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Structure and Coordinate Bonding Nature of Nickel(0) and Copper(I) Carbon Dioxide Complexes. An ab Initio Molecular Orbital Study

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Ab initio MO calculations and energy decomposition analyses were carried out for the complexes of $Ni^0(PH_3)_2$ and $Cu^I(PH_3)_2$ with CO_2. The coordinate bond is stabilized mainly by electrostatic and/or back-donative interactions. A side-on and an end-on coordination of CO_2 require a sufficient back-donative and an electrostatic stabilization, respectively. $Ni(PH_3)_2$ can form a side-on-coordinated carbon dioxide complex because of the ability of Ni(0) to provide π back-donation, whereas an end-on-coordination mode should be favorable for $Cu(PH_3)_2{}^+$ because of a strong electrostatic interaction between Cu(I) and the negatively charged O atom of carbon dioxide. The C-coordination mode is unfavorable due to a repulsive electrostatic interaction between the metal and the positively charged C atom. The distortion of the CO_2 ligand of $Ni(PH_3)_2(CO_2)$ enhances the stabilization by increasing a π back-donation.

Introduction

Some transition-metal ions in the low-valency state form complexes with carbon dioxide. Such carbon dioxide complexes have a potential for practical application in activating otherwise inactive carbon dioxide.[2] It is significant, therefore, to investigate theoretically their natures of coordinate bond and electronic structure. Only a few molecular orbital (MO) studies have been reported on the metal–carbon dioxide complexes.[3-5] In a CNDO–MO study on $Pt(PH_3)_2(CO_2)$,[3] it has been briefly studied why a carbon dioxide ligand is placed in the plane of $Pt(PH_3)_2$. In an ab initio MO study of Zn^{2+}–CO_2,[5] the nature of the coordinate bond has been discussed in detail on the basis of energy decomposition. There is no ab initio MO study on carbon dioxide complexes of transition metals.

Carbon dioxide complexes of transition metals pose several questions of theoretical interest. The first is coordinate bonding modes. One would like to find out which of the three coordination modes, the side-on mode, the C mode, or the end-on mode (see Chart I), is the most favorable.[2] The side-on mode has been known in $Ni(PCy_3)_2(CO_2)$ (Cy = C_6H_{11}).[6] The C-coordination mode has been presumed in $Ni(PCy_3)_3(CO_2)$,[7] $Ir(dmpe)_2Cl(CO_2)$ (dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$),[8] and $RhCl(CO_2)L_3$ (L = PR_nPh_{3-n}).[9] The end-on mode has been considered less probable than the others.[2b] The second problem is concerned with the CO_2 distortion caused by the coordination; in $Ni(PCy_3)_2(CO_2)$, the CO_2 ligand is substantially distorted (∠OCO = 133°).[6] We wish to investigate the driving force for the distortion, a direct evidence on the nature of the coordinate bond. The third is the nature of the coordinate bond. In olefin and acetylene complexes, the nature of the coordinate bond has been discussed in terms of the Dewar–Chatt–Duncanson model,[10] where the coordinate bond has been considered to consist of the σ-donative interaction and the π-back-donative interaction, as is shown in Chart II. Recently the relative importance of σ donation or π back-donation has been discussed semiquantitatively for $Ni(PH_3)_2(C_2H_4)$ and $Ni(PH_3)_2(C_2H_2)$ with the ab initio MO method[11] and for some transition-metal ethylene complexes with the Hartree–Fock–Slater method.[12] The coordinate bond of the CO_2 complex is also expected to be described by the Dewar–Chatt–Duncanson model. It is interesting to study theoretically which of the two, the σ-donative or the π-back-donative interaction, is more important in the coordination of carbon dioxide.

Chart I

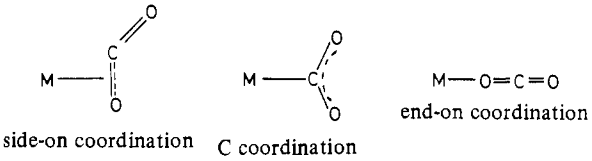
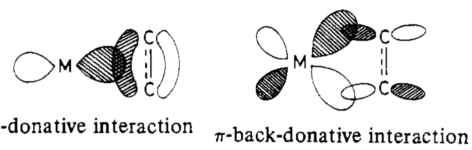


Chart II



In this paper two carbon dioxide complexes, $Ni(PH_3)_2(CO_2)$ and $[Cu(PH_3)_2(CO_2)]^+$, have been investigated with an ab initio MO method. The former is a model complex for $Ni(PCy_3)_2(CO_2)$, a well-studied carbon dioxide complex. $[Cu(PH_3)_2(CO_2)]^+$ is not a model for a real complex but is studied here because this complex is expected to have the same electron configuration as $Ni(PH_3)_2(CO_2)$ and yet its mode of coordination could be different because of a different charge. The authors intend (a) to compare three types of coordination modes and discuss which is the most stable and why the carbon dioxide coordinates to the Ni(0) through the side-on-coordination mode, (b) to investigate why the carbon dioxide is distorted in $Ni(PCy_3)_2(CO_2)$, and (c) to study the detailed nature of the coordinate bond of carbon dioxide.

Computational Details

MO Method. The ab initio LCAO–SCF–MO method was used. The computer program employed is IMSPACK,[13] which contains GAUSSIAN 70, HONDO, and many new routines.

