temperature factors. For example, the terminal carbon atoms of the ethyl groups (C_1 and C_2) have B values of about 5.4, whereas the methylene bridging carbon atoms, whose thermal motions are more restricted, have smaller values of B ($\sim$0–2). Similar trends may be noted among the atoms comprising the $[ReBr_4O(H_2O)]^-$ ion.

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The Infrared and Raman Spectra of a Triphenylphosphine Derivative of $Ni(CO)_4$[1]

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The infrared and Raman spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in cyclohexane were obtained for the identification of the modes of vibration localized in the $PNi(CO)_3$ group of $Ni(CO)_3P(C_6H_5)_3$. The Raman spectra were obtained by means of an electrodeless mercury arc powered by high-frequency radiation. The principal Raman exciting line was the 4358 Å. Hg line. The spectra are interpreted in terms of C_{3v} symmetry for the $PNi(CO)_3$ group and frequencies are assigned to the fundamentals. The nature of the bonding is discussed from a molecular orbital point of view and compared with that in $Ni(CO)_4$. The C–O stretching frequencies permit one to estimate the π^*_{CO} participation index as 0.28 compared with a PI value 0.19 for a CO in $Ni(CO)_4$. Thus, there is an increase of about 0.5 electron in the π^*_{CO} orbitals of the $Ni(CO)_3$ moiety on passing from $Ni(CO)_4$ to $Ni(CO)_3P(C_6H_5)_3$, much of which results from a substantial reduction in the charge back-transferred into the π acceptor orbitals of the $P(C_6H_5)_3$ ligand from the value for CO in $Ni(CO)_4$.

Introduction

Bonding in metal carbonyls is currently of interest. A molecular orbital description has been used in this laboratory to interpret the vibrational spectra of a number of metal carbonyls.[2–5] An important factor in this description is the extent of the presence of the carbon monoxide π^* orbitals in the electron-filled molecular orbitals of the metal carbonyl moiety or species. The π^* participation increases substantially in the isoelectronic series—$Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$—as the atomic number of the metal atom decreases. A consideration of the Hartree–Fock terms in the molecular orbital secular equation suggests that this will also happen in a given metal carbonyl moiety as negative charge on it is increased.

The purpose of this work was to study the complete infrared and Raman spectra of a metal carbonyl derivative in which a basic ligand is present to donate charge to the metal carbonyl group and to apply these spectra to a consideration of the bonding. A phosphine derivative, mono(triphenylphosphine)tricarbonylnickel, was chosen for this study. The primary interest lies in the nature of the bonding and the vibrations localized in the $PNi(CO)_3$ group.

The interest in substituted metal carbonyls is shown by several recent studies.[6–12] For the most part, the spectroscopic studies have been restricted to the C–O stretching vibrations, and most of the fundamental vibrations have been unobserved. While this study was in progress Bouquet and Bigorgne[11] reported a rather complete Raman spectrum of a nickel carbonyl–arsine derivative and interpreted their results in terms of valence bond theory.

Experimental

Chemicals.—Nickel tetracarbonyl (International Nickel), diethyl ether (Mallinckrodt, anhydrous), and nitrogen (Linde, high purity) were used as received. Triphenylphosphine (Eastman, White Label) was sublimed. Cyclohexane (Matheson, reagent grade) was distilled under nitrogen from lithium aluminum hydride.

Preparation of Mono(triphenylphosphine)tricarbonylnickel, $Ni(CO)_3P(C_6H_5)_3$.—The compound was prepared by a modification of the procedure given by Reppe and Schweckendiek.[13] Attention should be directed to the extreme toxicity of $Ni(CO)_4$, and the following reaction should be carried out in an efficient

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[1] Based upon the Ph.D. Thesis of M. P. Dunkle, Purdue University, Jan. 1964.

[2] W. F. Edgell, Abstracts, 134th National Meeting of the American Chemical Society, Sept. 1958; various papers presented before American Chemical Society local sections, 1958–1960; Abstracts, 139th National Meeting of the American Chemical Society, March 1961.

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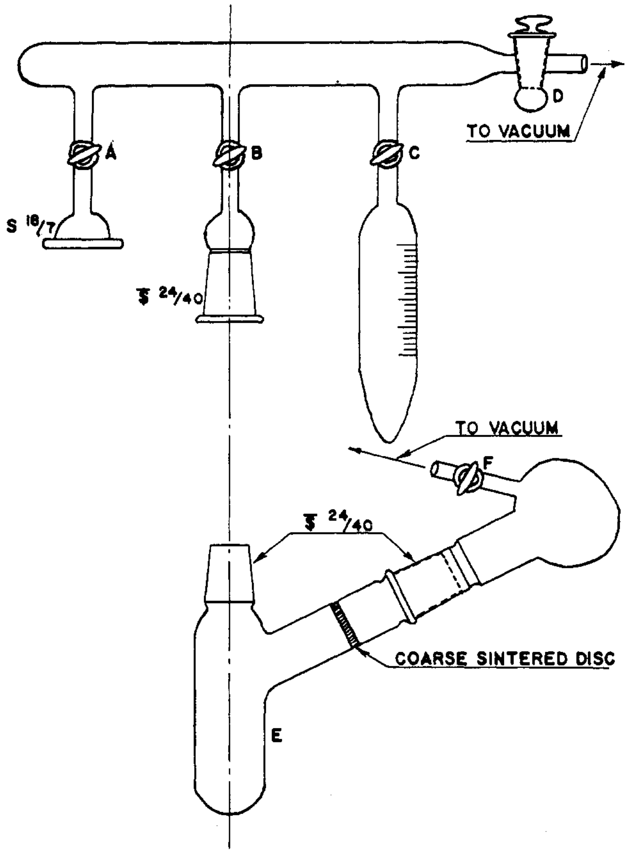

Figure 1.—Apparatus for preparation of $Ni(CO)_3P(C_6H_5)_3$.

hood! Triphenylphosphine (6.5 g., 0.025 mole) was transferred to a round-bottomed reaction container (see Figure 1) that attached to a vacuum system (0.1 mm. pressure). Ether (35 ml.) and then nickel carbonyl (3.0 ml., 0.024 mole) were distilled *in vacuo* into the vessel which was frozen with liquid nitrogen. The liquid nitrogen was replaced by an ice bath, and nitrogen was introduced into the reaction container. Carbon monoxide evolved and white crystals ($Ni(CO)_3P(C_6H_5)_3$) deposited as the mixture was stirred magnetically for 3 hr. The mixture was filtered under nitrogen through the side arm, and the product was dried *in vacuo* for 2 hr. The compound is stable for months when stored at *ca.* 5° free from oxygen and water. Polar organic solvents cause rapid decomposition as evidenced by gas evolution and the formation of a green gelatinous precipitate. Decomposition in nonpolar solvents under nitrogen is relatively slow. *Anal.* Calcd. for $C_{21}H_{15}O_3NiP$: C, 62.3; H, 3.73. Found: C, 63.0; H, 3.65.

