

CO, CS, N₂, PF₃, and CNCH₃ as σ Donors and π Acceptors. A Theoretical Study by the Hartree-Fock-Slater Transition-State Method

TOM ZIEGLER and ARVI RAUK*

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Hartree-Fock-Slater calculations have been carried out on Ni(CO)₃L for a number of different ligands (L) in order to investigate the abilities of the ligands to act as σ donors and π acceptors. The order, based on extent of electron transfer, for σ donation is CS \approx CO > CNCH₃ > N₂ \sim PF₃ and for π back-bonding is CNCH₃ > CS > CO > PF₃ > N₂. The contributions to the total bonding energy between Ni(CO)₃ and L from σ donation and π back-donation are evaluated by the Hartree-Fock-Slater transition-state method, and the same method is used to optimize the Ni-L bond distances. Calculations on the stretching frequency ν_{CO} of carbon monoxide complexed to Ni(CO)₃ showed that ν_{CO} is decreased by the π back-donation but is increased by the steric interaction energy between Ni(CO)₃ and CO. Thus the decrease in ν_{CO} is not a reliable measure of the extent of π back-bonding in the metal-ligand bond. The calculated influence on ν_{CO} from σ donation was negligible.

1. Introduction

A number of neutral molecules, notably CO, CS, N₂, substituted phosphines, and isocyanides, are able to form complexes in which the transition metal is stabilized in a low formal oxidation state. The highest occupied and lowest unoccupied orbitals in the neutral molecules are of σ and π symmetry, respectively. Thus the ligands have the potential for σ donation to the metal as well as π acceptance.

It is possible in the literature to find experiments in support of a bonding model in which only σ donation is important,¹ as well as experiments in support of a model that involves both σ donation and π back-donation.²

Theoretical discussions based on ab initio HF-SCF calculations^{3,4} as well as DVM-HFS calculations^{5,6} find for various carbonyl complexes that both σ and π bonding are important, and quite similar conclusions have been reached from molecular orbital calculations on complexes involving other ligands such as CS,⁷ N₂,⁸ and CNCH₃.⁹ One particular computational scheme, the multiple-scattering method, that has been used widely in recent years in transition-metal chemistry yields, on the basis of calculations on Cr(CO)₆,¹⁰ the result that the ligand to metal bonding primarily is σ in nature. It has been asserted^{2,10} that substantial π back-donation to the CO group, as found in various calculations, would result in a notable reduction of the CO stretching frequency as compared to the free ligand. The experimental finding that the CO frequency is roughly the same in Ni(CO)₄,¹¹ Cr(CO)₆,^{1b} and CO¹² may be taken as support for the dominance of σ bonding, since the σ orbital is primarily nonbonding in nature.

This paper gives an analysis of the relative importance of σ donation and π back-donation by considering the various ligands attached to the same metal fragment, Ni(CO)₃. The analysis is concerned with the contribution from these processes to the total bonding energy as well as the amount of charge donated and back-donated. It will be shown that σ bonding as well as π bonding is important for carbonyl complexes and that the back-donation indeed reduces the CO stretching frequency by a substantial amount. However, this reduction is canceled to a large extent by the influence of steric interactions.

2.1. Computational Details

All calculations were carried out by the HFS-DVM program system, with 0.7 as the exchange parameter. The orbitals 3s, 3p, 3d, 4s, and 4p on Ni were considered as valence and described by a double ζ basis, except for 3d where a third Slater component was used. The valence orbitals 1s on H, 2s and 2p on C, N, O, and F, and 3s and 3p on S and P were

described by a triple ζ basis. One 3d orbital was added to the basis of S and P. The core orbitals were represented by atomic orbitals from the tables of Roetti and Clementi¹³ and kept frozen. The geometries of N₂, CS, CO, and CNCH₃ were taken as those of the free ligands,¹⁴ and that of PF₃ was taken from the structure of Ni(PF₃)₄.¹⁵ The Ni to carbon distance in Ni(CO)₃ was taken from Ni(CO)₄¹⁶ and the CO-Ni-CO angle considered tetrahedral.