Basis Sets. For the first- and the second-row elements except for transition metals, the 4-31G split-valence basis set was used with standard parameters.[14,15] For Ni and Cu, the basis sets were taken from Roos, Veillard, and Vinot,[16] with some modifications and contractions. In the case of the s

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orbitals, the two most diffuse primitive Gaussians were excluded, and a primitive Gaussian with the exponent of 0.2 was added. In the cases of the p and d orbitals, primitive Gaussians with the exponent of 0.25 for p and 0.2 for d were added. The resultant primitives (11s7p5d) were contracted to a [4s3p2d] basis set.[17a]

So that the reliability of this basis set could be examined, a calculation for the side-on $Ni(PH_3)_2(CO_2)$ was carried out by using a larger basis set, i.e., a valence triple-ζ [6s5p3d] basis set[17b] for Ni and the 4-31G for the others. The usual [4s3p2d] basis set gave the Ni Mulliken population $d^{9.71}s^{6.03}p^{12.01}$ for $Ni(PH_3)_2$ and $d^{9.12}s^{6.10}p^{12.21}$ for $Ni(PH_3)_2(CO_2)$, while the larger [6s5p3d] basis set gave $d^{9.64}s^{6.23}p^{12.07}$ and $d^{9.00}s^{6.29}p^{12.30}$, respectively. PH_3 in $Ni(PH_3)_2$ has a Mulliken population of 18.13 in the usual basis set and 18.03 in the larger basis set, and CO_2 in $Ni(PH_3)_2(CO_2)$ has a Mulliken population of 22.69 in the usual set and 22.61 in the larger set. As expected, the Ni atom accepts more electron population in the larger basis set, but the effect is small. The change of population upon the CO_2 coordination is virtually identical in both basis sets; the decrease of the Ni atomic population is mainly due to a decrease in the $3d_{xz}$ orbital population. Furthermore, the calculated stabilization energy due to the CO_2 coordination, which is defined as INT in the following section, is not much different between the two basis sets: 61 kcal/mol in the usual set and 50 kcal/mol in the larger set. Therefore, the present basis set is expected to give the same bonding picture of CO_2 coordination as a larger basis set would give.

An even smaller basis set was used in some geometrical optimizations. The basis functions of the metal atoms were the above [4s3p2d], while the basis functions for other atoms were replaced by the STO-3G.[18] When the smaller basis set is used, it will be specifically mentioned. Otherwise, the [4s3p2d] + 4-31G basis set is used throughout this paper.

Energy Decomposition. So that the nature of coordinate bond could be investigated in detail, the decomposition of the interaction energy was carried out with a new variation[11] of the method of Kitaura and Morokuma.[19] In this analysis, $M(PH_3)_2(CO_2)$ is considered to be composed of the $M(PH_3)_2$ fragment and the CO_2 ligand. The binding energy, BE, the energy difference between the complex and the isolated fragments, is divided into two parts: the deformation energy, DEF, and the interaction energy, INT:

$$\mathrm{BE} = E_{\mathrm{total}}[\mathrm{M(PH_3)_2(CO_2)}] - E_{\mathrm{total}}[\mathrm{M(PH_3)_2}] - E_{\mathrm{total}}(\mathrm{CO_2}\text{ in the equilibrium structure}) = \mathrm{DEF} + \mathrm{INT}$$

DEF is the energy required to distort the ligand from its equilibrium structure to the structure it takes in the complex.

$$\mathrm{DEF} = E_{\mathrm{total}}(\text{distorted }\mathrm{CO_2}) - E_{\mathrm{total}}(\mathrm{CO_2}\text{ in the equilibrium structure})$$

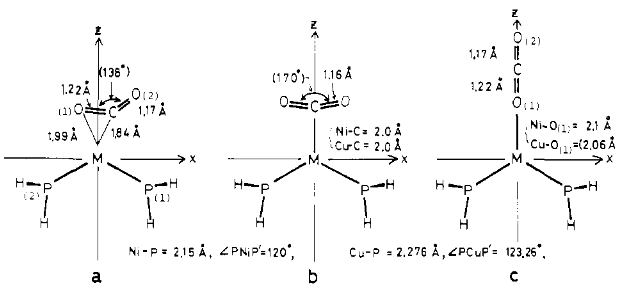

Figure 1. Assumed geometries of three types of complexes. Values in parentheses are optimized values. Total energies (au) of the complexes shown here are as follows: side-on $Ni(PH_3)_2(CO_2)$ = −2375.0310; C-coordinated $Ni(PH_3)_2(CO_2)$ = −2374.9797; end-on $Ni(PH_3)_2(CO_2)$ = −2374.9867 (Ni–O = 2.1 Å); side-on $Cu(PH_3)_2(CO_2)^+$ = −2506.6805; C-coordinated $Cu(PH_3)_2(CO_2)^+$ = −2506.7267; end-on $Cu(PH_3)_2(CO_2)^+$ = −2506.7936. Total energies (au) of important fragments are as follows: PH_3 = −342.0252; $Ni(PH_3)_2$ = −2187.6603; $Cu(PH_3)_2^+$ = −2319.4437; CO_2 for the side-on complex (∠OCO = 139°) = −187.2738, CO_2 for the C-coordination = −187.3254; CO_2 for the end-on coordination = −187.3209.