Infrared Spectra.—Solution spectra were desired in preference to spectra of the solid, and cyclohexane was found suitable as far as solubility and decomposition of $Ni(CO)_3P(C_6H_5)_3$ were concerned. To aid in the identification of the absorption bands of the $P(C_6H_5)_3$ group in $Ni(CO)_3P(C_6H_5)_3$, corresponding spectra of $P(C_6H_5)_3$ were obtained under the same set of experimental conditions used to obtain the $Ni(CO)_3P(C_6H_5)_3$ spectra, the concentrations being adjusted so that the number of $P(C_6H_5)_3$ molecules in the sample beam was equal to or greater than the number of $P(C_6H_5)_3$ groups in the sample beam for the corresponding spectral runs of $Ni(CO)_3P(C_6H_5)_3$. The primary purpose of the study was to obtain the frequencies of the bands due to the $PNi(CO)_3$ group, and a complete vibrational assignment of either $P(C_6H_5)_3$ or the $P(C_6H_5)_3$ ligand was not attempted. The spectra of the latter two were recorded, therefore, under survey instrumental conditions. Higher resolution spectra were obtained for the bands of the $PNi(CO)_3$ group.

Spectra from 290 to 900 cm.$^{-1}$ were recorded with a Beckman IR5A spectrophotometer and with a spectrophotometer built

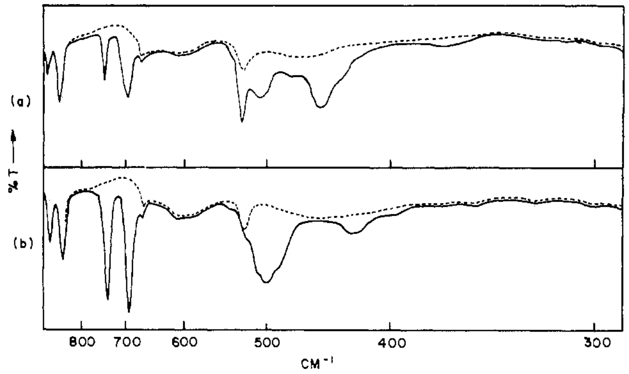

Figure 2.—Infrared spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in cyclohexane, 290–900 cm.$^{-1}$: (a) $Ni(CO)_3P(C_6H_5)_3$, (b) $P(C_6H_5)_3$.

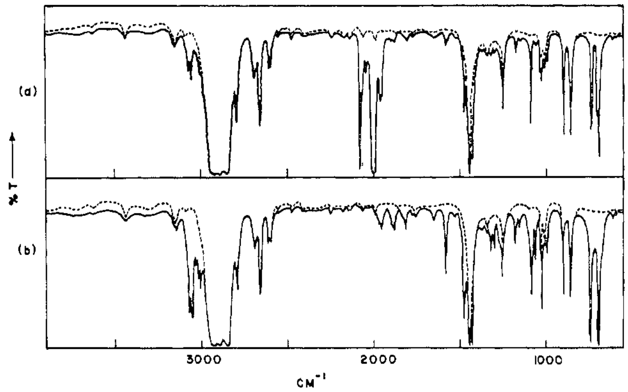

Figure 3.—Infrared spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in cyclohexane, 550–3900 cm.$^{-1}$: (a) $Ni(CO)_3P(C_6H_5)_3$, (b) $P(C_6H_5)_3$.

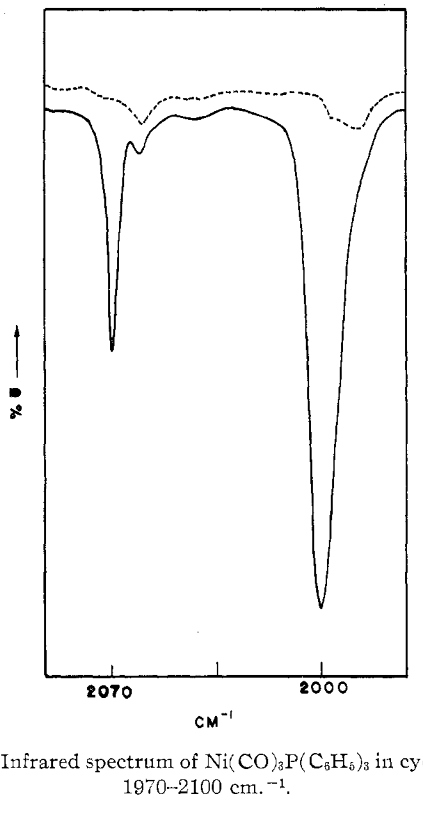

Figure 4.—Infrared spectrum of $Ni(CO)_3P(C_6H_5)_3$ in cyclohexane, 1970–2100 cm.$^{-1}$.

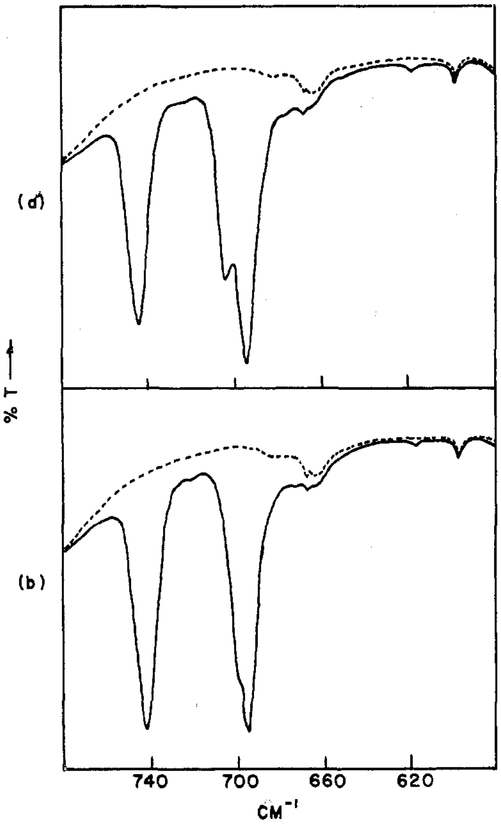

Figure 5.—Infrared spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in cyclohexane, 580–780 cm.⁻¹: (a) $Ni(CO)_3P(C_6H_5)_3$, (b) $P(C_6H_5)_3$.

around a Perkin-Elmer Model 99 monochromator. Both instruments were equipped with CsBr prisms. The spectra from the latter instrument were recorded with an effective band width (one-half spectral slit width) of *ca.* 1 cm.⁻¹ at 400 cm.⁻¹ and were calibrated with atmospheric CO_2 and H_2O.[14] The accuracy of the observed frequencies is believed to be ±2 cm.⁻¹. Spectra from 550 to 4000 cm.⁻¹ were recorded with a Perkin-Elmer 421 spectrophotometer equipped with a grating interchange. Survey spectra were calibrated with a polystyrene film and with the numerous solvent bands. The accuracy is believed to be ±2 cm.⁻¹. Spectra recorded from 1970 to 2100 cm.⁻¹ under higher resolution conditions, effective band width about 3 cm.⁻¹, were calibrated with atmospheric H_2O,[15] while the higher resolution spectra from 580 to 780 cm.⁻¹, effective band width about 1 cm.⁻¹, were calibrated with CO_2 and NH_3.[16] Frequency accuracy here is ±1 cm.⁻¹. The accuracy of sharp bands should be well within the stated limits; broader bands and shoulders are more difficult to determine.

Spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in cyclohexane are shown in Figure 2 (290–900 cm.⁻¹) and in Figure 3 (600–3900 cm.⁻¹). A higher resolution spectrum of $Ni(CO)_3P(C_6H_5)_3$ in cyclohexane is shown in Figure 4 (1970–2100 cm.⁻¹). This latter region covers the CO stretching domain, and a corresponding solution of $P(C_6H_5)_3$ in cyclohexane showed no bands here. Higher resolution spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in the 700 cm.⁻¹ region are shown in Figure 5. A careful study of this region was necessary in the determination of the origin of the 703 cm.⁻¹ band in $Ni(CO)_3P(C_6H_5)_3$. The measured frequencies and character of the infrared absorption bands are as follows (cm.⁻¹). **$Ni(CO)_3P(C_6H_5)_3$**: 365 (w), 413 (w, sh), 432 (w, sh), 450 (s), 476 (w), 501 (m, sh), 506 (s), 524 (s), 541 (w, sh), 619 (vw), 675 (vw), 693 (s), 703 (m), 720 (vw), 742 (s), 999 (w), 1029 (w), 1071 (vw), 1094 (m), 1157 (w), 1183 (w), 1306 (vw), 1329 (vw), 1382 (vw), 1435 (s), 1482 (m), 1591 (w), 1658 (vw), 1755 (vw), 1813 (vw), 1830 (vw), 1886 (vw), 1902 (vw, sh), 1951 (m), 1963 (m), 2000 (vs), 2042 (w), 2070 (s), 3006 (w, sh), 3020 (w, sh), 3035 (w, sh), 3059 (m), 3075 (m), 3145 (vw, sh). **$P(C_6H_5)_3$**: 395 (w), 425 (w), 487 (m, sh), 502 (s), 512 (s, sh), 541 (w), 616 (vw), 674 (vw), 694 (s), 699 (m, sh), 720 (vw), 740 (s), 1000 (w), 1028 (m), 1068 (w), 1088 (m), 1156 (w), 1182 (w), 1305 (w), 1327 (w), 1380 (vw), 1434 (s), 1481 (s), 1588 (m), 1654 (w), 1755 (vw), 1812 (w), 1830 (w, sh), 1885 (w), 1900 (w, sh), 1953 (w), 1966 (w, sh), 3003 (m), 3015 (m), 3030 (m), 3055 (s), 3071 (s), 3140 (w). The infrared bands assigned to the $PNi(CO)_3$ group are listed in Table I.

TABLE I

FREQUENCIES (IN CM.⁻¹) ASSIGNED TO THE $PNi(CO)_3$ GROUP

Infrared	Raman	Infrared	Raman
...	88 m	450 s	454 w
...	112 m	476 w	481 m
...	192 w[a]	2000 vs	1999 s
365 w	366 m	2142 w	2045 w
...	418 s	2070 s	2071 m

[a] Tentative, see text.

Raman Spectra.—An applied Research Laboratories spectrograph with a camera aperture of f/3.5 and a dispersion of 15 Å./mm. at 4358 Å. was used. The spectrograph was equipped with three flint-glass prisms. The Raman excitation unit consisted of a high-frequency electrodeless mercury arc similar to the type described recently,[17] but with certain modifications. The mercury toroid (26 cm. long, 11.5 cm. i.d., 15 cm. o.d.) was prepared by sealing *ca.* 3 g. of Hg in the toroid after the toroid had been evacuated for 20 hr. at 500°. The toroid was covered with a MgO asbestos reflector to increase the amount of light falling on the Raman tube. During operation, the toroid was inside an inductance coil which was fed with high-frequency power through a coaxial cable. The load was matched to the source by tuning the capacitor. The high-frequency source consisted of modified rectifier power and radio transmitter units of the Navy Model TDH-4 radio equipment manufactured by Collins Radio Co. The inductance coil was constructed from 25 ft. of 0.25-in. Cu tubing. A Variac in the primary of the high-voltage transformer regulated the voltage supply between 2000 and 4000 volts. The resonant frequency for the mercury excitation was 4936 kc. The heat generated by the arc in operation was dissipated in part by a fan and a cold Rhodamine (DuPont, 5DGN Extra) filter solution which circulated in a jacket inside the mercury toroid. Before entering the filter jacket the filter solution circulated through a coil immersed in an ice bath. Besides stabilizing the mercury arc, the Rhodamine filter system insulated the sample tube from most of the heat of the arc and decreased the background on the film by absorbing undesirable radiation. After runs of several hours, the temperature of the sample tube increased 5–10° above room temperature. The excitation unit was mounted upright (vertical Raman tube) on a Transite platform with adjustable Bakelite legs. The Raman tube (1.5 cm. o.d., 25 cm. long) had a 32-ml. capacity. A Kodak Wratten 2B gelatin filter was wrapped around the Raman tube for some runs to aid in the identification of Raman lines excited by the 4047 and 4078 Å. Hg lines. A Corning No. 3387 glass filter was placed against the slit for some runs to aid in the identification of Raman lines close to the principal mercury exciting line at 4358 Å. The spectra were recorded on Kodak Royal X and 103a-F[18] film. A reference spectrum of argon was used to calculate the Raman

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(16) "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," (IUPAC edition), Butterworths, London, 1961.

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(18) Thanks are due to Eastman Kodak Company for a sample of this film.

shifts by a graphical method, and the accuracy of the frequencies is believed to be within ±2 cm. for average lines.