2.2. Decomposition of the Bonding Energy

The transition-state method for calculation of bond energies has been described elsewhere.¹⁷

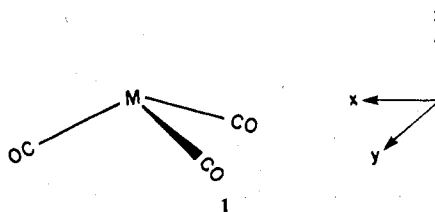
The bonding energy of \overline{AB} with respect to the two fragments A and B (molecules or atoms) is decomposed in the following way. First, a calculation is carried out on \overline{AB} in which only the occupied orbitals of A and B are used as a basis. The resulting bonding energy from this calculation, ΔE° , is referred to as the steric interaction energy. This energy can further be decomposed into ΔE_{el} , the electrostatic interaction between A and B, and ΔE_{er} , the exchange repulsion between A and B. Second, a calculation is carried out on \overline{AB} in which occupied as well as virtual orbitals on A and B are included in the basis. The virtual orbitals in each symmetry representation Γ of the point group to which \overline{AB} belongs contribute to the total bonding energy ΔE^{Γ} . The sum of all such contributions $\sum_{\Gamma} \Delta E^{\Gamma}$ is referred to as the electronic interaction energy, and the total bonding energy is given as in eq 1. A detailed

$$\Delta E = \Delta E_{\text{el}} + \Delta E_{\text{er}} + \sum_{\Gamma} \Delta E^{\Gamma} = \Delta E^{\circ} + \sum_{\Gamma} \Delta E^{\Gamma} \quad (1)$$

description of this decomposition scheme with application to transition-metal complexes of ethylene is given elsewhere.¹⁸

3.1. Electronic Structure of the Ni(CO)₃ Fragment

The Ni(CO)₃ fragment is a d¹⁰ complex with C_{3v} symmetry (see structure 1). The five d orbitals of Ni are divided into



one a₁ component, d_{z²}, two e_x components, d_{y²-x²} and d_{xz}, and two e_y components, d_{xy} and d_{yz}.

From the results of the HFS calculation, the highest occupied a₁ orbital, 1a₁ shown in Figure 1, is identified as d_{z²}.

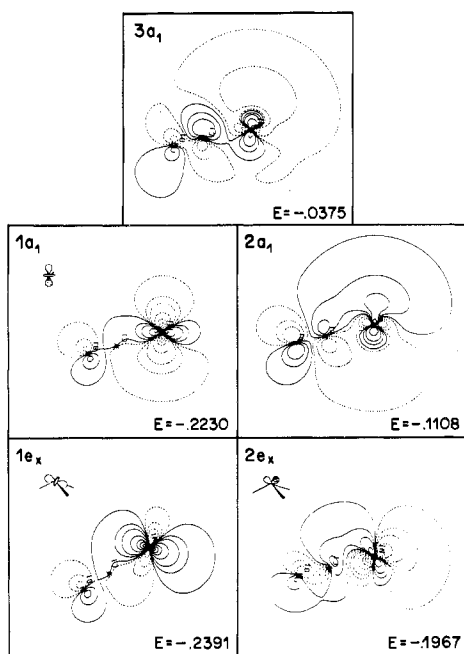
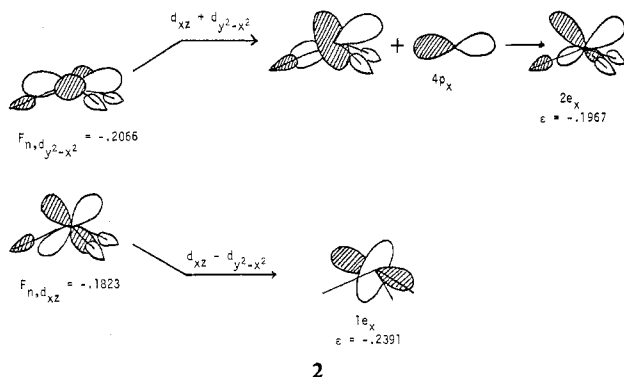


Figure 1. Molecular orbitals of the Ni(CO)₃ fragment. Contour values: 0.75, 0.5, 0.25, 0.1, 0.05, 0.025, 0.01. The dashed lines correspond to negative values and the solid lines to positive values. The orbital energies (*E*) are in atomic units.

