$.

The computed binding energy and components are shown in Table II. The binding energy of $\text{Ni}(\text{PH}_3)_2-\text{C}_2\text{H}_2$ is obtained to be -37 kcal/mol. Though the corresponding experimental

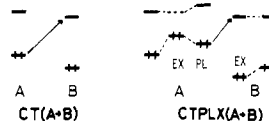


Figure 6. Schematic illustration of the orbital energy diagram for $\text{CT}(\text{A} \rightarrow \text{B})$ and $\text{CTPLX}(\text{A} \rightarrow \text{B})$.

value is not available, our calculation suggests that the $\text{Ni}-\text{C}_2\text{H}_2$ bond is stronger than the $\text{Ni}-\text{C}_2\text{H}_4$ bond.

The relative importance of donative and back-donative interactions is similar to that in the ethylene complex. The interaction energy is about 1.5 times larger in the acetylene complex. The components also reflect the stronger interaction between $\text{Ni}(\text{PH}_3)_2$ and C_2H_2 . The smaller Ni-C distance and the larger bending angle may be responsible for the stronger interaction. The former increases the overlap integrals between interacting orbitals. The latter lowers the π^* energy level for easier interaction with metal d orbitals (Figure 5).

Changes in Mulliken population are shown in Table IV. The change of the total population on Ni is not much different from that of the ethylene complex. The changes of individual Ni s-, p-, and d-orbital populations, however, are larger in the acetylene complex. Both the donative (mainly an increase in the population on p orbitals) and the back-donative (mainly a decrease in the populations on the d_{xz} orbital) interactions are responsible for the larger charge transfer. The larger increase in Ni-P overlap populations is realized in the acetylene complex since the acetylene ligand draws more electrons than ethylene from the d_{xz} orbital, which has an antibonding character between Ni and P.

In this section we have revealed a great similarity of bonding schemes between Ni-acetylene and -ethylene through the analysis of binding energy and electron populations.

Donative (FCTPLX) and Back-Donative (BCTPLX) Interactions.

The FCTPLX or BCTPLX interaction defined by scheme b in Figure 2 includes higher order interaction terms in addition to the second-order terms pertaining to perturbation expansion. The interaction may be approximately regarded as a kind of overall charge-transfer interaction, that is, the charge-transfer interaction with the simultaneous inclusion of the exchange-repulsion and polarization interaction. The interaction, for instance, FCTPLX or CTPLX($\text{A} \rightarrow \text{B}$) may be qualitatively understood by the orbital-interaction diagram shown in Figure 6. The occupied orbital energy of A is shifted by the interaction with occupied orbitals of B(EX) and

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unoccupied orbitals of A(PL). It is noted that PL used here just refers to an interaction mode that mixes unoccupied orbitals of A into occupied orbitals of A. Hence, the PL interaction may take place to reduce the exchange repulsion as well as to stabilize the electrostatic field of partner molecule B, depending on the relative magnitude of overlap repulsion and electrostatic field. CTPLX(A → B) may have a modified orbital energy gap from CT(A → B) in the energy expression of perturbation expansion. When A is an electron donor and B is an acceptor, CTPLX(A → B) is expected to be larger than CT(A → B) and CTPLX(B → A) may be smaller than CT(B → A). Actually, we have obtained -41, -16, -44, and -54 kcal/mol for FCT, FCTPLX, BCT, and BCTPLX, respectively, for Ni(PH₃)₂(C₂H₄) at $\theta = 26^\circ$.

Concluding Remarks

The bonding between Ni(PH₃)₂ and C₂H₄ was analyzed in terms of the donative and the back-donative interactions. The back-donative interaction was proved to be the major contributor to the binding energy as well as to the electron dis-

tribution in the complex. The bent-back structure of coordinated ethylene was shown to be favored due to the favored back-donative interaction. The substitution of PH₃ with NH₃, which is more electron donative, greatly strengthened the back-donative interaction in the Ni-C₂H₄ bond. The bonding scheme of Ni-C₂H₂ was revealed to be similar to that of Ni-C₂H₄, though the magnitude of each energy component was larger in the former than in the latter. The RHF approximation provides a simple model that can describe the bonding nature of transition-metal-olefin complexes, as demonstrated in this work. It is no doubt true, however, that the electron correlation should be taken into account for a more quantitative description of bonding.

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Luminescence, Absorption, MCD, and NQR Study of the Cis and Trans Isomers of Dichlorodiammineplatinum(II)

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Luminescence, absorption, magnetic circular dichroism (MCD), and nuclear quadrupole resonance (NQR) experiments are reported for the cis and trans isomers of dichlorodiammineplatinum(II). Extended Hückel molecular orbital calculations, using nonrelativistic and relativistic HF basis functions for Pt, have been made to correlate the experimental data. Analysis of the luminescence intensity and lifetime data vs. temperature for the trans isomer allows us to determine the energy separation of the low-lying triplet d states. The solution MCD spectra indicate the presence of transitions which do not show a maxima in the absorption spectra but which are predicted from the MO calculations. The ³⁵Cl NQR results for the cis and trans isomers allow a comparison of the ground electronic state chemical bonding for the two isomers; also, since the NQR coupling constant MO calculations are a more sensitive test of the MO wave functions than energy calculations, the NQR data can be used to judge our MO models.

Introduction

In a series of studies¹⁻⁶ we have reported the absorption and luminescence spectra of selected platinum complexes. In this paper we consider the cis and trans isomers of dichlorodiammineplatinum(II). The cis isomer is of current interest because of its anticancer activity. ³⁵Cl NQR measurements have been made to probe the ground electronic state bonding while luminescence, MCD, and absorption measurements have been used to determine the excited electronic state ordering in both solution and solid-state environments.

Previously Chatt et al.⁷ have reported the solution spectra of cis- and trans-Pt(NH₃)₂Cl₂ and assigned the low-energy transitions as d-d on the basis of the extinction coefficients.

Also, Martin and co-workers^{8,9} have reported the solution and polarized single-crystal absorption spectra of Pt(en)Cl₂ and discovered significant differences in the two spectra. These differences were assigned to the presence of inter- and intramolecular excitonic transitions in the solid state. Recently, Martin et al.¹⁰ have compared the Pd(en)Cl₂ spectra with the platinum results.

Experimental Methods

cis-Pt(NH₃)₂Cl₂ was prepared by the method of Dhara.¹¹ K₂PtCl₄ was converted to K₂PtI₄ and then to cis-Pt(NH₃)₂I₂ by addition of NH₄OH. Reaction with AgNO₃ produced cis-[Pt(NH₃)₂(H₂O)₂](NO₃)₂, which upon addition of KCl produced the final product. Purification was accomplished by successive recrystallization from a 0.1 N HCl solution. The trans-Pt(NH₃)₂Cl₂ isomer was prepared with use of the method of Kauffman and Cowan.¹² The product was purified from 0.1 N HCl.

In order to obtain luminescence spectra in the limit of zero Pt-Pt interaction, we rapidly froze solutions containing the cis or trans

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