

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860, Japan, and the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Ab Initio MO Study of Nickel(0) Complexes: Stereochemistry of Ni(PH₃)₂L (L = H₂CO or (CO)₂) and Comparison of Coordinate Bonds of Various Ligands

SHIGEYOSHI SAKAKI,*^{1a} KAZUO KITAURA,^{1b,c} KEIJI MOROKUMA,^{1b} and KATSUTOSHI OHKUBO^{1a}

Received March 1, 1982

The stereochemistry of Ni(PH₃)₂(H₂CO) and Ni(PH₃)₂(CO)₂ was studied with the ab initio MO method. In Ni(PH₃)₂(H₂CO) the energy decomposition analysis shows that, due to stronger back-donation, the planar side-on-coordinated complex is more stable than both the pseudotetrahedral side-on and the end-on complex. The H₂CO ligand is greatly distorted in the side-on complex, for the distortion relieves the exchange repulsion and enhances the back-donation. In Ni(PH₃)₂(CO)₂, the pseudotetrahedral structure is more stable than the planar one, owing to smaller exchange repulsion. Coordinate bonds of C₂H₄, C₂H₂, CO₂, H₂CO, and CO with Ni(PH₃)₂ are compared with each other. In the side-on-coordination mode, the back-donation increases in the order CO < C₂H₄ < C₂H₂ < H₂CO < CO₂, which agrees with the decreasing order of their π* orbital energies. The electrostatic interaction becomes larger in the order CO₂ << H₂CO << CO < C₂H₄ ≈ C₂H₂, roughly the increasing order of the negative charge on the coordinating atoms. A weaker back-donation makes the end-on-coordination mode less stable than the side-on mode. Exceptional characteristics of the CO ligand are also discussed and explained.

Introduction

The goal of this series of papers² is to answer questions regarding the coordinate-bond nature and stereochemistry of Ni(PR₃)₂L (L = H₂CO, C₂H₄, C₂H₂, CO₂, (CO)₂).³ Why does the L ligand coordinate to Ni in the side-on-coordination mode rather than the end-on mode except for CO?³⁻⁷ Why is the L ligand greatly distorted?³⁻⁷ Why is Ni(PR₃)₂L (L = C₂H₄, C₂H₂, CO₂, H₂CO) planar,³⁻⁷ though Ni(PR₃)₂(CO)₂ is pseudotetrahedral?⁸ Can these coordinate bonds be described by the Dewar-Chatto-Duncanson model?⁹ The above questions are not limited to the chemistry of Ni(PR₃)₂L but are applicable generally to the chemistry of low-valent organo-transition metal complexes.

In this article, Ni(PH₃)₂(H₂CO) and Ni(PH₃)₂(CO)₂ are studied with the energy decomposition analysis¹⁰ in the ab initio MO method to answer the above-mentioned questions. Although the H₂CO complex has been postulated as an intermediate of an interesting catalytic reaction by transition-metal complexes,¹¹ no MO theoretical study on it has been carried out. The other emphasis of this work, the point of departure from our previous papers,² lies in comparing systematically the coordinate-bond nature of C₂H₄, C₂H₂, CO₂, H₂CO, and CO ligands.

Computational Procedures

Ab initio SCF-MO calculations¹² were performed for the closed-shell (singlet) state by using a double-ζ quality basis

set.¹³ As has been shown in the previous papers,² this basis set and a triple-ζ quality basis set give a similar binding energy and electron distribution for bonding between Ni(PH₃)₂ and a π ligand.

Although ³D(3d⁹4s¹), ³F(3d⁸4s²), and ¹S(3d¹⁰) lie energetically very close to each other in the free Ni atom, the ground state of Ni(PH₃)₂L is considered to be a closed-shell singlet, which has been discussed in detail^{2b} and will not be repeated. The essence is that phosphine ligands stabilize the Ni d¹⁰ electron configuration relative to d⁹s and d⁸s². Some experimental results suggest that Ni(PR₃)₂(R'₂CO) and Ni(PR₃)₂(CO)₂ are indeed diamagnetic.^{4b,14} This is in contrast to the high spin state of ligand free π complexes such as Ni(C₂H₄)_n (n = 1, 2).¹⁵

The energy decomposition analysis (EDA)¹⁰ was carried out in order to investigate the coordinate-bond nature in detail. In the EDA scheme, the binding energy (BE) between Ni(PH₃)₂ and L is defined as

$$BE = INT + DEF \quad (1)$$

where DEF is the destabilization energy caused by the geometrical deformation of L and Ni(PH₃)₂,¹⁶ INT is the stabilization energy resulting from the interaction between Ni(PH₃)₂ and the deformed L, and, consequently, BE is the stabilization energy relative to Ni(PH₃)₂ and the undeformed L. INT is further divided into various interaction components such as the electrostatic (ES), the exchange repulsion (EX), the donative or forward charge-transfer polarization (FCTPLX), the back-donative or back-charge-transfer polarization (BCTPLX), and the higher order mixing (R) term.^{2b} In this paper FCTPLX is the donative interaction from L to Ni(PH₃)₂ and BCTPLX is the back-donative interaction from Ni(PH₃)₂ to L. Details of the EDA scheme are given elsewhere.^{2,10}