Of the six occupied molecular orbitals of *e* symmetry, the two highest occupied are essentially linear combinations of the Ni *d* orbitals whose particular composition arises as a result of minimizing repulsive interactions with the occupied *e* combination of ligand nonbonded $\sigma(n)$ orbitals. The *x* components of the two highest MO's of *e* symmetry, identified as 1e_x and 2e_x and displayed in Figure 1, are composed of $d_{y^2-x^2}$, d_{xz} , and 4p_x. As it is these orbitals which may participate in π back-bonding to ligands, it is important to appreciate how they arise. Each of the two *d* orbitals interacts to about the same extent with the *e* combination of CO nonbonded σ orbitals as judged by the respective HFS matrix elements (F_{ij} , where *i* is the e_x combination of CO *n* orbitals and *j* is either $d_{y^2-x^2}$ or d_{xz} ; see structure 2). Thus the combination $d_{xz} - d_{y^2-x^2}$ will



have an almost negligible ligand interaction and give rise to the second highest occupied *e_x* orbital, 1e_x (Figure 1). In effect, a nodal surface is created at the position of the ligand *n* orbitals, and some additional stabilization is obtained by a small admixture of the CO π^* orbitals. There remains for the highest occupied Ni(CO)₃ orbital the combination $d_{xz} + d_{y^2-x^2}$ which is highly destabilizing as it directs *d* electron density toward the ligand σ orbitals in an antibonding manner. This interaction is reduced by a small admixture of the 4p_x orbital which serves to polarize charge away from the CO σ orbitals.

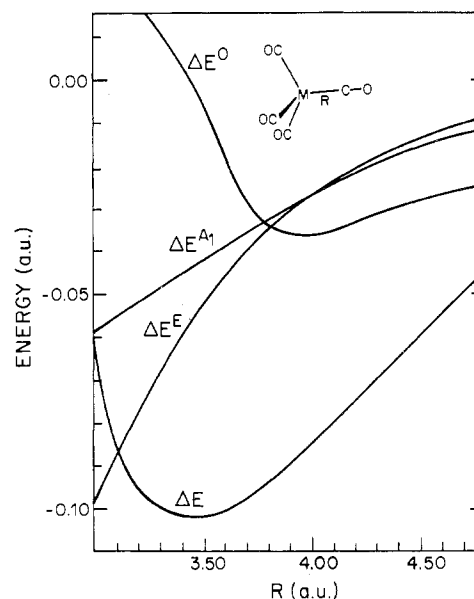


Figure 2. The bonding energy between Ni(CO)₃ and CO. The figure shows the different contributions as a function of the distance, *R*, between Ni(CO)₃ and CO. Here ΔE° is the steric energy, ΔE^{A1} the σ -donation energy, and ΔE^E the π -back-donation energy.

A direct consequence of the charge polarization is that the resulting orbital, 2e_x in Figure 1, can have better overlap with ligand π^* orbitals. We shall see below that most of the π back-bonding will involve the 2e orbitals for this reason.

The two virtual orbitals of interest for the σ bonding in Ni(CO)₃-L are shown in Figure 1 as 2a₁ and 3a₁. The first orbital is mainly a σ^* orbital and the second mainly a 4s orbital.

3.2. The Bonding between Ni(CO)₃ and CO

The bonding energy,¹⁹ $\Delta E \approx \Delta E^\circ + \Delta E^{A1} + \Delta E^E$, as well as the different components ΔE° , ΔE^{A1} , and ΔE^E are shown in Figure 2 as a function of *R*, where *R* is the Ni to CO distance.

The steric interaction $\Delta E^\circ = \Delta E_{el} + \Delta E_{er}$ is attractive at large distances where ΔE_{el} is dominant and repulsive at small distances where ΔE_{er} prevails. The steric energy term considered alone results in a stable complex with a bonding energy of 21.7 kcal at *R* = 3.9 au.

The electronic part of the bonding energy $\Delta E^{A1} + \Delta E^E$ is divided by symmetry into a σ contribution, ΔE^{A1} , and a π contribution ΔE^E . Close inspection shows that ΔE^{A1} involves three orbitals, namely, the highest occupied and lowest unoccupied orbitals of Ni(CO)₃ and the highest occupied orbital of CO (3σ); see Figures 3 and 4. Charge is donated from both 1a₁ and 3σ to 2a₁ (which has a large contribution of π^* orbitals from the backside CO ligands on Ni(CO)₃ in order to decrease the four-electron destabilizing interaction between 1a₁ and 3σ). Thus the main feature of the Ni(CO)₃ to CO σ -bond interaction is the removal of charge from the region between Ni(CO)₃ and CO and its delocalization into the backside π^* -CO orbitals of Ni(CO)₃, as shown in the density difference map of Figure 5a. It was found that 3a₁ is of little importance for the σ bonding.