The $M(PH_3)_2$ part is assumed to be rigid. INT is the stabilization energy resulting from the coordination of the distorted CO_2 to the $M(PH_3)_2$ fragment:

$$\mathrm{INT} = E_{\mathrm{total}}[\mathrm{M(PH_3)_2(CO_2)}] - E_{\mathrm{total}}[\mathrm{M(PH_3)_2}] - E_{\mathrm{total}}(\text{distorted }\mathrm{CO_2})$$

The present analysis allows INT to further decompose into physically meaningful components: the electrostatic interaction energy, ES; the exchange repulsion energy, EX; the donative interaction energy, FCTPLX; the back-donative interaction energy, BCTPLX; and the remaining energy, R.[11] The present scheme, details of which have been given elsewhere,[11] differs from the traditional decomposition scheme[19] in which the interaction is divided into the electrostatic (ES), the exchange (EX), the polarization (PL), the charge transfer (CT), and the coupling term (MIX) and is appropriate and convenient for describing a weak molecular interaction. When the interaction is strong, however, a substantial coupling between the charge transfer and the polarization takes place, making MIX large and, therefore, the analysis less meaningful. In the present scheme,[11] the wave function of the supermolecule Hartree–Fock calculation describing the donative interaction is given in the form

$$\Psi_{\mathrm{FCTPLX}} = C_0 A(\Psi^0{}_{\mathrm{A}}\cdot\Psi^0{}_{\mathrm{B}}) + \sum_{i}^{\mathrm{occA}}\sum_{l}^{\mathrm{vacB}} C_{il} A[\Psi_{\mathrm{A}}(\mathrm{i_A} \rightarrow \mathrm{l_B})\cdot\Psi^0{}_{\mathrm{B}}] + \sum_{k}^{\mathrm{occB}}\sum_{l}^{\mathrm{vacB}} C_{kl} A[\Psi^0{}_{\mathrm{A}}\cdot\Psi_{\mathrm{B}}(\mathrm{k_B} \rightarrow \mathrm{l_B})] + \text{higher order terms}$$

where $A(\Psi^0{}_A\cdot\Psi^0{}_B)$ is the antisymmetrized product of the monomer wavefunctions, $A[\Psi_A(i_A \rightarrow l_B)\cdot\Psi^0{}_B]$ is the wave function in which a charge transfer from an occupied MO i_A of A to a vacant MO l_B of B is allowed, and $A[\Psi^0{}_A\cdot\Psi_B(k_B \rightarrow l_B)]$ allows a (polarization) excitation within the molecule B. The energy of this wave function relative to the energy of $A(\Psi^0{}_A\cdot\Psi^0{}_B)$ gives the donative interaction energy FCTPLX:

$$\mathrm{FCTPLX} = \langle \Psi_{\mathrm{FCTPLX}}|H|\Psi_{\mathrm{FCTPLX}}\rangle - \langle A(\Psi^0{}_{\mathrm{A}}\cdot\Psi^0{}_{\mathrm{B}})|H|A(\Psi^0{}_{\mathrm{A}}\cdot\Psi^0{}_{\mathrm{B}})\rangle$$

The donative interaction energy thus includes the charge-transfer energy from A to B, the polarization energy of B, and the coupling among the exchange, polarization, and charge-transfer terms. The back-donative interaction is also defined similarly, including the charge transfer from B to A, the polarization energy of A, and the coupling terms. The present definition of donative and back-donative interactions corresponds very well to the concept of interactions used in inorganic chemistry.[11]

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(17) (a) The 11s primitives are contracted as groups of 6s, 2s, 2s, and 1s in a decreasing order of exponents with the contraction coefficients taken from ref 16. Similarly, the 7p and the 5d primitives are grouped into 4p, 2p, 1p and 4d, 1d, respectively. The spherical part of d functions was removed from the calculations. (b) A triple-ζ basis set of Hay, which consists of five primitives, was used for the Ni 3d orbital (Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377). For the Ni s orbital, a primitive with an exponent of 0.2 was added to (12s) primitives of ref 16, and the resultant (13s) primitives were contracted to 6s, 2s, 2s, 1s, 1s, and 1s with the decreasing order of exponents. For the Ni 4p orbital, the most diffuse primitives of the Ni s orbital (exponent = 0.125 776 and 0.047 955) were added to the (6p) primitives of ref 16 to represent the 4p orbital of atomic Ni, and further a primitive with the exponent 0.25 was also added to represent a coordinate bond. The resultant (9p) primitives were contracted to 4p, 2p, 1p, 1p, and 1p. The contraction coefficients for s and p orbitals were taken from ref 16. Overall, (13s9p5d) primitives were contracted to [6s5p3d].

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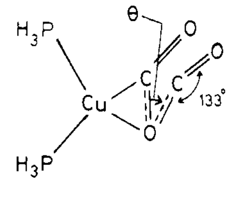
Table I. Energy Components (kcal/mol)[a] for the Interaction between $M(PH_3)_2$ and CO_2 ($M = Ni$ or Cu^+)

	$Ni(PH_3)_2(CO_2)$							$Cu(PH_3)_2(CO_2)^+$			
	side-on			end-on			C coord	side-on		end-on	C coord
	180°[b]	147°	139°	2.0 Å[c]	2.1 Å[c]	1.7 Å[c,d]	2.0 Å[e]	139°[b]	+0.4 Å,[d,f] 139°[b]	2.06 Å[c]	2.0 Å[e]
total bonding energy (BE)	19	−22	−27	1	1	17	5	57	38	−14	28
def energy (DEF)	4	22	34	4	4	4	1	34	34	4	1
interaction energy (INT)	15	−44	−61	−3	−3	13	4	23	4	−18	27
electrostatic (ES)	−71	−73	−76	−21	−14	−75	...	−31	6	−22	...
exchange repulsion (EX)	148	131	131	36	24	131	...	105	20	20	...
donation (FCTPLX)	−12	−15	−16	−5	−4	−13	...	−13	−12	−4	...
back-bonding (BCTPLX)	−41	−64	−70	−9	−7	−27	...	−35	−10	−8	...
remainder (*R*)	−9	−23	−30	−4	−3	−3	...	−3		−3	...