For Ni(PH₃)₂(CO)₂, where an ambiguity of three-body interaction exists, the following definitions are used: DEF = $\frac{1}{2}\{E[(CO)_2 \text{ in the complex}] - 2E[\text{free CO}] + E[\text{Ni(PH}_3)_2]$

- (1) (a) Kumamoto University. (b) Institute for Molecular Science. (c) Present address: Department of Chemistry, Osaka City University, Osaka, Japan.
- (2) (a) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292. (b) Sakaki, S.; Kitaura, K.; Morokuma, K. *Ibid.* **1982**, *21*, 760.
- (3) Jolly, P. W.; Wilke, G. "Organic Chemistry of Nickel"; Academic Press: New York, 1974.
- (4) (a) Countryman, R.; Penfold, B. P. *J. Chem. Soc. D* **1971**, 1598. (b) Tsau, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311.
- (5) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Chem. Commun.* **1975**, 636.
- (6) (a) Brauer, D.; Krüger, C., unpublished data cited in ref 3 (p 249). (b) Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 5333.
- (7) Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* **1972**, *36*, 191.
- (8) Jarvis, J. A. J.; Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1970**, 1867.
- (9) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18c*, 79. Chatt, J.; Duncanson, J. A. *J. Chem. Soc.* **1953**, 2939.
- (10) (a) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294. (b) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.
- (11) (a) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816. (b) Chen, A. S. C.; Halpern, J. *Ibid.* **1980**, *102*, 838. (c) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1979**, *101*, 503. (d) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045.
- (12) The program used for calculations was IMSPACK (Morokuma, K.; Kato, S.; Kitaura, K.; Ohmine, I.; Sakai, S.; Obara, S. IMS Computer Center Program Library, Institute for Molecular Science, 1980; No. 0372), consisting of GAUSSIAN70, HONDO, and many other of our own routines.

- (13) For ligand atoms: Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Lathan, W. A. *Ibid.* **1972**, *56*, 5255. For the Ni atom: Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta* **1971**, *20*, 1. The basis set was used after a slight modification.²
- (14) Ogilvie, F.; Clark, R. J.; Verkade, J. G. *Inorg. Chem.* **1969**, *8*, 1904.
- (15) Upton, T. H.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 321. Ozin, G. A.; Power, W. J.; Upton, T. H.; Goddard, W. A., III. *Ibid.* **1978**, *100*, 4750. Basch, J.; Newton, M. D.; Moskowitz, J. W. *J. Chem. Phys.* **1978**, *69*, 584. Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 7176.
- (16) The DEF of Ni(PH₃)₂ was considered only in Ni(PH₃)₂(CO)₂. In all other complexes the structure of the Ni(PH₃)₂ part does not vary much, and therefore a standard structure (∠PNiP = 120°) is used without deformation.

Table I. Energy Components (kcal/mol) and Mulliken Population Changes^a for Interaction between Ni(PH₃)₂ and L (L = H₂CO or (CO)₂)

	Ni(PH ₃) ₂ (H ₂ CO)							
	Ni(PH ₃) ₂ (CO) ₂ ^b		side-on			end-on		
	p-Td	PI ^c	p-Td $\theta^d = 32^\circ$	PI $\theta = 32^\circ$	PI $\theta = 0^\circ$	$R_{\text{Ni-O}} = 1.97 \text{ \AA}$ $R = 1.66 \text{ \AA}$		
	Energy Components							
BE	-23	17	-14	-42	-32	-7	5	
DEF	3	14	20	20	11	0	0	
INT	-26	3	-34	-62	-44	-7	5	
ES	-102	-115	-96	-102	-101	-27	-95	
EX	136	175	155	157	161	42	157	
BCTPLX	-42	-41	-55	-74	-67	-13	-39	
FCTPLX	} -18	} -16	-13	-17	-15	-7	-17	
R				-25	-25	-21	-2	0
	Changes in Mulliken Populations							
Ni	-0.21	-0.22	-0.39	-0.35	-0.30	-0.09		
d	-0.43	-0.39	-0.60	-0.61	-0.54	-0.13		
s	+0.02	+0.02	+0.05	+0.06	+0.05	0.0		
p	+0.20	+0.15	+0.16	+0.20	+0.18	+0.04		
L	+0.21	+0.18	+0.58	+0.66	+0.59	+0.06		