The Raman samples of $P(C_6H_5)_3$ in cyclohexane were prepared by vacuum distilling cyclohexane into the Raman tube which contained $P(C_6H_5)_3$. The tube was immersed in an ice bath for the distillation and was then sealed under vacuum. This technique was unsuitable for $Ni(CO)_3P(C_6H_5)_3$, because rapid decomposition of $Ni(CO)_3P(C_6H_5)_3$ occurred when its solution was subjected to a vacuum. Therefore, the Raman tubes with $Ni(CO)_3P(C_6H_5)_3$ in cyclohexane were prepared by sealing the tube under a pressure of nitrogen after the solution was centrifuged to remove decomposition product which formed initially. Additional decomposition product which formed after several hours Raman exposure was also removed by centrifugation. The colloidal decomposition product caused a large increase in the background darkening on the film.

Solutions of $Ni(CO)_3P(C_6H_5)_3$ in cyclohexane (20%) and solutions of $P(C_6H_5)_3$ in cyclohexane (30%) were examined. Exposure times varied from 1 to 12 hr. with slit widths 50–200 μ. The observed Raman lines (shifts from 4358 Å.) are as follows (cm.$^{-1}$). **$Ni(CO)_3P(C_6H_5)_3$**: 88 (m), 112 (m), 192 (m), 206 (m), 254 (w), 366 (m), 418 (s), 454 (w), 481 (m), 525 (m), 602 (vw), 620 (m), 691 (vw), 704 (m), 867 (vw), 1000 (s), 1097 (m), 1532 (vw), 1574 (vw), 1590 (s), 1949 (w), 1967 (w), 1999 (s), 2045 (w), 2071 (m), 3006 (w), 3057 (s), 3146 (w), 3173 (w). **$P(C_6H_5)_3$**: 188 (w), 205 (m), 246 (m), 400 (vw), 507 (m), 617 (m), 679 (vw), 697 (m), 842 (vw), 997 (s), 1093 (m), 1527 (vw), 1572 (vw), 1585 (s), 3002 (w), 3050 (s), 3136 (w), 3167 (w).

Several points concerning the Raman data warrant discussion. First, the frequencies for the lines in the spectrum of cyclohexane fall within ±2 cm.$^{-1}$ of the average of values reported by Rasmussen.[19] The following frequencies were also observed as Stokes lines excited by the 4046 Å. Hg line: 1000, 1097, 1999, 2071, and 3057 cm.$^{-1}$ for $Ni(CO)_3P(C_6H_5)_3$; 617, 697, 997, 1093, and 3050 cm.$^{-1}$ for $P(C_6H_5)_3$. The frequency shift, 997 cm.$^{-1}$, for $P(C_6H_5)_3$ was observed also as a Stokes line from the 4078 Å. Hg line, and 248 cm.$^{-1}$ was observed as an anti-Stokes line from 4358 Å. The frequencies listed above for $Ni(CO)_3P(C_6H_5)_3$ without corresponding frequencies listed for $P(C_6H_5)_3$ are those which arise from the $PNi(CO)_3$ group, except for the lines at 602, 1949, and 1967 cm.$^{-1}$. The Raman lines at 1949 and 1967 cm.$^{-1}$ in the spectrum of $Ni(CO)_3P(C_6H_5)_3$ correspond to the 1951 and 1963 cm.$^{-1}$ infrared bands of $Ni(CO)_3P(C_6H_5)_3$ and to the 1953 and 1966 cm.$^{-1}$ infrared bands of $P(C_6H_5)_3$. Hence, the 1949 and 1967 cm.$^{-1}$ lines are interpreted as arising from the $P(C_6H_5)_3$ group. The Raman line of $Ni(CO)_3P(C_6H_5)_3$ which corresponds to the weak 400 cm.$^{-1}$ $P(C_6H_5)_3$ line is very likely buried under the strong 418 cm.$^{-1}$ line of $Ni(CO)_3P(C_6H_5)_3$. On the whole, the relative intensities of the lines assigned to the $P(C_6H_5)_3$ group in the spectrum of $Ni(CO)_3P(C_6H_5)_3$ are nearly the same as the relative intensities of the lines for $P(C_6H_5)_3$ itself. However, the 192 cm.$^{-1}$ line for $Ni(CO)_3P(C_6H_5)_3$ is stronger than the corresponding line at 188 cm.$^{-1}$ in $P(C_6H_5)_3$. This may result from another line near this frequency in the spectrum of $Ni(CO)_3P(C_6H_5)_3$ which contributes to the intensity. Therefore, a line at 192 cm.$^{-1}$ is tentatively assigned to the $PNi(CO)_3$ group. The 602 cm.$^{-1}$ line for $Ni(CO)_3P(C_6H_5)_3$ appeared only during the longest exposure of $Ni(CO)_3P(C_6H_5)_3$, and corresponding spectra of $P(C_6H_5)_3$ and cyclohexane were not obtained for this run. Because of a very weak band at this frequency in the infrared spectrum of cyclohexane and the fact that no infrared bands were observed at this frequency which could be assigned to either $P(C_6H_5)_3$ or $Ni(CO)_3P(C_6H_5)_3$, one is led to assign the 602 cm.$^{-1}$ line as probably arising from cyclohexane. The Raman lines assigned to the $PNi(CO)_3$ group are listed in Table I.

The Assignment of the Vibrational Spectra

A general feature of the vibrational spectra of large molecules is the appearance of frequencies which are characteristic of vibrations of certain groups in the molecule. In such vibrations, atoms in the remainder of the molecule have relatively little or no amplitude of vibration. The primary interest of this study concerns the vibrational modes localized in the $PNi(CO)_3$ group. The $PNi(CO)_3$ group vibrations are those modes in which the atomic displacements are confined primarily to the atoms in this group. Therefore, the symmetry and selection rules for these vibrations may be approximated by considering only this group and neglecting any influence of the remainder of the molecule.

The $PNi(CO)_3$ group is assumed to belong to the C_{3v} point group. The structure of the reduced representation for the normal modes of vibration of the group under localized-mode C_{3v} selection rules may be written as

$$\Gamma = 5A_1 + A_2 + 6E$$

All vibrations except the A_2 mode are both infrared and Raman active. An approximate description of each mode is given in Table II. These descriptions have been arrived at by considering the results of calculations made in this laboratory for other metal carbonyls.[20] These descriptions refer to the actual displacements and are not to be interpreted as meaning that a single type of bond or other structural unit is being deformed. In the C–O stretching vibrations the C and O atoms move in opposite directions along the NiCO lines, and the Ni–C bond is compressed somewhat more than one-half as much as the C–O bond is extended. The NiCO lines almost remain straight in the $Ni(CO)_3$ deformations. The amplitude of the C atom is expected to be of the order of twice that of the O atom with the two atoms moving in opposite directions perpendicular to the NiCO line in the Ni–C–O bending modes of vibration. The C and O atoms move almost as a unit in the Ni–CO stretching motion. It should be noted that the Ni–CO stretching and Ni–C–O bending motions are strongly mixed in both ν_2 and ν_3 with the latter dominating in ν_2 and the former in ν_3. A similar mixing is expected in the asymmetric modes ν_8, ν_9, and ν_{10}. The assignment of the fundamental modes of the $PNi(CO)_3$ group is based upon analogy with the as-