[a] A negative (positive) energy designates stabilization (destabilization). [b] ∠OCO′ angle. [c] R_{M-O}. [d] For equal EX comparison. [e] R_{M-C}. [f] CO_2 is removed away from Cu^+ by 0.4 Å along the *z* axis.

Chart III



In the present system the donative interaction FCTPLX is from CO_2 to $M(PH_3)_2$, and the back-donative interaction BCTPLX is from $M(PH_3)_2$ to CO_2. Though the present analysis does not separate σ and π contributions, FCTPLX roughly corresponds to the σ-donative interaction and BCTPLX to the π-back-donative interaction in the Dewar–Chatt–Duncanson model.

Geometries and Geometry Optimization. Three types of coordination, the side-on coordination, the C coordination, and the end-on coordination, shown in Figure 1, were examined for both Ni and Cu complexes. The geometry of the side-on-coordinated $Ni(PH_3)_2(CO_2)$ was taken from the X-ray study of $Ni(PCy_3)_2(CO_2)$,[6] with the following modifications. The Ni–P bond length, not reported for this complex, was assumed to be 2.15 Å, referring to the X-ray study of $Ni(PPh_3)_2(C_2H_4)$.[20] Although the OCO′ angle has been experimentally known to be 133°,[6] it was varied in the calculation in order to examine the predictability of the present MO method and also to elucidate the angular dependency of the energy components. The optimization gave the angle of 138°, in good agreement with the experiment.[6] Subsequently the distance between Ni and CO_2 was optimized roughly by moving CO_2 in the direction of the *z* axis in Figure 1; the optimized Ni–C = 1.87 Å and Ni–O = 2.02 Å agree well with the experimental values (Ni–C = 1.84 Å and Ni–O = 1.99 Å). For the side-on-coordinated $Cu(PH_3)_2(CO_2)^+$, the geometry of the $Cu(PH_3)_2$ part was taken from the X-ray study of $Cu(PPh_3)_2(BH_4)$.[21] The CO_2 coordination at the relative geometry taken from the Ni complex gives a large destabilization energy. A deviation from this geometry by an increase of the θ in Chart III reduces the destabilization but did not result in any stable complex.

Both in the end-on-coordination and in the C-coordination modes, the geometries of $Ni(PH_3)_2$ and $Cu(PH_3)_2$ were assumed to be the same as those described above. In the end-on mode, the C–O bond lengths were assumed to be the same as those of the side-on coordination ($C–O_1 = 1.22$ Å, $C–O_2 = 2.06$ Å). Two bond lengths, 2.0 and 2.1 Å, were examined for the $Ni–O_1$ bond, both giving almost the same total energy. Without further optimization, we assumed the equilibrium distance is 2.1 Å and used it for the discussion of the electronic structure.

In the C coordination, there are two possible structures: one in which the OCO′ plane is perpendicular to the MPP′ plane and the other in which they lie in the same plane. The geometry of the C-coordinated $Ni(PH_3)_2(CO_2)$ was optimized with the smaller basis set, where the C–O and Ni–C distances are assumed to be 1.16 and 2.0 Å, respectively. The in-plane structure was found to be more stable by about 5 kcal/mol than the perpendicular structure at ∠OCO = 160 and 170°. In the in-plane structure, ∠OCO = 170° was found to be optimal. The structure thus obtained was used for MO calculation with the larger basis set. In the C-coordinated $[Cu(PH_3)_2(CO_2)]^+$, the structure of the $Cu(CO_2)$ part was assumed to be the same as in the C-coordinated $Ni(PH_3)_2(CO_2)$.

Electronic State of $Ni(PH_3)_2(CO_2)$. Because ^3D ($3d^94s^1$), ^3F ($3d^84s^2$), and ^1S ($3d^{10}$) lie energetically close to each other in the free nickel atom, the ground state of a zerovalent nickel complex is expected to have an electron configuration corresponding to one of the above three states. For example, the ground state of $Ni(C_2H_4)$ has been reported to be $^3A_1$ ($3d^94s^1$).[22,23] Similarly, $^3B_{3u}$ ($3d^94p$) has been calculated to be the most stable state in $Ni(C_2H_4)_2$ without electron correlation.[24] In the present study, as well as in the other study of the series, MO calculations were carried out for the singlet state of $Ni(PH_3)_2L$ ($L = C_2H_4$, C_2H_2, CO_2, H_2CO, or $(CO)_2$), which experimental results such as ESR and ^1H NMR spectra[25-27] suggest to be the ground state. Although neither a ^1H NMR nor ESR study has been reported for $Ni(PR_3)_2(CO_2)$, MO calculations show that this complex has essentially the same electron distribution and bonding nature as $Ni(PH_3)_2(C_2H_4)$, $Ni(PH_3)_2(C_2H_2)$,[11] and $Ni(PH_3)_2(H_2CO)$.[28]

It can also be suggested theoretically that $Ni(PR_3)_2L$ has a d^{10} ground-state configuration rather than one of d^9s, d^9p, and d^8s^2 configurations. In $Ni(PR_3)_2L$, the more diffuse 4s and 4p orbitals are destabilized to a larger extent than the 3d by two PR_3 and the L ligand. Furthermore, the 3d destabilization is partially compensated by a large π back-donation