^a [Mulliken population of the complex] - [Mulliken population of fragments, Ni(PH₃)₂ or L]. ^b Energy per Ni(PH₃)₂-CO pair. ^c $\angle\text{CNiC} = \angle\text{PNiP} = 90^\circ$. Though the optimum angles of $\angle\text{CNiC}$ and $\angle\text{PNiP}$ are slightly different from 90° (see Figure 1), the difference in energy is very small. ^d The distortion angle between the CH₂ plane and the C=O bond in H₂CO.

in the complex] - $E[\text{Ni}(\text{PH}_3)_2, \text{"standard"}]$; INT = INT₁ - INT₂; INT₁ = $1/2\{E[\text{complex}] - E[\text{Ni}(\text{PH}_3)_2 \text{ in the complex}] - 2E[\text{CO in the complex}]\}$; INT₂ = $1/2\{E[\text{CO}_2 \text{ in the complex}] - 2E[\text{CO in the complex}]\}$. The energy components are calculated for INT₁ and INT₂ and subtracted to obtain those for INT. INT₂ components (kcal/mol), representing the CO-CO interaction in the complex, are small (ES = 0, EX = 3, FCTPLX + BCTPLX = -1, and R = 0 for the pseudotetrahedral structure; ES = -2, EX = 15, FCTPLX + BCTPLX = -3, and R = 0 for the planar structure) and are of minor significance.

Geometries and Their Optimization

For Ni(PH₃)₂(H₂CO) the side-on-coordinated planar (PI), the side-on-coordinated pseudotetrahedral (p-Td), and the end-on-coordinated structures, shown in Figure 1, were examined. The geometry of the Ni(PH₃)₂ part was same as in previous work.^{2,16} The CH bond length and the HCH angle of H₂CO were taken from the experimental structure of free H₂CO.¹⁷ The structure of the side-on-coordinated PI Ni(PH₃)₂(H₂CO) was constructed from the above-described Ni(PH₃)₂ and H₂CO with the Ni-C, Ni-O, and C=O bond lengths taken from the corresponding experimental values of Ni(PPh₃)₂[(CF₃)₂C=O],^{4a} with the assumption that the CO double bond is placed perpendicular to the bisector of $\angle\text{PNiP}$. The distortion angle, defined as an angle between the CH₂ plane and the C=O bond, was optimized to be 32° , which agrees well with experimental values⁴ as described later. The same geometry of H₂CO was used in the side-on p-Td Ni(PH₃)₂(H₂CO). In the end-on-coordinated complex, the C=O bond length was taken to be 1.20 Å, which is the optimized bond length of free H₂CO. H₂CO was placed on the bisector of $\angle\text{PNiP}$. Of two possible structures, one where H₂CO lies in the xz and the other with it in the yz plane, the latter is more stable than the former by about 3 kcal/mol at $R_{\text{Ni-O}} = 2.0 \text{ \AA}$. This small energy difference suggests that H₂CO can rotate easily around the Ni-O axis. The Ni-O distance was optimized to be 1.97 Å in the structure having H₂CO in the yz plane.

In Ni(PH₃)₂(CO)₂, both p-Td and PI structures were examined. The Ni-C and C-O bond lengths were taken to be

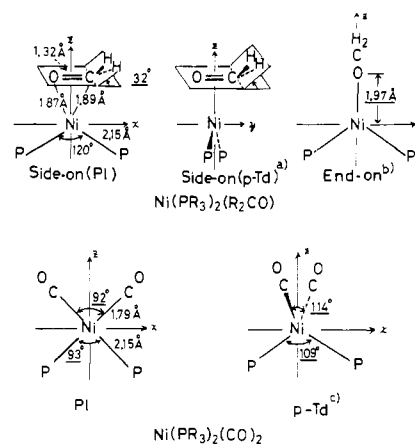


Figure 1. Coordinate systems of the complexes Ni(PH₃)₂(H₂CO) and Ni(PH₃)₂(CO)₂. Optimized geometrical parameters are underlined. Explanation for superscripts: (a) same bond length and bond angle used as those of the side-on (PI) structure; (b) geometry of the Ni(PH₃)₂ part taken as the same as for the side-on complex; (c) Ni-P, Ni-C, and CO bond lengths taken as the same as those of the planar structure.

1.79 and 1.13 Å, respectively, on the basis of the experimental values of Ni(PPh₃)₂(CO)₂.⁸ The Ni-P bond length was assumed to be the same as in the Ni(PH₃)₂(H₂CO). In both structures, the CNiC and PNiP angles were optimized to be $\angle\text{CNiC} = 114^\circ$ and $\angle\text{PNiP} = 109^\circ$ for p-Td, and $\angle\text{CNiC} = 92^\circ$ and $\angle\text{PNiP} = 93^\circ$ for PI. The optimized value of $\angle\text{CNiC}$ in the p-Td structure is larger than the experimental value (104°) of Ni(PPh₃)₂(CO)₂, estimated from an IR study.¹⁸ The optimized geometrical parameters are outlined in Figure 1.