TABLE II

ASSIGNMENT OF THE VIBRATIONAL SPECTRA FOR THE $PNi(CO)_3$ GROUP

ν_i	Species	Description	Frequency, cm.$^{-1}$	
			Infrared	Raman
ν_1	A_1	C–O stretch	2070	2071
ν_2	A_1	Ni–C–O bend	476	481
ν_3	A_1	Ni–CO stretch	....	418
ν_4	A_1	Ni–P stretch	....	192?
ν_5	A_1	$Ni(CO)_3$ def.	....	112
ν_6	A_2	Ni–C–O bend	Inactive	Inactive
ν_7	E	C–O stretch	2000	1999
ν_8	E	Ni–C–O bend	?	?
ν_9	E	Ni–CO stretch	450	454
ν_{10}	E	Ni–C–O bend	365	366
ν_{11}	E	$Ni(CO)_3$ rock	....	88
ν_{12}	E	$Ni(CO)_3$ def.	?	?

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[19] R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943).

[20] W. F. Edgell and P. Cecchi, unpublished results.

signment of the spectra of other metal carbonyls which have been studied in this laboratory.[3–5] The frequencies are divided naturally into three regions: high-frequency region (1900–2100 cm.$^{-1}$), middle-frequency region (300–700 cm.$^{-1}$), and low-frequency region (0–200 cm.$^{-1}$).

The two C–O stretching modes, ν_1 (A_1) and ν_7 (E), are the fundamentals in the high-frequency region. The infrared spectrum of $Ni(CO)_3P(C_6H_5)_3$ shows a strong band at 2000 cm.$^{-1}$ and a band of medium intensity at 2070 cm.$^{-1}$. These two bands are by far the most intense bands in this region and must be the two fundamentals. The Raman spectrum is in good agreement and shows a strong line at 1999 cm.$^{-1}$ and a line of medium intensity at 2071 cm.$^{-1}$. The difference in intensity of the infrared bands corresponding to the two C–O stretching modes may be predicted by considering the dipole moment changes in these vibrations. The over-all molecular dipole moment change is much less for the symmetric C–O stretching mode than for the asymmetric mode, due to the substantial cancellation of the bond dipole moment change in the in-phase motion. Thus, the intensity of the A_1 mode is expected to be less than that of the E mode. For other metal carbonyls[4,21] considerations such as these and others concerning interaction constants have led to the assignment of the highest frequency in the C–O stretching region to the symmetric C–O stretching mode. Therefore, the less intense infrared band at 2070 and the Raman line at 2071 cm.$^{-1}$ are assigned to ν_1, while the more intense infrared band at 2000 cm.$^{-1}$ and the Raman line at 1999 cm.$^{-1}$ are assigned to ν_7.

The middle-frequency region includes the two Ni–CO stretching modes, ν_3 (A_1) and ν_9 (E), and the three Ni–C–O bending modes, ν_2 (A_1), ν_3 (E), and ν_{10} (E). The assignment in this region is facilitated by consideration of the results obtained[2–5,6,22] for the spectra of metal carbonyls and series such as $Ni(CO)_4$, $Co(CO)_4^-$, and $Fe(CO)_4^{2-}$. With increasing negative charge on the $M(CO)_4$ moiety, the C–O frequencies decrease and the M–C frequencies increase. These results are useful here for a prediction of the Ni–C frequencies in $PNi(CO)_3$. Since the C–O frequencies for the $PNi(CO)_3$ group shift about 60 cm.$^{-1}$ to lower frequencies compared to those in $Ni(CO)_4$, the Ni–C frequencies are expected to shift about 30 cm.$^{-1}$ to higher frequencies. The two Ni–CO stretching modes in $Ni(CO)_4$ occur at 379 cm.$^{-1}$ (A_1) and 423 cm.$^{-1}$ (F_2). The strongest Raman line for $PNi(CO)_3$ in this region falls at 418 cm.$^{-1}$ and is assigned to ν_3, the symmetric Ni–C stretching mode, both on position and intensity grounds. The 450(infrared)–454(Raman) cm.$^{-1}$ pair is assigned to the asymmetric Ni–C stretching mode ν_9 on the basis of position. No infrared band was observed which could be unambiguously assigned to ν_3. The intensity of this vibration in the infrared is expected to be less than that of ν_9 from considerations similar to those discussed for the C–O stretching modes.

A frequency of 332 cm.$^{-1}$ has been selected[23] for the inactive (F_1) Ni–C–O bending mode in $Ni(CO)_4$ from a detailed study of the spectra. This mode is expected to split into an A_2 mode (ν_6) and an E mode (ν_{10}) in $PNi(CO)_3$. The 365(infrared)–366(Raman) cm.$^{-1}$ is assigned to ν_{10} while ν_6 is inactive in both Raman and infrared spectra. The remaining observed frequency pair, 476(infrared)–481(Raman) cm.$^{-1}$, is taken for the symmetric bending mode, ν_2, since a similar bending mode in $Ni(CO)_4$ lies at 461 cm.$^{-1}$. No frequency has yet been assigned to ν_8, an asymmetric Ni–C–O bending mode. This mode has been assigned[2,23] to a weak line at 600 cm.$^{-1}$ in $Ni(CO)_4$. One would therefore expect the frequency of ν_8 for $PNi(CO)_3$ to lie between 610 and 630 cm.$^{-1}$. There is a Raman line (620 cm.$^{-1}$) of medium intensity and a weak infrared band (619 cm.$^{-1}$) in the spectra of $Ni(CO)_3P(C_6H_5)_3$. However, a corresponding line is also observed in the spectra of $P(C_6H_5)_3$ and consequently the above frequencies are believed to arise from a mode localized in the $P(C_6H_5)_3$ group. A second weak frequency in this region would be very difficult to detect. A weak Raman line is found at 602 cm.$^{-1}$. However, there is a weak infrared band in cyclohexane at 599 cm.$^{-1}$ and, as mentioned in the Experimental section, the Raman line at 602 cm.$^{-1}$ is perhaps better assigned to this cause. Thus, no frequency was observed in either the infrared or Raman spectra which could be assigned unequivocally to ν_8. This is, perhaps, not unexpected in view of the weak intensity of the corresponding mode in $Ni(CO)_4$ and the presence of other bands which tend to mask this spectral region.