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Table II. Atomic and Overlap Electron Populations of $Ni(PH_3)_2(CO_2)$

		$Ni(PH_3)_2(CO_2)$		
	fragment[a]	side-on	C coord	end-on
Ni	27.746	27.431	27.727	27.701
s	6.030	6.102	6.046	6.030
p	12.007	12.214	12.047	12.028
d	9.709	9.115	9.634	9.643
Δd_β[b]		−0.687 (*xz*)	−0.092 (z^2)	−0.016 (*xz*)
			~0 (*yz*)	−0.010 (*yz*)
$PH_3(1)$[c]	18.127	17.924	18.074	18.140
$PH_3(2)$[d]	18.127	17.955	18.074	18.140
CO_2	22.000	22.689	22.125	22.018
Ni–P_1	−0.127	0.008	−0.109	−0.123
Ni–P_2	−0.127	−0.029	−0.109	−0.123
Ni–C		0.111	0.043	−0.006
Ni–O_1		0.032	−0.040	−0.063

[a] $Ni(PH_3)_2$ and distorted CO_2. [b] The decrease in electron population of the d orbital contributing to back-bonding. [c] PH_3 cis to the C atom. [d] PH_3 trans to the C atom.

Table III. Atomic and Overlap Electron Populations of $Cu(PH_3)_2(CO_2)^+$

		$Cu(PH_3)_2(CO_2)^+$		
	fragment[a]	side-on	C coord	end-on
Cu	28.163	28.216	28.246	28.150
s	6.131	6.153	6.138	6.117
p	12.107	12.245	12.163	12.126
d	9.925	9.819	9.945	9.907
Δd_β[b]		−0.116 (*yz*)	−0.035 (z^2)	−0.001 (*xz*)
			~0 (*yz*)	−0.003 (*yz*)
$PH_3(1)$[c]	17.919	17.816	17.898	17.933
$PH_3(2)$[d]	17.919	17.884	17.898	17.933
CO_2	22.000	22.083	21.959	21.983
Cu–P_1	0.016	0.060	0.031	0.007
Cu–P_2	0.016	0.041	0.031	0.007
Cu–C		0.008	0.005	0
Cu–O_1		0.021	0	−0.028

[a] $Cu(PH_3)_2$ and distorted CO_2. [b] The decrease in electron population of the d orbital contributing to back-bonding. [c] PH_3 cis to the C atom. [d] PH_3 trans to the C atom.

to L.[11,28] In $Ni(C_2H_4)$, on the other hand, only a C_2H_4 ligand destabilizes nickel orbitals and the π back-donation is weak, and therefore, 4s and 3d lie energetically close to each other, stabilizing $3d^94s$ relative to $3d^{10}$. In conclusion, two PR_3 ligands would play an important role in destabilizing $3d^94s$ and $3d^94p$ states to make $3d^{10}$ the ground state of $Ni(PR_3)_2L$.

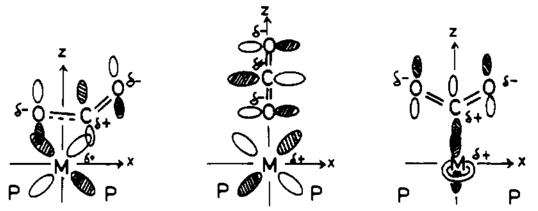
Results and Discussion

Comparison of Coordination Modes. Values of INT, DEF, and BE for $M(PH_3)_2(CO_2)$ (M = Ni(0) or Cu(I)) are given in Table I. The BE value for the side-on-coordinated $Ni(PH_3)_2(CO_2)$ at $\angle OCO = 139°$ is −27 kcal/mol. The calculated BE values indicate that the C-coordinated and the end-on-coordinated $Ni(PH_3)_2(CO_2)$ are substantially less stable than the side-on complex and are probably unbound for the CO_2 complexation. There is no available experimental value for the binding energy; however, this result agrees with the fact that the side-on coordination is the only mode found experimentally for Ni(0) complexes. In contrast, the Cu(I) complex has the largest stabilization (−14 kcal/mol) in the end-on mode, whereas the side-on and the C-coordination modes are probably repulsive.

First, let us investigate why the side-on mode is best for the Ni(0) complex but the end-on mode is preferred in the Cu(I) complex. Mulliken populations of $M(PH_3)_2$ and $M(PH_3)_2(CO_2)$ (M = Ni(0) or Cu(I)) are given in Tables II and III. The Ni 3d orbital population and the CO_2 atomic population suggest that the π back-bonding decreases in the order side-on >> C coordination > end-on and Ni(0) >> Cu(I). Thus, π back-bonding appears to be important in stabilizing the side-on Ni complex, and some other factor is important in the end-on $Cu(PH_3)_2(CO_2)^+$.