Total energies (in hartrees) of complexes and important fragments are as follows: Ni(PH₃)₂ = -2187.6603 for the fragment in Ni(PH₃)₂(H₂CO), -2187.6543 in the p-Td Ni(PH₃)₂(CO)₂, and -2189.6314 in the PI Ni(PH₃)₂(CO)₂; H₂CO = -113.6582 in the side-on complex ($R_{\text{C=O}} = 1.32 \text{ \AA}$ with the CH₂ bending angle 32°), -113.6906 in the end-on complex ($R_{\text{C=O}} = 1.204 \text{ \AA}$); CO = -112.5524 ($R_{\text{C=O}} = 1.13 \text{ \AA}$); Ni(PH₃)₂(H₂CO) = -2301.4177 for the PI side-on structure, -2301.3727 for the p-Td side-on structure, and

(17) Sutton, E. "Tables of Interatomic Distances and Configuration in Molecules and Ions"; The Chemical Society: London, 1958.

(18) Beck, W.; Melnikoff, A.; Stahl, R. *Chem. Ber.* 1966, 99, 3721.

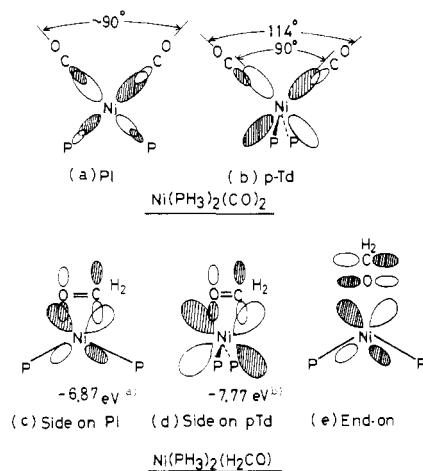


Figure 2. Schematic pictures of the exchange repulsion between $\text{Ni}(\text{PH}_3)_2$ and CO and of the back-donation from $\text{Ni}(\text{PH}_3)_2$ to H_2CO . Explanation for superscripts: (a) orbital energy of d_{xz} ; (b) orbital energy of d_{yz} .

-2301.3628 for the end-on structure; $\text{Ni}(\text{PH}_3)_2(\text{CO})_2 = -2142.8381$ for the p-Td structure ($\angle\text{PNiP} = 109.46^\circ$, $\angle\text{CNiC} = 114.0^\circ$) and -2412.7120 for the PI structure ($\angle\text{PNiP} = \angle\text{CNiC} = 90.0^\circ$).

Results and Discussion

Pseudotetrahedral (p-Td) and Planar (PI) Structures of $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ and $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$. Table I lists the BE, DEF, INT, energy components, and Mulliken populations of various structures of $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ and $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$. The p-Td $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ is substantially more stable than the PI structure, while the PI $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$ is more stable than the p-Td structure. These results agree well with experimental results.^{4,5} As is clearly shown by energy components, the PI $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ is much more destabilized by EX than the p-Td complex; a difference in EX is as large as 38 kcal/mol per $\text{Ni}(\text{PH}_3)_2\text{-CO}$ pair. The PI structure has the optimized CNiC and PNiP angles of 92 and 93°, respectively, perhaps trying to minimize the steric repulsion between ligands. However, this structure gives rise to a large overlap and hence a large EX repulsion between CO lone pairs and the occupied Ni d_{xz} , as is schematically shown in Figure 2a. In the p-Td structure, on the other hand, the CNiC angle can become larger (114°) than 90° without causing large ligand-ligand repulsion, resulting in a small lone-pair-Ni d_{yz} overlap (Figure 2b) and hence a small EX repulsion. Both the PI and the p-Td structures of $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ have four occupied d orbitals ($d_{x^2-y^2}$, d_{z^2} , d_{yz} , and d_{xy} for the PI structure; d_{z^2} , $d_{x^2-y^2}$, d_{xy} , and d_{xz} for the p-Td structure) that can participate in the π back-bonding and have a similar value of BCTPLX.