The three CO–Ni–CO bending modes, ν_5 (A_1), ν_{11} (E), and ν_{12} (E), and the Ni–P stretching mode, ν_4 (A_1), are expected to occur in the low-frequency region. Since the infrared instrumentation available did not permit the observation of bands which occur below 290 cm.$^{-1}$, the assignments in this region are made solely from the Raman data. The two CO–Ni–CO deformation modes in $Ni(CO)_4$ occur at 65 cm.$^{-1}$ (E) and 79 cm.$^{-1}$ (F_2). Following the method used for the assignments in the middle-frequency region, the two Raman lines of medium intensity at 88 and 112 cm.$^{-1}$ are assigned to ν_{11} and ν_5, respectively. No line was observed which can be assigned to ν_{12}.

The Ni–P stretching mode in molecules such as $Ni(PF_3)_4$[24] and $Ni[P(OCH_3)_4]$[25] has been assigned to frequencies which fall around 190 cm.$^{-1}$. Thus, the Raman line at 192 cm.$^{-1}$ is tentatively assigned to ν_4. These assignments are collected together in Table II.

The weak Raman line at 2045 cm.$^{-1}$ and a weak infrared band at 2042 cm.$^{-1}$ correspond to a combination band. One possible explanation is that this band arises from a combination of ν_9 with the 1591 cm.$^{-1}$

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(21) W. F. Edgell, C. Magee, and G. Gallup, *J. Am. Chem. Soc.*, **78**, 4185 (1956).

(22) (a) L. H. Jones, *J. Chem. Phys.*, **28**, 1215 (1958); (b) H. Stammreich, K. Kawai, and O. Sala, *ibid.*, **35**, 2168 (1961).

(23) W. F. Edgell, unpublished work.

(24) L. A. Woodward and J. R. Hall, *Nature*, **181**, 831 (1958); *Spectrochim. Acta*, **16**, 654 (1960).

(25) M. Bigorgne, *Compt. rend.*, **250**, 3484 (1960).

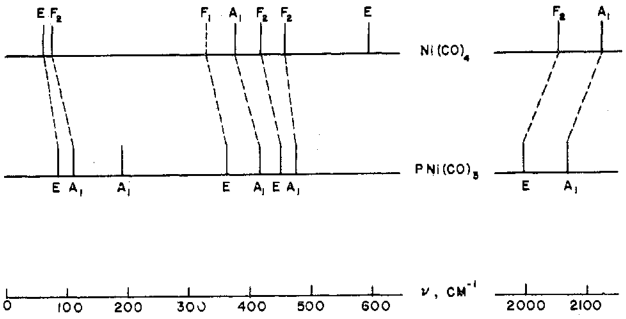

Figure 6.—Correlation of the fundamental frequencies for $Ni(CO)_4$ and the $PNi(CO)_3$ group.

band of $P(C_6H_5)_3$ (infrared; $1591 + 450 = 2041$: Raman; $1590 + 454 = 2044$).

Discussion

A comparison of the fundamental frequencies of the $PNi(CO)_3$ group with those of $Ni(CO)_4$ is given in Figure 6. Large shifts to lower frequencies occur on going from $Ni(CO)_4$ to $PNi(CO)_3$ in the high-frequency region and smaller though definite shifts to higher frequencies occur in the middle- and low-frequency regions. The correlation is good even though there is a change in symmetry from $Ni(CO)_4$ (T_d) to the $PNi(CO)_3$ group (C_{3v}). These frequency shifts are similar to those found in the isoelectronic series, $Ni(CO)_4$, $Co(CO)_4^-$, and $Fe(CO)_4^{2-}$, which have been discussed by Edgell, *et al.*,[2–5] in terms of a molecular orbital description of the bonding. The shifts in such a series are interpreted as resulting from the pronounced increase in π^*_{CO} participation in the electron-filled molecular orbitals of the species as one passes along the series. They are a direct consequence of the decrease in metal–C antibonding character and the increase in C–O antibonding character which accompanies the increase in π^*_{CO} participation. The primary factor causing these changes in the isoelectronic series is the changing atomic number of the metal atom—a factor not present in going from $Ni(CO)_4$ to $Ni(CO)_3P(C_6H_5)_3$.

It is useful to consider the molecular orbitals involved in the bonding in the $PNi(CO)_3$ group. The relevant metal orbitals are classified on the basis of symmetry as follows: $3d(a_1 + 2e)$, $4s(a_1)$, and $4p(a_1 + e)$. Similar classification for the pertinent CO orbitals gives: lone-pair $\sigma(a_1 + e)$, $\pi(a_1 + a_2 + 2e)$, and $\pi^*(a_1 + a_2 + 2e)$. The relevant orbitals for the phosphine group are classified as lone-pair $\sigma(a_1)$ and $\pi(2e)$, the latter orbitals being the empty $3d\pi$ orbitals of phosphorus. Only metal and ligand orbitals of the same symmetry may combine to form the bonding and the antibonding orbitals of the molecule. A schematic correlation diagram is given in Figure 7, where the molecular orbitals are divided according to symmetry species. Since there are no a_2 metal orbitals, the CO orbital of this symmetry is nonbonding and is not shown. The thirty electrons which occupy the orbitals of the metal atom and the ligands in the separated species occupy the 15 lowest-energy molecular orbitals of the $PNi(CO)_3$ group. Each "x" in Figure 7 represents an electron pair. In addition to these, the nonbonding $a_2(\pi)$ orbital is filled.

The extent of the presence of the π^*_{CO} and $3d\pi_P$ orbitals in the electron-filled molecular orbitals of the metal carbonyl is an important factor in this bonding description. The effects of the participation may be seen readily by considering first the limiting or hypothetical case where the π^*_{CO} and the $3d\pi_P$ orbitals are too high in energy to mix with the other orbitals. Then the $1a_1$, $2a_1$, $3a_1$, $1e$, $2e$, and $3e$ molecular orbitals would be antibonding between the metal and the ligands. The energies of the $4a_1$, $4e$, and $5e$ orbitals in the limiting state are indicated schematically by dashed lines in Figure 7. The difference between the number of occupied bonding orbitals and the number of occupied antibonding orbitals gives essentially a net of four bonding orbitals between the nickel and the ligands or one per ligand. These are the dative bonds. Since the $4a$, $4e$, and $5e$ orbitals will have some σ_{CO} as well as π_{CO} character, the dative bond from a CO group to the metal will have a small amount of π character along with its dominant σ character! The CO groups do not share their "dative electrons" equally with the nickel atom so the CO dative bond has a bond order definitely less than one.