The energy components in Table I give a clearer picture. The side-on complex is stabilized mainly by the electrostatic interaction ES and the back-donative interaction BCTPLX, supplemented by the smaller donative interaction FCTPLX. On the other hand, in the end-on complex the stabilization comes principally from ES, augmented by BCTPLX and FCTPLX. Thus the stable side-on $Ni(PH_3)_2\cdots(CO_2)$ complex is an "ES–BCTPLX" complex, whereas the end-on $Cu(PH_3)_2^+\cdots(CO_2)$ is an "ES" complex. Each energy component for the side-on-coordinated $Ni(PH_3)_2(CO_2)$ is substantially larger than for the end-on complex at 2.0 or 2.1 Å; $Ni(PH_3)_2$ and CO_2 fragments interact more strongly in the side-on mode. This is true not only for the Ni complex, for which the side-on mode is favorable, but also for the Cu^+ complex, where the end-on mode is preferred. This difference of energy characteristics between the two modes essentially comes from the fact that in the side-on mode the metal–CO_2 distance is smaller than in the end-on mode. For a clarification of the intrinsic difference between the two modes, a comparison of energy components at the same interfragment contact will be helpful. It is not easy, however, to define "the same interfragment separation" for different modes, but, considering the exchange repulsion EX as the measure of contact of electron clouds, we compare two modes when EX is the same. We choose, somewhat arbitrarily, 131 kcal/mol, the EX value for the best side-on Ni complex, as the reference in comparing the two modes of the Ni(0) complex. Calculations for the end-on Ni complex at various R_{Ni-O} give this EX value at $R_{Ni-O} = 1.7$ Å; the energy components at this geometry are shown in Table I, to be compared with the side-on values at $\theta = 139°$. The two complexes have nearly the same ES and the same FCTPLX; the principal difference between the two comes from BCTPLX supplemented in part by R, which also includes, as will be described in the following paragraph, the back-bonding coupling term. A similar comparison is made also in Table I for the Cu complex at EX = 20 kcal/mol between the most stable end-on mode and the side-on mode, which is obtained by moving CO_2 away from Cu in Figure 1a by 0.4 Å. While BCTPLX as well as FCTPLX + R is nearly the same in the two modes, the ES stabilization strongly favors the end-on mode. Thus, the side-on coordination is stable when the back-donation gives a large stabilization as in the $Ni(PH_3)_2\cdots(CO_2)$ complex. The end-on coordination is stable when the electrostatic energy causes a large stabilization. As is shown in Chart IV the side-on coordination mode has a favorable overlap between the metal $d\pi$ and the CO_2 π^* orbital, whereas the end-on mode has the small overlap. When the metal ion has a sufficiently large positive charge, the side-on mode is unfavorable due to a repulsive interaction between the $M^{\delta+}$ and $C^{\delta+}$, while the end-on mode is electrostatically favorable. Thus, the end-on mode is stabilized in the Cu(I) complex. If the metal fragment has a sufficient Lewis basicity as in $Ni(PH_3)_2$, the strong π back-bonding would be formed to stabilize the side-on mode. In such a case, however, the end-on mode would not be stable, because the metal atom

Chart IV



side-on coordination C coordination end-on coordination

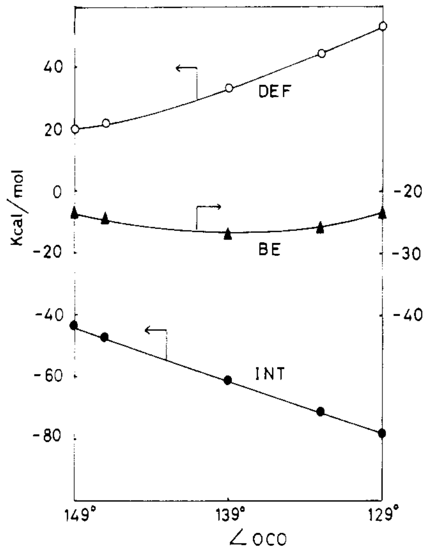


Figure 2. OCO angle vs. the deformation energy (DEF) of CO_2, interaction energy (INT), and binding energy (BE) of $Ni(PH_3)_2(CO_2)$.

would have a considerable electron population, as shown for the Ni complex in Table II, to form only a weak electrostatic interaction between Ni and O. Thus, the side-on mode is stable in the Ni(0) complex. In $Cu(PH_3)_2^+$ the Cu $3d_{xz}$ orbital lies at −15.8 eV (d_{xz}–PH_3 antibonding orbital) and at −20.2 eV (d_{xz}–PH_3 bonding orbital), which are much lower in energy than the Ni $3d_{xz}$ orbital of $Ni(PH_3)_2$ (−6.9 eV for the d_{xz}–PH_3 antibonding orbital). Thus, the back-bonding from the Cu $3d_{xz}$ to the CO_2 π^* orbital would be difficult and the side-on coordination mode, which needs to be stabilized by the back-bonding, would be unstable.

We will now examine the reason why the C-coordination mode is unfavorable for both Ni(0) and Cu(I) complexes. An energy analysis has not been carried out since a qualitative argument appears to be sufficient. In $Cu(PH_3)_2(CO_2)^+$ the ES stabilization is expected to be rather unfavorable in this mode, as the positively charged C lies near the positively charged Cu^+ atom (Chart IV). When the metal atom has a sufficient donor ability and less positive charge, as does $Ni(PH_3)_2$, there would not be such a repulsion. However, the π back-donative interaction in this mode is expected to be worse than in the side-on mode, since the overlap between C p_π and Ni d_{z^2}, as schematically shown in Chart IV, is modest. Thus, the C-coordination mode is comparable in stability to the end-on mode in $Ni(PH_3)_2(CO_2)$. The side-on mode, however, provides a more favorable back-donative interaction to be the most stable coordination mode. Consequently, there is a possibility that the C coordination is substantially stabilized, when the metal has little positive charge and a strong donor ability, and simultaneously the side-on coordination is not allowed for some reason such as coordination numbers. In fact, the C-coordination mode has been experimentally proposed for complexes with large coordination numbers such as $Ni(PCy_3)_3(CO_2)$,[7] $Ir(dmpe)_2Cl(CO_2)$,[8] and $[Co(Pr(sal\text{-}en))K(CO_2)(THF)]_n$.[32] $RhCl(CO_2)L_3$ ($L = PR_nPh_{3-n}$) has been proposed as a C-coordinated complex, although the coordination number is small.[9] Otsuka et al., however, have reported that all attempts to isolate similar $RhH(CO_2)L_3$ had failed and $RhH_2(HCO_3)L_2$ had been isolated.[29]