In $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$, on the contrary, the PI is more stable than the p-Td structure, due to a larger BCTPLX stabilization of the former, as shown in Table I. Mulliken populations in Table I also suggest the stronger back-donation in the PI structure. In the PI structure the Ni $3d_{xz}$ orbital (HOMO) of $\text{Ni}(\text{PH}_3)_2$ interacts with the $\text{H}_2\text{CO} \pi^*$ orbital to form π back-bonding as is shown in Figure 2c,d, whereas in the p-Td structure the Ni $3d_{yz}$ orbital, lying lower in energy than Ni $3d_{xz}$, interacts with the $\text{H}_2\text{CO} \pi^*$ orbital. Consequently, the BCTPLX is larger in the PI than in the p-Td structure. The EX repulsion of the PI structure is similar to that of the p-Td, unlike the case of $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$; this can be understood easily by considering that the electron cloud of H_2CO overlaps with Ni $3d_{xz}$ in the PI structure as well as it does with Ni $3d_{yz}$ in the p-Td structure.

Coordination Mode and Ligand Distortion in $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$. The side-on-coordination mode is somewhat more stable than the end-on mode, as is shown in Table I. This

Table II. Mulliken Population Changes for the PI Side-On $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$ at $\theta = 32^\circ$

	EX	BCTPLX	FCTPLX	R
Gross Populations				
Ni	-0.01	-0.33	+0.06	-0.07
d	-0.01	-0.33	-0.04	-0.23
s	0.0	~0	+0.01	+0.05
p	0.0	~0	+0.09	+0.10
$\text{PH}_3(1)$	+0.1	-0.06	+0.02	-0.11
$\text{PH}_3(2)$	0.0	-0.04	-0.02	-0.11
H_2CO	0.0	+0.43	-0.05	+0.29
Overlap Populations				
Ni-C	-0.08	+0.05	-0.02	+0.11
Ni-O	-0.10	+0.04	+0.05	+0.09
C=O	+0.01	-0.05	-0.01	-0.08
Ni-P(1)	~0	+0.03	+0.02	+0.08
Ni-P(2)	~0	+0.03	-0.03	+0.05

result agrees well with the experimental results that the side-on-coordinated $\text{Ni}(\text{PPh}_3)_2[(\text{CF}_3)_2\text{CO}]$ and $\text{Ni}(\text{PET}_3)_2(\text{Ph}_2\text{CO})$ have been isolated and that no end-on complex has been isolated, though it has been postulated as a reaction intermediate.^{11,19}

The end-on-coordinated $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$ at the optimized structure has substantially smaller energy components and smaller population changes than the side-on complex (see Table I), suggesting a weak interaction between $\text{Ni}(\text{PH}_3)_2$ and H_2CO in the end-on mode. This result, however, does not explain why the end-on mode is unfavorable relative to the side-on mode, for the end-on mode has both a smaller EX repulsion and a smaller ES, FCTPLX, and BCTPLX stabilization. For the explanation, we employ the same procedure as used in the previous work;^{2b} energy components of the end-on complex were calculated at various interfragment distances, and its energy components were compared with those of the side-on complex at the interfragment distance giving the same EX repulsion or the same contact. Energy components at the same EX value (157 kcal/mol) are given in Table I. The side-on mode is more favorable due to BCTPLX and R terms. As an aid in the identification of the meaning of the higher order mixing term R, the Mulliken population analysis was carried out for the side-on complexes (Table II). As expected, charge transfer occurs from H_2CO to $\text{Ni}(\text{PH}_3)_2$ through FCTPLX and from $\text{Ni}(\text{PH}_3)_2$ to H_2CO through BCTPLX. The R term moves electron population from the Ni $3d_{xz}$ orbital to the Ni s and p orbitals and the H_2CO ligand, indicating that R has, to a large extent, a character of back-donation. Thus, the side-on complex is more stable due to stronger back-donation (BCTPLX and R) than the end-on complex. Figure 2d,e explains schematically why the overlap is smaller and, therefore, the back-donation is weaker in the end-on complex.

The ligand distortion was also examined in the PI side-on $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$. Optimized distortion angles are compared with experimental values in Table III for this complex as well as those studied previously.² The agreement is very good, suggesting the basis set used in this series of work is expected to offer good results regarding ligand distortion. Energy components of the undistorted ($\theta = 0^\circ$) and the distorted ($\theta = 32^\circ$) complex are given also in Table I. The distortion makes the back-donative BCTPLX and R stabilization larger and the EX repulsion smaller. Though both factors contribute to stabilize the distorted structure, the back-donative stabilization, 3 times as large as the reduction of EX repulsion, is the principal driving force for distortion. The H_2CO distortion lowers the π^* orbital energy and promotes back-donative stabilization.

(19) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045.