The π contribution, ΔE^E , can be described by two sets of orbitals, 2e_x, 2e_y, of Ni(CO)₃ shown in Figure 1 and π_x^* , π_y^* of CO displayed in Figure 4. Charge is back-donated from 2e_x, 2e_y to π_x^* , π_y^* as shown in the density difference map of Figure 5b. The actual amount of charge transferred is given in Table I.

It was found that the 1e_x, 1e_y set has a minor importance in the back-donation process primarily because the overlaps

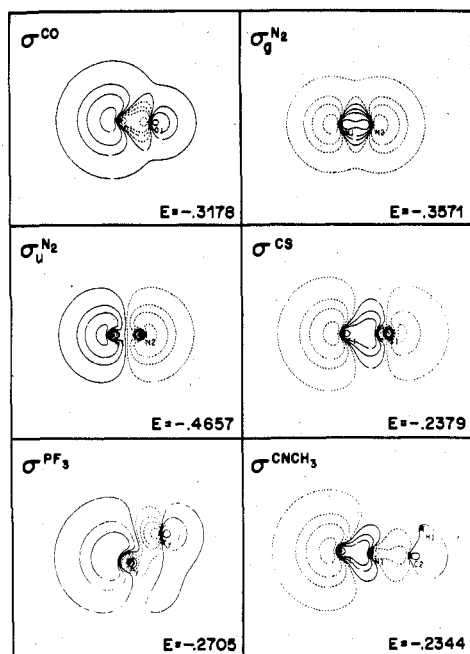


Figure 3. Molecular orbital contour plots of σ orbitals for different ligands. Contour values: 0.75, 0.5, 0.25, 0.1, 0.05, 0.025, 0.01. Dashed lines correspond to negative values and solid lines to positive values. Orbital energies (E) are in atomic units.

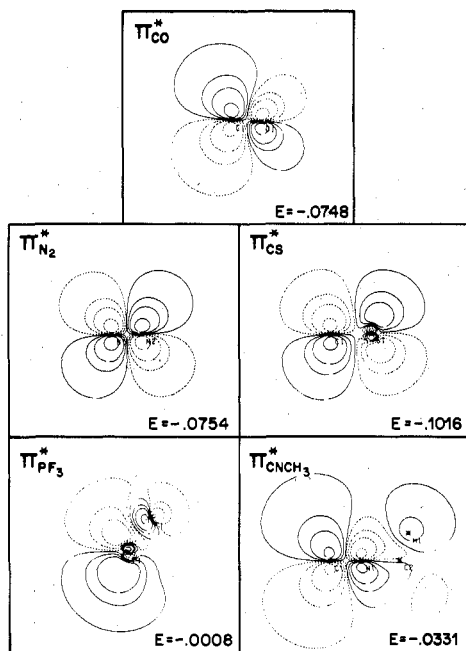


Figure 4. Molecular orbital contour plots of π^* orbitals of different ligands. Contour values: 0.75, 0.5, 0.25, 0.1, 0.05, 0.025, 0.01. Dashed lines correspond to negative values and solid lines to positive values. Molecular orbital energies (E) are in atomic units.

Table I. Orbital Populations of Some $\text{Ni}(\text{CO})_3\text{L}$ Complexes in Terms of the Orbitals from $\text{Ni}(\text{CO})_3$ and the Free Ligand L

orbitals	CO	CS	N_2	CNCH_3	PF_3
$1a_1$	1.92	1.91	1.91	1.86	1.90
σ_L	1.69	1.69	1.89, ^a 1.95 ^b	1.72	1.89
$2a_1$	0.37	0.37	0.17	0.40	0.17
$2e$	3.70	3.65	3.72	3.62	3.68
π_L^*	0.38	0.42	0.29	0.44	0.34

^a Population of σ_g . ^b Population of σ_u .

with the π_x^*, π_y^* set are smaller than the overlaps between $2e_x, 2e_y$ and π_x^*, π_y^* for reasons cited in the previous section.