In conclusion, the side-on coordination is favorable when a large back-donative stabilization is accomplished. A metal with a diffuse and high-energy d orbital such as Ni(0) can form a stable side-on complex. The end-on coordination needs to be stabilized by the electrostatic interaction. The Cu(I) ion would prefer the end-on mode, for this ion has a considerable positive charge.

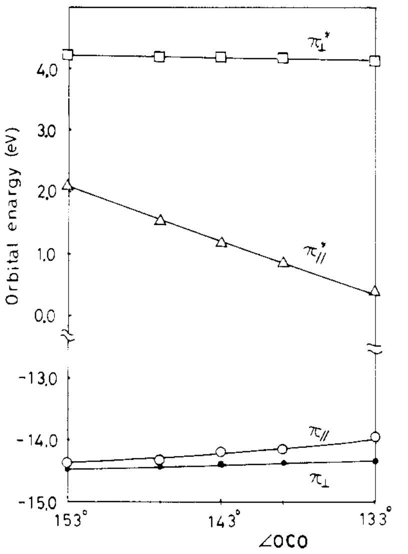


Figure 3. π and π^* energy levels of CO_2 vs. ∠OCO.

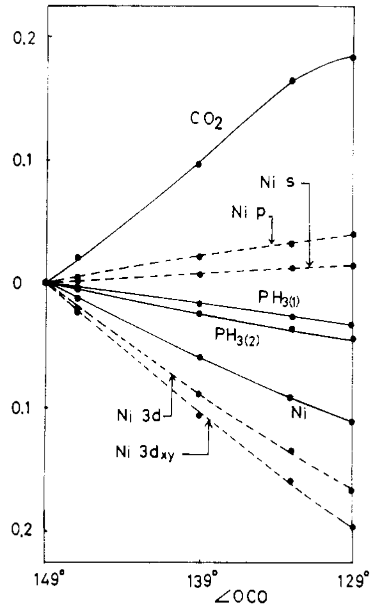


Figure 4. Changes in Mulliken populations caused by the carbon dioxide distortion.

CO_2 Distortion in the Side-On-Coordinated $Ni(PH_3)_2(CO_2)$. In order to investigate why the CO_2 ligand in the side-on-coordinated $Ni(PH_3)_2(CO_2)$ is substantially distorted from its linear geometry, it was necessary to carry out calculations for various OCO angles. The obtained CO_2 deformation energy DEF, the interaction energy INT, and BE (=DEF + INT) are shown in Figure 2. The DEF increases nearly quadratically with an increase in distortion, i.e., a decrease in the OCO angle from 180°. The INT, on the other hand, becomes more negative (attractive) almost linearly with the distortion. The BE, determined as a balance of these two quantities, has a quadratic shape, with its minimum at around 138°. The most stable structure in Table I (139°) is stabilized predominantly by BCTPLX and *R*, relative to the undistorted (180°) and the less distorted structure (147°). As shown in Figure 3 the $\pi^*_{\parallel}$ orbital, lying in the *xz* plane, is stabilized remarkably with a decrease in ∠OCO. This lowering facilitates π back-bonding and results in a large BCTPLX stabilization of the distorted structure. Changes in Mulliken populations are shown in Figure 4. With a decrease in ∠OCO the CO_2 population increases, while the Ni atomic population decreases, owing to a decrease in the 3d, in particular $3d_{xz}$, orbital population.

Table IV. Component Analysis of Mulliken Populations for $Ni(PH_3)_2(CO_2)$ at $\theta = 139°$[a]

	EX	FCTPLX	BCTPLX	*R*
Ni	−0.008	0.096	−0.314	−0.089
s	−0.002	0.016	0.0	0.057
p	0.010	0.077	0.003	0.124
d	−0.011	0.003	−0.317	−0.269
d_{xz}	−0.002	−0.028	−0.303	−0.354
$PH_3(1)$	0.131	−0.020	−0.078	−0.127
$PH_3(2)$	0.131	−0.043	−0.030	−0.103
CO_2	0	−0.033	0.421	0.301
Ni-C	−0.077	−0.025	0.058	0.155
Ni-O_1	−0.077	0.026	0.030	0.053
C-O_1	0.016	−0.006	−0.125	−0.088

[a] See Table II for an explanation of conventions.

Phosphines also lose electrons slightly. These changes in Mulliken populations are a reflection of increase in the π back-bonding caused by the CO_2 distortion.

The remaining term *R* also favors the CO_2 distortion. Though a simple picture cannot be drawn, a detailed analysis of this higher-order coupling term for other systems[11,30] suggests that it consists mainly of an additional back-charge-transfer type interaction coupled with the polarization of the $Ni(PH_3)_2$ fragment, consistent with the changes in electron populations due to this component to be described in Table IV.

In conclusion, the CO_2 distortion stabilizes its π^* orbital, to strengthen π back-bonding, which is reflected in an increase in BCTPLX and *R*. The loss due to distortion, DEF, is more than compensated by the favorable back-donative interaction.