The modifications that would occur in the limiting state when the π^*_{CO} orbitals participate in the bonding will now be considered. One modification that results is the lowering of the energy of the occupied molecular orbitals. This π^*_{CO} stabilization is expected to be greater for the antibonding orbitals than for the bonding orbitals, since the π^*_{CO} orbitals are closer in energy to the former than to the latter. We indicate this by dropping the energies of the $4a_1$, $4e$, and $5e$ antibonding orbitals in Figure 7 for the case of π^*_{CO} participation below the dashed lines (which indicate the limiting-state energies). A second modification due to the π^*_{CO} participation in the a_1 and e molecular orbitals is a transfer of charge from Ni to the CO groups; there is an increase in electron density between Ni and C and a decrease in density between C and O. Thus, the Ni–C antibonding character decreases while that of C–O increases. The effect is to strengthen the bonding of the CO groups to the Ni atom and weaken the bonds between the C and O atoms. The features are similar to those found earlier for $Ni(CO)_4$ by the same procedure.[2]

The participation of the $3d\pi_P$ orbitals would also lead to the stabilization of electron-filled orbitals, especially the $4e$ and $5e$, and would remove charge from the Ni atom to strengthen the Ni–P bond (π bonding). This would also lead to a reduction of π^*_{CO} participation and a shift of the C–O stretching frequencies to higher values. If there is any participation of the electrons transferred to phosphorus in the π bonding of the phenyl rings, this would alter the ring stretching and P–C frequencies.

The problem is how to estimate the amount of π^*_{CO} and $3d\pi_P$ participation. A useful quantity has been proposed[2–5] to relate spectroscopic data for metal

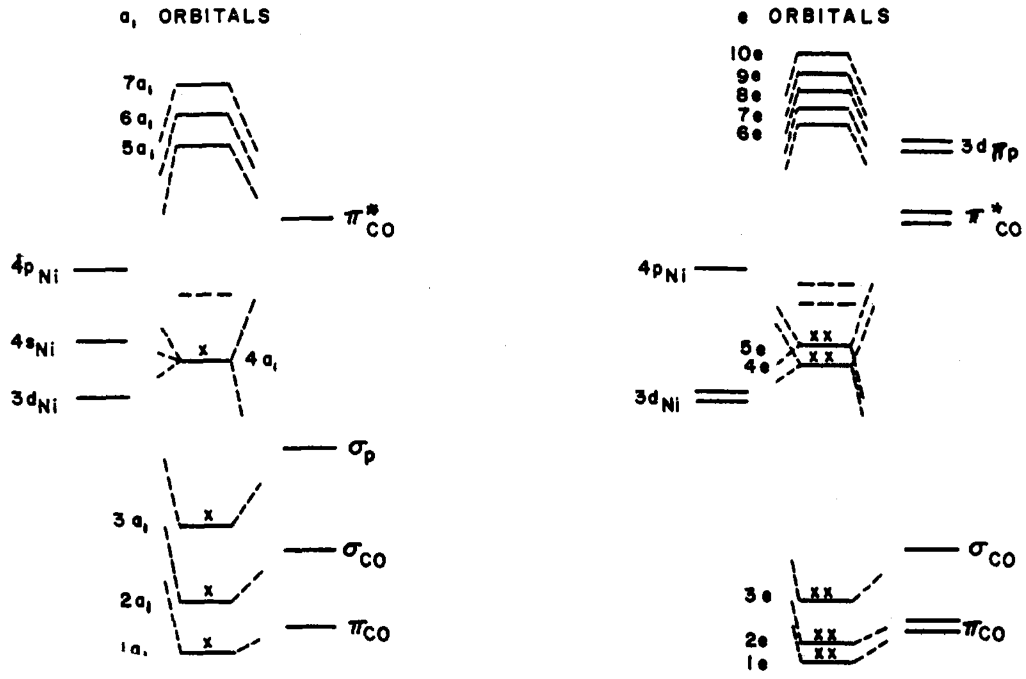

Figure 7.—Schematic correlation diagram for molecular orbitals of the PNi(CO)$_3$ group.

carbonyls to the amount of π^*_{CO} participation. This quantity, called the π^* participation index (*PI*), is defined as

$$PI = (k^0_{CO} - k_{CO})/(k^0_{CO} - k^*_{CO}) \quad (1)$$

where k_{CO} is the stretching force constant of the CO group in the compound, k^0_{CO} that for the limit case of no π^*_{CO} participation, and k^*_{CO} that when one electron pair has been transferred back to the π^*_{CO} orbital of the CO group. The quantity k^0_{CO} is approximated by the force constant for carbon monoxide (18.56 mdynes/Å.) while ($k^0_{CO} - k^*_{CO}$) is estimated as about 8.3 mdynes/Å. from a consideration of the force constants in a number of molecules. An approximate and simplified molecular orbital treatment of the CO force constant in metal carbonyls[23] equates *PI* to one-half the charge on the CO in π^* orbitals as given by the population analysis. Thus, one expects *PI* to approximate one-half the number of electrons in the π^*_{CO} orbitals.

TABLE III

CO STRETCHING FREQUENCIES AND *PI* VALUES FOR SOME METAL CARBONYLS

Molecule or moiety	ν, cm.$^{-1}$	PI
Ni(CO)$_4$	2128 2058	0.19[a]
PNi(CO)$_3$	2070 2000	0.28
Co(CO)$_4^-$	1918 1883	0.49[a]
Fe(CO)$_4^{2-}$	1730	0.72[a]

[a] W. F. Edgell, quoted in ref. 4; the Ni(CO)$_4$ value is based upon new force constant considerations.

An accurate value of the *PI* in (C$_6$H$_5$)$_3$PNi(CO)$_3$ must await force constant calculations now in progress in this laboratory. However, *PI* may be estimated as *ca.* 0.28 from a comparison of the C–O stretching frequencies with those of other metal carbonyls for which *PI* has been calculated. This is to be compared with *PI* for other four-coordinated compounds in Table III. Thus the nickel atom (3d^{10}) transfers about 0.56 electron to each CO group in Ni(CO)$_3$P(C$_6$H$_5$)$_3$ *via* back bonding into the π^*_{CO} orbitals. We shall assume, as a first estimate, that the CO dative bonding is the same as that calculated for the Ni(CO)$_4$, Co(CO)$_4^-$, Fe(CO)$_4^{2-}$ series.[26] In this event, each CO group of Ni(CO)$_3$P(C$_6$H$_5$)$_3$ transfers about 0.67 electron (0.55 as σ and 0.12 as π) to the nickel atom (4s, 4p) in dative bonding. Following Nieuwpoort's definition, this could be described as a Ni–CO "bond order" of 1.23 (0.67 + 0.56). For comparison, each CO in Ni(CO)$_4$ transfers about 0.67 electron to Ni in dative bonding and receives about 0.38 electron in back bonding to the π^*_{CO} orbitals, for a Ni–CO bond order of 1.05. The moderate frequency increases found for the vibrations of the middle- and low-frequency range in the Ni(CO)$_3$ moiety on passing from Ni(CO)$_4$ to Ni(CO)$_3$P(C$_6$H$_5$)$_3$ are due to the increase in stiffness of the Ni–CO bond accompanying the increase in Ni–CO back bonding; the more substantial drop in the C–O stretching frequencies results from the sensitivity of the C–O bond strength to the presence of π^* character in the C–O bond.