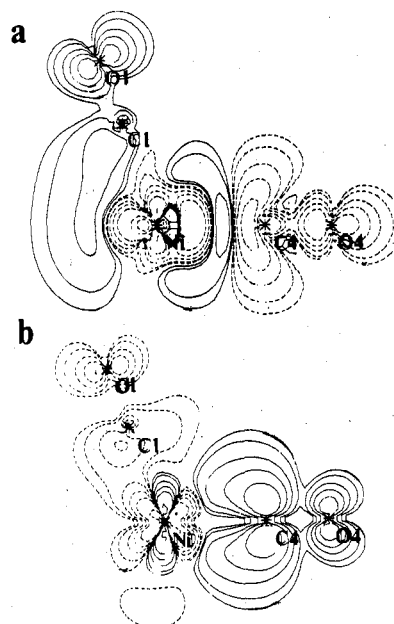


Figure 5. The electron density differences refer to three densities. ρ_1 is the sum of the CO and $\text{Ni}(\text{CO})_3$ densities. ρ_2 is the density from the combined complex described by the occupied orbitals on CO and $\text{Ni}(\text{CO})_3$, as well as the virtual orbitals of $\text{Ni}(\text{CO})_3$. ρ_3 is the density of the combined complex described by the occupied orbitals of CO and $\text{Ni}(\text{CO})_3$ as well as the virtual orbitals of CO. Diagram a refers to $\rho_2 - \rho_1$ and diagram b to $\rho_3 - \rho_1$. The plot is in the xz plane with contour values 0.01, 0.005, 0.0025, 0.001, and 0.0005.

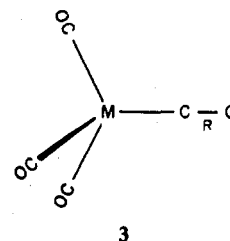
Table II. Contributions from the Steric Interaction Energy ΔE^S , the σ -Donation Energy E^{A_1} , the π -Back-Donation Energy ΔE^E , and the Bonding Energy of Free CO (E^{CO}) to the Force Constant F_{CO} and Bond Distance R_{CO} of $\text{Ni}(\text{CO})_4$

contribution	$F_{\text{CO}},^a$ mdyn/Å	$R_{\text{CO}},$ au
E^{CO}	18.6 (19.0 ^b)	2.17 (2.14 ^d)
$E^{\text{CO}} + \Delta E^S$	20.8	2.15
$E^{\text{CO}} + \Delta E^{A_1}$	18.6	2.17
$E^{\text{CO}} + \Delta E^E$	16.4	2.21
$E^{\text{CO}} + \Delta E^S + \Delta E^{A_1} + \Delta E^E$	18.5 (17.9 ^c)	2.19 (2.17 ^e)

^a The force constant is taken as the second derivative of $E(R)$ at the minimum distance, R_{CO} , where $E(R)$ is a cubic function of R determined by a least-squares fit to at least five values of the C-O distance. ^b Experimental; ref 12. ^c Experimental force constant of $\text{Ni}(\text{CO})_4$ from ref 11. ^d Experimental; ref 14. ^e Experimental; ref 16.

3.3. The Relation between ΔE^S , ΔE^{A_1} , ΔE^E and the CO Stretching Frequency in $\text{Ni}(\text{CO})_4$

Jones et al.¹¹ have determined the force constant F_{CO} of $\text{Ni}(\text{CO})_4$, corresponding to a stretch of a single carbonyl bond with the rest of the molecule fixed including the Ni to C bond distance, 3. The force constant in $\text{Ni}(\text{CO})_4$ was found to be



slightly smaller than that of the free CO ligand, 17.9 mdyn/Å as compared to 19.0¹² mdyn/Å (Table II). In order to understand how the chemical bond modifies F_{CO} , consider

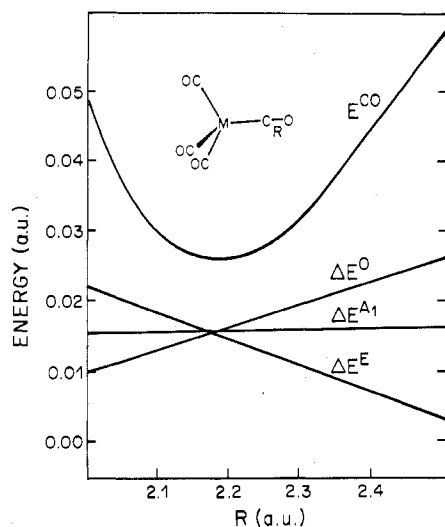


Figure 6. The steric interaction energy, ΔE^σ , the σ -donation energy, ΔE^{A_1} , the π -back-donation energy, ΔE^E , and the bonding energy, E^{CO} , of the free CO ligand as a function of R . Here R is the CO distance, and the variation of R takes place in such a way that the Ni to carbon distance is fixed. All contributions are given within a constant, and absolute values can be found in Table II.