Table III. Distortion of Ligands in Ni(PH₃)₂L (L = C₂H₄, C₂H₂, CO₂, H₂CO)

L	distortion angle, ^a deg	
	calcd	obsd
H ₂ CO	32	42 ^b (Ni(PPh ₃) ₂ [(CF ₃) ₂ CO])
		26.6 ^c (Ni(PEt ₃) ₂ (Ph ₂ CO))
C ₂ H ₄	26	28.4 ^d (Ni(CN- <i>t</i> -Bu) ₂ (TCNE))
		26 ^e (Ni[(Cy) ₂ PC ₂ H ₄ P(Cy) ₂](C ₂ Me ₄))
C ₂ H ₂	40	31 ^f (Ni(CN- <i>t</i> -Bu) ₂ (C ₂ Ph ₂))
CO ₂	42	47 ^g (Ni[P(Cy) ₃] ₂ (CO ₂))

^a The angle between the CH₂ plane and the C=O or C=C bond for L = H₂CO or C₂H₄; the angle is 180° - ∠HCC for L = C₂H₂ and is 180° - ∠OCO for L = CO₂. ^b Reference 4a. ^c Reference 4b. ^d Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* 1970, 92, 5333. ^e Brauer, D.; Kruger, C., unpublished data cited in ref 3, Vol. 1, p 249. ^f Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* 1972, 36, 191. ^g Aresta, M.; Nobile, C. F. *J. Chem. Soc., Chem. Commun.* 1975, 636.

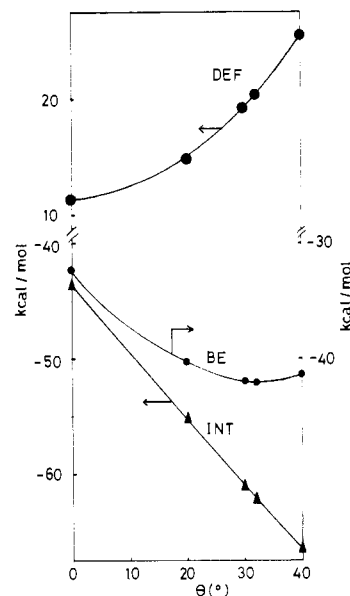
Figure 3 shows the dependence of BE, DEF, and INT on the ligand distortion. The same dependency has been found in both Ni(PH₃)₂(C₂H₄) and Ni(PH₃)₂(CO₂),² suggesting that this is a general feature regarding ligand distortion. By using this feature, the degree of ligand distortion can easily be predicted; a curve of DEF is obtained by a few MO calculations for the distorted ligand, a straight line of INT is given by two MO calculations on the complex, and the degree of distortion is predicted from a balance between DEF and INT. Now we show that the above dependency is justifiable. The dependence of DEF on the ligand distortion seems reasonable, for the potential curve is usually quadratic near the equilibrium structure. The dependence of INT, however, requires a detailed examination. The change of INT mainly comes, as shown above, from an increased back-donation caused by the lowering of π* orbital energy and can be roughly estimated by a simple second-order perturbation theory:

$$\Delta(\text{INT}) \approx \sum_i^{\text{OCC}} [\beta_{i\pi^*}^2 / (\epsilon_i - \epsilon_{\pi^*}) - \beta_{i\pi^*0}^2 / (\epsilon_i - \epsilon_{\pi^*0})] \quad (2)$$

where ϵ_i is the energy of an occupied orbital of Ni(PH₃)₂, ϵ_{π^*} is the ligand π* orbital energy, $\beta_{i\pi^*}$ is the resonance integral, and a subscript 0 means the undistorted structure. With the assumption that $\beta_{i\pi^*} \approx \beta_{i\pi^*0}$ and with the property $\Delta\epsilon_{\pi^*0} (= \epsilon_{\pi^*} - \epsilon_{\pi^*0}) \ll \Delta\epsilon_{i\pi^*0} (= \epsilon_i - \epsilon_{\pi^*0})$, eq 2 is rewritten as

$$\Delta(\text{INT}) \approx \sum_i^{\text{OCC}} (\beta_{i\pi^*0}^2 / \Delta\epsilon_{i\pi^*0}) \Delta\epsilon_{\pi^*0} \quad (3)$$

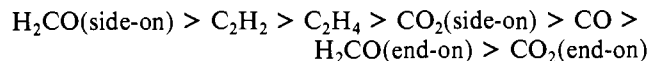
This equation suggests that Δ(INT) decreases in parallel with a decrease in ϵ_{π^*} . It has been shown^{2b} that the π* orbital

**Figure 3.** INT, DEF, and BE of side-on-coordinated Ni(PH₃)₂(H₂CO) vs. the H₂CO distortion angle θ , the angle between the CH₂ plane and the C=O bond.

energy linearly decreases with increasing ligand distortion in a wide range of distortion.

Comparison of Coordinate-Bond Nature of Various Ligands.