Coordinate Bonding Nature of the Side-On-Coordinated $Ni(PH_3)_2(CO_2)$. Here we present a detailed discussion on the nature of the coordinate bond of the side-on-coordinated $Ni(PH_3)_2(CO_2)$, the only isolated complex. As was discussed, this is an "ES–BCTPLX" complex. At first sight it might seem strange that there is a strong electrostatic interaction between neutral fragments. However, as electrons are distributed closer in space to the partner fragment than nuclei are, the electron–nucleus attraction supersedes the nucleus–nucleus and the electron–electron interaction. The repulsion due to the contact of electron clouds is included in EX and should be considered simultaneously with ES.[19] The contribution of the donative interaction FCTPLX is much smaller than that of ES and BCTPLX but is still an essential part of bonding. Table I indicates that total loss of FCTPLX would result in a very weak bonding (BE = −22 + 15 = −7 kcal/mol) at this geometry.

Mulliken populations and their components are given in Tables II and IV, respectively.

It is seen that the side-on CO_2 coordination causes the following changes: (1) The total electron population on Ni decreases. The decrease in the d, in particular d_{xz}, orbital population is predominant. Table IV shows that the decrease in the d_{xz} orbital population is, as expected, due to the back-bonding interaction (BCTPLX). (2) CO_2 receives about 0.7 e from $Ni(PH_3)_2$, reflecting the decrease in the Ni d_{xz} orbital population. The HOMO of $Ni(PH_3)_2$ is predominantly Ni d_{xz} in character; it contains $0.81d_{xz}$ and $0.24d_{xz}'$, where d_{xz}' means the more diffuse d orbital. A back-donation from it to the LUMO of CO_2 qualitatively explains the above changes. (3) Both the donative and the back-donative interactions accumulate electrons at the Ni–C bonding region, as seen in Figure 5. It is noted, however, that the change in overlap population does not reflect this trend in FCTPLX; the Ni–C overlap population is decreased by FCTPLX, shown in Table IV, which may be due to the diffuse nature of the Ni sp outer orbital.[31] A detailed inspection of Figure 5 shows that electron accumulation caused by FCTPLX seems as if electrons of Ni are attracted to the positively charged C atom; i.e., it is attributable to the polarization of $Ni(PH_3)_2$ under the electrostatic field of the positive C. It has been recognized that the major electron redistribution is usually due to polarization.[19] The difference density map corresponding to BCTPLX gives the normal feature of back-bonding that Ni d_{xz} loses electrons, which CO_2 receives. Electrons are accumulated more in the Ni–C than in the Ni–O region because of the larger contributions of the C p_π orbital in the CO_2 LUMO, the closer Ni–C distance and the proper directionality of C p_π. This results in a larger overlap population for Ni–C than for Ni–O_1, as shown in Table II. (4) The C–O_1 overlap population decreases drastically, which is mainly caused by the BCTPLX interaction as is shown in Table IV.

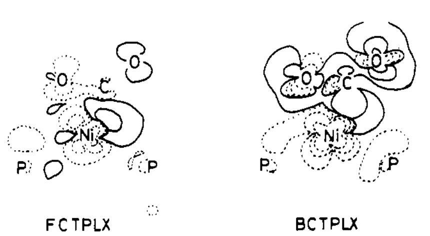


Figure 5. Difference density maps due to various interactions in the side-on coordinated $Ni(PH_3)_2(CO_2)$. A solid line indicates an increase in the electron density and a dashed line a decrease in the electron density.

Concluding Remarks

Several important points noted in the present work are summarized as follows. (1) Three coordination modes, the side-on, the end-on, and the C-coordination modes, were examined. A critical contrast was found between the Ni(0) and the Cu(I) complex; in the Ni(0) complex, while the side-on mode is stable, the other two modes are unfavorable. On the other hand, the end-on mode is best and the others are unstable in the Cu(I) complex. The back-bonding stabilizes the side-on mode, whereas the electrostatic interaction favors the end-on mode. When the metal ion has a sufficient Lewis basicity such as in $Ni(PH_3)_2$, BCTPLX becomes large to favor the side-on coordination. When the metal ion has a considerable positive charge such as in $Cu(PH_3)_2^+$, the end-on coordination mode is preferred by the electrostatic interaction. The C coordination would not be very bad but not be as good as the side-on mode, when the metal ion has a strong Lewis basicity but a small positive charge. Thus, the C coordination may actually occur only when the side-on coordination is difficult for some reason such as coordination numbers. (2) A detailed investigation was carried out on the distortion of CO_2 in the side-on-coordinated $Ni(PH_3)_2(CO_2)$. The calculated CO_2 distortion angle (∠OCO) of 138° agrees well with the experimental value (133°). The distorted structure is stabilized by the BCTPLX and *R* components. The CO_2 distortion stabilizes the CO_2 π^* orbital energy to strengthen the π-back-donative interaction.

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Registry No. $Ni(PH_3)_2(CO_2)$, side-on, 79953-45-0; $Ni(PH_3)_2(CO_2)$, end-on, 79953-46-1; $Ni(PH_3)_2(CO_2)$, C-coord., 79953-47-2; $Cu(PH_3)_2(CO_2)^+$, side-on, 79953-48-3; $Cu(PH_3)_2(CO_2)^+$, end-on, 79953-49-4; $Cu(PH_3)_2(CO_2)^+$, C-coord., 79953-50-7.

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