Figure 6, where the different components in the total energy expression for $\text{Ni}(\text{CO})_4$ (eq 2) are given as a function of R .

$$E(R) = E^{CO}(R) + \Delta E^\sigma(R) + \Delta E^{A_1}(R) + \Delta E^E(R) + C \quad (2)$$

Here C is a constant independent of R and $E^{CO}(R)$ the bonding energy of the free CO ligand; the other terms have been defined in the previous sections. The σ donation $\Delta E^{A_1}(R)$ is constant in the whole R range, Figure 6, and does not contribute to the change in the force constant, ΔF_{CO} , or the bond distance, ΔR_{CO} , Table II. The π back-donation is almost linear in R with a negative slope (Figure 6). Thus the contribution from $\Delta E^E(R)$ is to increase the equilibrium bond length. The calculated decrease in F_{CO} , Table II, is a consequence of smaller curvature in the E^{CO} component of $E(R)$, a reflection of the anharmonicity of the E^{CO} potential. The steric interaction energy $\Delta E^\sigma(R)$ is also nearly linear in R but with a positive slope. The contributions to ΔF_{CO} and ΔR_{CO} are of the same order of magnitude as $\Delta E^E(R)$ but of opposite signs, Table II.

Erroneous conclusions may be reached if one attempts to deduce the nature of the metal-ligand bonding from changes in F_{CO} expected from changes in occupancy of the isolated ligand orbitals. This is tantamount to considering electronic factors, ΔE^{A_1} and ΔE^E , and neglecting steric factors, ΔE^σ . For instance, the influence of the σ donation (ΔE^{A_1}) could be assessed by considering F_{CO} and R_{CO} of CO^+ corresponding to the configuration σ^1 and the effect of the π back-donation by considering F_{CO} from the excited states $^1\Pi$ and $^3\Pi$ corresponding to the configuration $\sigma^1\pi^1$. The calculated results are shown in Table III. From such an analysis one may be led to conclude that substantial π back-donation, as found in most theoretical works (say 0.5 electron/CO), would reduce F_{CO} in $\text{Ni}(\text{CO})_4$ by several millidynes per angstrom in contrast to experimental findings. We have shown above that if $\Delta E^\sigma(R)$ is taken into consideration, substantial back-donation can take place (Table I) without a large change in F_{CO} (Table II) or R_{CO} . The dependence of $\Delta E^\sigma = \Delta E_{el} + \Delta E_{er}$ on R is somewhat complex to analyze. The exchange repulsion, ΔE_{er} , is reduced when the CO bond is stretched, since electrons are moved away from the region between Ni and CO. On the other hand, stretching the CO bond reduces the attractive electrostatic term, ΔE_{el} , as one would expect from a simple

Table III. Force Constants F_{CO} and Bond Distances R_{CO} for Different States of CO^c

species	confign	state	F_{CO} , mydn/A	R_{CO} , ^b au
CO	$(5\sigma)^2$	$^1\Sigma^+$	19.0 ^a (18.6)	2.14 (2.17)
CO^+	$(5\sigma)^1$	$^2\Sigma^+$	19.8 ^a (19.3)	2.10 (2.16)
CO	$(5\sigma)^1(2\pi)^1$	$^1\Pi$	12.9 ^b (13.7)	2.33 (2.34)
CO	$(5\sigma)^1(2\pi)^1$	$^3\Pi$	14.9 ^b (15.2)	2.28 (2.32)

^a Reference 12. ^b Experimental values deduced from ref 10. ^c The calculated values are given in parentheses.