Now we will compare the nature of the coordinate bond of various ligands in Ni(PH₃)₂L. BE, INT, DEF, and energy components are taken from this work and our previous papers² and are for the best complex geometries, except for those in parentheses. The binding energy BE is found to decrease in the order



Since neither enthalpy nor equilibrium constants have been reported for these complexes, it is difficult to compare the above order with experiments in detail. However, the above order is compatible with experimental findings that no end-on complexes of CO₂ and R₂CO have been isolated, while side-on complexes of C₂H₄, C₂H₂, CO₂, and R₂CO and an end-on complex of CO have been isolated.³ Paying attention to energy components in Table IV, we find the following characteristics in the side-on complexes: (1) a coordinate bond is stabilized mainly by ES and BCTPLX, (2) the FCTPLX energy is about one-third to one-fifth of BCTPLX and depends little on lig-

Table IV. Energy Components for Interaction between Ni(PH₃)₂ and L (L = C₂H₄, C₂H₂, CO₂, H₂CO, or CO) (kcal/mol) and Ligand Properties

L	side-on				end-on		
	H ₂ CO	CO ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂ CO	CO ₂
(a) Energy Components							
BE	-42	-27	-37	-30	-23 ^a	-7 (3) ^b	1 (20) ^b
DEF	20	34	40	15	3 ^a	0	4
INT	-62	-61	-77	-45	-26 ^a	-7 (3) ^b	-3 (16) ^b
ES	-102	-76	-148	-132	-101	-27 (-83) ^b	-14 (-78) ^b
EX	157	131	189	168	136	42 (136)	24 (136)
BCTPLX	-74	-70	-75	-54	-43	-13 (-35)	-7 (-28)
FCTPLX	-17	-16	-24	-16	-19	-7 (-16)	-4 (-13)
R	-26	-30	-19	-11		-2 (-1)	-3 (-3)
(b) Properties of Deformed Ligands							
π*, eV	2.27	0.85	2.59	3.84	4.05	3.60	4.31
Mulliken Population							
C	5.87	5.09	6.25	6.33	5.61	5.83	5.01
O	8.50	8.48	8.40	8.48	8.52

^a Values for a Ni-CO interaction. ^b Energy component at R_{Ni-O} = 1.69 Å for both Ni(PH₃)₂(CO₂) and Ni(PH₃)₂(H₂CO).

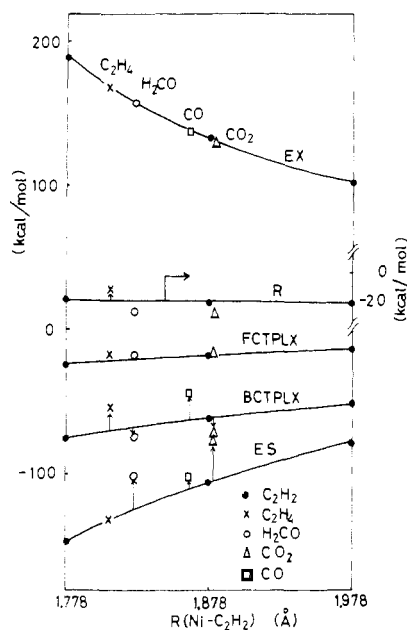


Figure 4. Dependence of energy components on the interfragment distance in $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$ and energy components of various complexes. $R(\text{Ni}-\text{C}_2\text{H}_2)$ denotes the distance between Ni and the center of the $\text{C}\equiv\text{C}$ triple bond.

ands, (3) C_2H_2 , H_2CO , and CO_2 complexes have a similar BCTPLX energy, while C_2H_4 and CO complexes have less, and (4) the ES stabilization decreases in the order $\text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{H}_2\text{CO} \gg \text{CO}_2$. Among the end-on complexes, the CO complex is distinctly different from the H_2CO and the CO_2 complexes. The former is a stronger complex with a larger ES and BCTPLX stabilization and also with large EX destabilization, while the latter two are weaker complexes with smaller energy components.

We see two problems to be examined regarding the nature of the coordinate bond of various ligands. (1) Why can CO form a stable complex with $\text{Ni}(0)$ but the other two ligands cannot in the end-on coordination mode? (2) What relationship can be found between the coordinate-bond nature and ligand properties? When we examine these problems, it is best to compare various complexes, as discussed above and in a previous paper,^{2b} at geometries that give the same EX value or the same "contact". In an approach to the first problem, i.e., a comparison between the CO complex and the other two end-on complexes, energy components for each complex were calculated at an interfragment distance which gives the same EX value, arbitrarily chosen to be 136 kcal/mol, the EX value of optimized $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$. As shown in parentheses in Table IV, H_2CO and CO_2 complexes have substantially smaller ES stabilization and somewhat smaller BCTPLX stabilization than the CO complex. The large ES stabilization in the CO complex is attributable to the large σ polarity $\text{C}^\delta-\text{O}^{\delta+}$ or the existence of the σ lone pair on C. Though CO has a small overall polarity, the rich electron density on the C σ lone-pair orbital makes CO a favorite end-on ligand. A favorable BCTPLX stabilization in the CO complex can be explained in terms of the distribution of the π^* orbital; the π^* orbitals of these ligands are localized more on C than on O, and CO , coordinating on the C end, has a more favorable overlap than the other two, which coordinate on the O end.