As pointed out, the primary cause of the increased π^*_{CO} participation on going from Ni(CO)$_4$ to Ni(CO)$_3$P(C$_6$H$_5$)$_3$ cannot be that involved on going from Ni(CO)$_4$ to Co(CO)$_4^-$. In connection with this question, we now examine the broad character of the changes in bonding which can take place when a ligand replaces a CO group in Ni(CO)$_4$. The molecular orbitals for LNi(CO)$_3$ (see Figure 7) can be written as

$$\phi_i = \sum_q \chi_q c_{qi} \quad (2)$$

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(26) W. C. Nieuwpoort, private communication.

where the χ_q are the nickel and ligand orbitals discussed above. They are solutions, along with the orbital energies ϵ_i, of the equations (one for each value of p)

$$\sum_q (F_{pq} - \epsilon_i S_{pq})c_{qi} = 0 \qquad (3)$$

and are self-consistent in that the constants c_{qi} which enter the Fock matrix F (*via* the ϕ_i) are the same as those obtained with its use from these equations. S_{pq} is the overlap integral between χ_p and χ_q.

The orbitals obtained when L is CO, $\phi^0{}_i$, can be used to construct a first approximation set $\phi^1{}_i$ for LNi(CO)$_3$ with which the first approximation to the Fock matrix for LNi(CO)$_3$ is formed. An insight into the problem can be obtained by considering the case where the π acceptor orbitals of L are less available to the nickel atom than those of the CO it replaces for whatever reason. Form the $\phi^1{}_i$ from the $\phi^0{}_i$ by reducing the value of the c_{qi} for the π acceptor orbitals of L from its L = CO value, retain the values of all other c_{qi} except those for the 3d nickel orbitals which (strongly) overlap the π acceptor orbitals of L, and finally increase the c_{qi} for these last (Ni) orbitals until the $\phi^1{}_i$ are again normalized to unity. This redistributes the charge lost from the π acceptor orbitals of L, when it was CO, over the rest of the molecule, placing most of it on the nickel atom. The first correction to the $\phi^1{}_i$ is obtained by solving eq. 3 for the c_{qi} (and ϵ_i) using the Fock matrix based upon the $\phi^1{}_i$, *i.e.*

$$F^1{}_{pq} = H^1{}_{pq}(1) + 2J^1{}_{pq}(1) - K^1{}_{pq}(1) \qquad (4)$$

$$J^1{}_{pq}(1) = \sum_i \int \bar{\phi}_i(2)\phi_i(2)\bar{\chi}_p(1)\chi_q(1)r_{12}{}^{-1}\,\mathrm{d}r_1r_2$$

Here H is the Hamiltonian matrix for an electron in the field of the nuclei plus its interaction with the core electrons, J is the Coulomb energy matrix, and K is the exchange matrix. We concern ourselves with the terms involving the χ_q of the nickel atom and CO groups, and more specifically how these $F^1{}_{pq}$ compare with the corresponding ones when L is CO, *i.e.*, $F^0{}_{pq}$. It is apparent that $H^1{}_{pq} \doteq H^0{}_{pq}$. Since K is much smaller than J, we may concern ourselves only with changes in the Coulombic terms. Since the $\phi^1{}_i$ differ from the $\phi^0{}_i$ by putting more charge on the metal atom, the diagonal terms for the metal orbitals (χ_m) and the CO orbitals (χ_n) increase in value. When χ_n is a lone-pair σ orbital, $(J^1{}_{mm} - J^0{}_{mm})$ is of the same order as $(J^1{}_{\sigma\sigma} - J^0{}_{\sigma\sigma})$ because the σ is concentrated toward the metal atom. Since the π^* orbitals are distributed at ends of the CO group, one sees that $(J^1{}_{mm} - J^0{}_{mm})$ is greater than $(J^1{}_{\pi^*\pi^*} - J^0{}_{\pi^*\pi^*})$. One concluces that: the relevant F^1 matrix elements lie at higher energies than those of F^0; the diagonal metal terms $F^1{}_{mm}$ are shifted upward definitely more than the diagonal CO terms $F^1{}_{\pi^*\pi^*}$; the diagonal σ CO terms $F^1{}_{\sigma\sigma}$ are shifted upward approximately as much as the $F^1{}_{mm}$ terms for the metal orbitals with which they strongly interact; the changes in the off-diagonal terms connecting metal and CO orbitals are the smallest but are largest for some 3d–π^* interactions. These changes lead to greater participation of the $\pi^*{}_{\mathrm{CO}}$ orbitals in the bonding orbitals of LNi(CO)$_3$ while suggesting that the change in the Ni–CO σ bonds is much smaller. Thus the correction reduces the charge on the nickel atom in 3d orbitals and places it in the $\pi^*{}_{\mathrm{CO}}$ orbitals.

Now suppose that the ligand L differs from CO by forming a better σ bond with the nickel atom. The same kind of consideration leads to the conclusion that the effects will be similar to those discussed above. However, since the $\phi^1{}_i$ now puts the extra charge on the metal in those (combinations of) metal orbitals involved in the σ bond to the ligand, the increase in $\pi^*{}_{\mathrm{CO}}$ participation is smaller than in the first case for the same (change in) charge transfer to the metal. This follows from the expectation that the Coulombic energy terms of 3d orbitals will be raised more by the transfer of a given charge into 3d orbitals than into the (combination of) metal orbitals involved in the σ bond to the ligand.

The increase in *PI* from 0.19 to 0.28 when a CO in Ni(CO)$_4$ is replaced by a P(C$_6$H$_5$)$_3$ group, when interpreted in the light of the above analysis, implies that the latter ligand transfers more charge to the Ni(CO)$_3$ moiety than the CO group it replaces. The total increase in charge which appears in $\pi^*{}_{\mathrm{CO}}$ orbitals of Ni(CO)$_3$ is about 0.5 electron. One notes that if the π acceptor strength of P(C$_6$H$_5$)$_3$ should be zero without an increase in donation into the σ orbitals, the additional electrons in the Ni(CO)$_3$ moiety would have been 0.4. While one cannot be certain how much of the 0.5 electron comes from the decrease in π acceptor strength compared with CO and how much from an increase in σ donor strength, the implication of the analysis is that there has been a substantial reduction in the charge in the π acceptor orbitals in P(C$_6$H$_5$)$_3$ from the 0.4 electron when L is CO.

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