Table IV. Calculated Bonding Energies and Bond Distances for the Complex $\text{Ni}(\text{CO})_3\text{-L}^c$

ligand	ΔE^σ , kcal	ΔE^{A_1} , kcal	ΔE^E , kcal	ΔE^{A_2} , kcal	ΔE , kcal	$R_{\text{Ni-L}}$, au
CO	0.00	-25.1	-35.1	-2.5	-62.7	3.44 ^a
N_2	3.1	-23.8	-23.8	-3.8	-48.3	3.45
CS	3.8	-31.4	-38.2	-5.1	-70.9	3.42
PF_3	-16.3	-32.0	-35.1	+0.6	-82.8	3.83 ^b
CNCH_3	-9.4	-38.9	-37.0	-0.3	-85.6	3.27

^a Experimental bond distance is 3.44 au.¹⁶ ^b Experimental bond distance in $\text{Ni}(\text{PF}_3)_4$ is 3.97 au.¹⁵ ^c Negative values for the bonding energy (ΔE) indicate that the complex is stable with respect to its components L and $\text{Ni}(\text{CO})_3$.

point-charge model in which Ni is positive and oxygen negative. The overall effect is an approximately linear dependence of ΔE^σ on R with a positive slope (Figure 6).

In summary, slightly more charge is transferred via π back-donation than σ donation (0.38 e vs. 0.31 e, Table I), and the contribution to the bond energy is greater in π than in σ bonding (35.1 vs. 25.1 kcal, Table IV). Both results are entirely consistent with the observation that the stretching force constant of CO does not change much upon complexation (Table II).

4.1. N_2 , CS, CNCH_3 , and PF_3 as σ Donors and π Acceptors in $\text{Ni}(\text{CO})_3\text{L}$

Comparisons between N_2 , CS, CNCH_3 , and PF_3 as σ donors or as π acceptors are often done in cases where the ligands are attached to different fragments. In the following sections the analysis will be based on the $\text{Ni}(\text{CO})_3\text{L}$ system in which the ligands are all attached to the same fragment. The electronic structure of $\text{Ni}(\text{CO})_3$ has been discussed in section 3.1.

4.2. The π Bond in $\text{Ni}(\text{CO})_3\text{L}$

The π bond involves a transfer of charge from the 2e orbital of $\text{Ni}(\text{CO})_3$ to the π^* orbital on the ligand L, as illustrated in the electron density difference map of Figure 5b for the $\text{Ni}(\text{CO})_3\text{-CO}$ system. The actual amount of charge transferred for each ligand can be seen in Table I. On the basis of the calculated occupation of the π^* orbitals upon complex formation, one may deduce that CNCH_3 and CS are better π acceptors than CO and PF_3 and that N_2 is the weakest π acceptor among the five ligands.

The energy contribution from the π back-donation to the total bonding energy between $\text{Ni}(\text{CO})_3$ and L is shown in Table IV as ΔE^E along with the calculated bond distances. The weak π acceptor N_2 contributes with 23.8 kcal, whereas ΔE^E for the other ligands is in the narrow range between 35.1 and 38.2 kcal.

4.3. The σ Bond in $\text{Ni}(\text{CO})_3\text{L}$

The σ bond in $\text{Ni}(\text{CO})_3\text{L}$ is not a simple buildup of charge between $\text{Ni}(\text{CO})_3$ and L or a transfer of electrons from L to Ni. Rather, electrons are promoted from $1a_1$ on the $\text{Ni}(\text{CO})_3$ fragment (corresponding to a rehybridization) and donated from the highest occupied σ orbital of L to the vacant $2a_1$ orbital on $\text{Ni}(\text{CO})_3$ which is made up in large part from the π^*_{CO} orbitals of the fragment CO ligands as is apparent from

Figure 1. The charge transfer is illustrated in the electron density difference map of Figure 5a for the $\text{Ni}(\text{CO})_3\text{-CO}$ system.

Population analysis shows that PF_3 and N_2 both are weaker σ donors than CO , CS , and CNCH_3 (Table I).

The electronic effect in $\text{Ni}(\text{CO})_3\text{L}$ has been studied for a variety of ligands in connection with the A_1 carbonyl stretching frequency²⁰ ν_{CO} . Attempts have been made to correlate ν_{CO} to the σ donation from L as well as the π back-donation to L.

According to the present calculations, the back-donation from $2e$ to π^* on the ligand should have only a minor influence on ν_{CO} since the contribution from π^*_{CO} on $\text{Ni}(\text{CO})_3$ to $2e$ is only 12%. The σ donation from $1a_1$ and σ_L to $2a_1$ has on the other hand a substantial influence on ν_{CO} since the contribution from π^*_{CO} on $\text{Ni}(\text{CO})_3$ to $2a_1$ is 81%. A strong σ donor would then tend to populate π^*_{CO} and decrease ν_{CO} . In the present calculations CNCH_3 is found to be a strong donor compared to N_2 as well as PF_3 . Consequently, CNCH_3 forms a complex with a low experimental stretching frequency (ν_{CO} 2073 cm^{-1})²¹ compared to the weak σ donors N_2 and PF_3 , where the experimental values for ν_{CO} are 2098²² and 2111²³ cm^{-1} , respectively.