In an approach to the second problem, energy components of $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$ were first obtained at three interfragment distances and are connected as the "reference curves", as shown in Figure 4. Energy components of any other complex at its optimized geometry are then plotted in Figure 4 at the interfragment distance $R_{\text{Ni}-\text{C}_2\text{H}_2}$, where $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$ has the same EX energy as that of the complex in question. Whether

a plot of an energy component for a complex is below or above the reference curve tells whether this energy component favors or disfavors the complex over the reference C_2H_2 complex. Apparently FCTPLX makes no difference between the complexes examined here. Compared with the C_2H_2 complex, the H_2CO and CO_2 complexes have slightly better BCTPLX stabilization, while the C_2H_4 and CO complexes receive less favorable BCTPLX stabilization. The π^* orbital energy of the deformed ligand increases, as shown in Table IV, in the order $\text{CO}_2 < \text{H}_2\text{CO} < \text{C}_2\text{H}_2 < \text{C}_2\text{H}_4 < \text{CO}$ and dictates, as expected, the preference of back-donation.

The ES stabilization of the CO_2 and H_2CO complexes is substantially less favorable, and that of the CO complex is only slightly less favorable than those of the C_2H_4 and C_2H_2 complexes. Because the Ni atom in $\text{Ni}(\text{PH}_3)_2$ is somewhat positively charged, the ES stabilization is expected to become less favorable with a decreasing sum of negative net charges of the coordinating atoms, $\text{C}_2\text{H}_4 > \text{C}_2\text{H}_2 > \text{H}_2\text{CO} \approx \text{CO} > \text{CO}_2$. The actual order of ES agrees roughly with this order, though some discrepancies are found for C_2H_2 and CO . Such discrepancies are, however, understandable; CO has a lone-pair electron cloud extending to Ni and the largely distorted C_2H_2 also has its π electron cloud extended to Ni. These two ligands would give rise to a stronger electrostatic attraction with Ni than the simple net point charge attraction would predict.

Concluding Remarks

The structure and bond nature of $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$ and $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ were investigated by using the ab initio MO method with double- ζ basis sets. Their most stable structures calculated here agree well with experiments. A discussion is presented explaining the relationship between the structure and the coordinate-bond nature. For example, $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$ is the most stable at a planar structure with a side-on-coordinated H_2CO ligand, which has a stronger back-donation than p-Td side-on and end-on structures. The most stable structure of $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$ is p-Td, as it has less EX repulsion than Pl. It should be noted that the ligand distortion of $\text{Ni}(0)$ complexes was successfully reproduced in this series of studies. The driving force for the distortion is shown clearly to be the strengthening of back-donation.

A discussion is also presented on the coordinate-bond nature of $\text{Ni}(\text{PH}_3)_2\text{L}$ ($\text{L} = \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \text{CO}_2, \text{H}_2\text{CO},$ and $(\text{CO})_2$). The back-donation and the electrostatic interaction mainly contribute to the coordinate bond. In side-on complexes, the back-donation is strong when the π^* orbital is low in energy, and the electrostatic interaction is large when the coordinating atom is negatively charged. In end-on complexes, the back-donation is more unfavorable than in side-on complexes because of small overlap between the Ni d π and the ligand π^* orbital. A stable end-on complex is formed when the p π orbital of the coordinating atom has a large weight in the ligand π^* orbital to favor its overlap with the Ni d π orbital and when the ligand lone-pair orbital extends to Ni to cause a strong electrostatic interaction. The CO ligand satisfies these conditions, and consequently its end-on complex is stable, while the H_2CO and CO_2 ligands cannot satisfy these conditions.

We have studied the structure and bond nature of $\text{Ni}(\text{PH}_3)_2\text{L}$ ($\text{L} = \text{C}_2\text{H}_4, \text{C}_2\text{H}_2,$ etc.) in this series of papers. We feel that results and implications obtained here are of general significance and applicability to other low-valent transition-metal complexes.

Acknowledgment. S.S. is grateful for support through the IMS Joint Studies Program and a Ministry of Education grant. Numerical calculations were carried out at the IMS Computer Center.

Registry No. $\text{Ni}(\text{PH}_3)_2(\text{H}_2\text{CO})$, 83365-29-1; $\text{Ni}(\text{PH}_3)_2(\text{CO})_2$, 83365-30-4; C_2H_4 , 74-85-1; C_2H_2 , 74-86-2; H_2CO , 50-00-0; CO_2 , 124-38-9; CO , 630-08-0.