It is of interest to examine the ν_{CO} of $\text{Ni}(\text{CO})_3\text{L}$ for some other ligands (in CH_2Cl_2):²³ PCl_3 , 2097 cm^{-1} ; PH_3 , 2081 cm^{-1} ; $\text{P}(\text{C}_6\text{H}_5)_3$, 2070 cm^{-1} ; $\text{P}(\text{CH}_3)_3$, 2064 cm^{-1} ; $\text{P}(\text{C}_2\text{H}_5)_3$, 2062 cm^{-1} ; $\text{P}(t\text{-C}_4\text{H}_9)_3$, 2056 cm^{-1} . According to this analysis, PCl_3 should be the weakest σ donor and $\text{P}(t\text{-C}_4\text{H}_9)_3$ the strongest σ donor in the list above.

4.4. Relative Stabilities

The dinitrogen complex with $\text{Ni}(\text{CO})_3$ is, in accord with theory (Table IV), less stable than three of the other $\text{Ni}(\text{CO})_3\text{L}$ complexes under consideration and has only been isolated at low temperatures (-100°C) in an inert-gas matrix.²² The π^* orbital of N_2 , Figure 4, and the two σ orbitals, Figure 3, are all somewhat contracted, and the overlaps with $2a_1$ and $2e$ on $\text{Ni}(\text{CO})_3$ are consequently small. This, in conjunction with the low energy of σ_u , Figure 3, results in a relatively small bonding energy between N_2 and $\text{Ni}(\text{CO})_3$.

$\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{CO})_3\text{PF}_3$, and $\text{Ni}(\text{CO})_3\text{CNCH}_3$ are all stable at room temperature.²⁴ The complex $\text{Ni}(\text{CO})_3\text{CS}$ has not been prepared.²⁵ The energy of dissociation for the process $\text{Ni}(\text{CO})_3\text{L} \rightarrow \text{Ni}(\text{CO})_3 + \text{L}$ is not known. Exchange reactions between free CO and $\text{Ni}(\text{CO})_3\text{L}$, where the rate-determining step is dissociation of one ligand from $\text{Ni}(\text{CO})_3\text{L}$, result in exchange of CO molecules rather than L when L is either PF_3 or CNCH_3 , indicating that the Ni-PF_3 and the Ni-CNCH_3 bonds are both stronger than the Ni-CO bond,²¹ as suggested by HFS results, Table IV. In other thiocarbonyl complexes CO is displaced rather than CS .²⁷

It is important to point out that the similarities between PF_3 , CO , CS , and CNCH_3 as ligands in the $\text{Ni}(\text{CO})_3\text{L}$ complex are more striking than the differences. All ligands have a σ orbital (Figure 3) with the right energy and right shape for

interaction with $\text{Ni}(\text{CO})_3$, as well as a suitable set of π^* orbitals. The contribution from the σ donation as well as the π back-donation to the bonding energy is as a consequence important for all the ligands, Table IV.

Albright, Hofmann, and Hoffmann²⁸ have recently published a detailed analysis of the orbitals in the $\text{M}(\text{CO})_3$ fragment based on the Hückel method in connection with rotational barriers in polyene- ML_3 complexes. The orbitals in ref 19 are in qualitative agreement with those presented in Figure 1 of the present work. The minor differences are probably due to the choice of an CO-M-CO angle of 90° compared to an CO-M-CO angle of 109° in the present work rather than a consequence of the parametrization.

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Registry No. $\text{Ni}(\text{CO})_4$, 13463-39-3; $\text{Ni}(\text{CO})_3\text{N}_2$, 37936-21-3; $\text{Ni}(\text{CO})_3\text{CS}$, 70130-57-3; $\text{Ni}(\text{CO})_3\text{PF}_3$, 14264-32-5; $\text{Ni}(\text{CO})_3\text{CNCH}_3$, 16787-44-3; CO , 630-08-0; CO^* , 12144-04-6.

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