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IX. SYNTHESIS AND IR STUDY OF $Ni(CO)_3L$ WHERE L IS A TERTIARY SUBSTITUTED ARYL GROUP VB DERIVATIVE

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Summary

The synthesis of a series of compounds of general formula $LNi(CO)_3$ is presented, the ligands employed being aryl Group VB derivatives of formulae $(C_6H_5)_3E$, $(4\text{-}XC_6H_4)_3E$ and $(3\text{-}XC_6H_4)_3E$, with E = P, As, Sb and X = Cl, F. The CO stretching frequencies and their shifts have been discussed for these compounds in terms of the σ bonding involved and a correlation between the CO force constants and the bonding suggests some interesting conclusions regarding the bonding in analogous $LCr(CO)_5$ derivatives.

In a previous paper [1] the synthesis and IR spectra of a series of compounds of general formula $LCr(CO)_5$ were described, L being a tertiary substituted aryl Group VB compound. The same ligands have now been used in the preparation of the analogous $LNi(CO)_3$ derivatives.

The characteristic CO vibrations of these compounds are discussed below with reference to the σ- and π-bonding characteristics of the ligands, the discussion being extended to include analogous $L(CO)_5Cr$ systems.

I. Synthesis

The ligand (0.025 mole) dissolved in dry ether was added dropwise to 0.023 mole of $Ni(CO)_4$ also in dry ether solution. After completion of the addition, the mixture was stirred at room temperature for 2 — 3 h and then evaporated in vacuo to remove the ether and the unreacted $Ni(CO)_4$. A green residue resulted which could be separated from the excess ligand by washing several times with ethanol. The residue proved to be $LNi(CO)_3$ as confirmed by an analysis of the CO stretching frequency in the IR spectrum. The compounds synthesized and the assigned CO stretching frequencies are summarized in Table 1. All spectra were measured in cyclohexane solution.

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TABLE 1

ASSIGNMENT OF CO STRETCHING FREQUENCIES FOR $LNi(CO)_3$ COMPOUNDS

L in $LNi(CO)_3$	ν(CO)		L in $LNi(CO)_3$	ν(CO)	
	A_1	E		A_1	E
$(C_6H_5)_3P$	2069.8	1998.5	$(4\text{-}ClC_6H_4)_3As$	2076.6	2005.3
$(4\text{-}FC_6H_4)_3P$	2072.8	2002.6	$(3\text{-}ClC_6H_4)_3As$	2077.6	2006.4
$(3\text{-}FC_6H_4)_3P$	2075.3	2006.2			
$(4\text{-}ClC_6H_4)_3P$	2073.7	2004.3	$(C_6H_5)_3Sb$	2073.8	2004.1
$(3\text{-}ClC_6H_4)_3P$	2075.3	2007.3	$(4\text{-}FC_6H_4)_3Sb$	2076.3	2007.8
			$(3\text{-}FC_6H_4)_3Sb$	2078.2	2009.5
$(C_6H_5)_3As$	2072.7	2000.8	$(4\text{-}ClC_6H_4)_3Sb$	2077.3	2008.5
$(4\text{-}FC_6H_4)_3As$	2075.8	2003.6	$(3\text{-}ClC_6H_4)_3Sb$	2078.5	2010.6
$(3\text{-}FC_6H_4)_3As$	2077.7	2007.3			

II. Metal—ligand bonding in $LNi(CO)_3$ compounds

Correlations between the CO frequency shifts and the bonding in substituted metal carbonyls have been studied by several authors. Thus by assuming a constant σ-donor ability for L, Horrocks et al. [2] through a study of ν(CO) and ν(NO) for the complexes of the type $Co(CO)(NO)L_2$ and $Co(CO)_2(NO)L$ have suggested a spectrochemical series of π-acceptor capacities for the ligands used. Using the CO frequency positions in the spectra of $M(CO)_5L$, $Ni(CO)_3L$ and $Fe(CO)_4L$, Strohmeier and Muller [3] have demonstrated that phosphines when used as ligands in these complexes may be classified according to their π-acceptor capacity. In contrast, Bigorgne [4] has shown that it is possible to duplicate the spectrochemical series of Horrocks by assuming constant π-acceptor participation for the ligands ER_3 when E = P, As, Sb and Bi. This result is possible because of the very good correlation between the sum of the σ_I parameters of the groups R in R_3E and the carbonyl stretching frequencies of $(R_3E)M(CO)_x$.

Since π bonding is generally thought to be negligible in Ni—L linkages [5], it is also possible to correlate the σ parameters and the CO frequencies for the $LNi(CO)_3$ compounds studied in this work. These data are summarized in Table 2. Hammett σ parameters are based on the transmission of inductive effects through the carbon atom but in this case inductive effects are transmitted to the atom E in ER_3 and for this reason a correlation between ν(CO) and Kabachnik [6,7] σ_{HK} parameters is also included. Obviously the latter correlation is only meaningful for phosphine ligands.

Although the differences in CO A_1 fundamental frequencies are small, the following general trends for the σ-donor capacity have been found in all cases for phosphines as well as for arsines and stibines: (1) $C_6H_5 > 4\text{-}FC_6H_4 > 4\text{-}ClC_6H_4 > 3\text{-}FC_6H_4 \geqslant 3\text{-}ClC_6H_4$ and (2) P > As > Sb respectively for the groups R and for the atoms E in R_3E ligands.

Sequence (2) is in complete agreement with those found by Ephstein [8] based on the electron-donor capacities of PPh_3, $AsPh_3$ and $SbPh_3$, and also with the study of the stablity of addition complexes by Stone [9].

The general trend observed for the groups attached to the P, As or Sb atoms seems to be questionable since the introduction of a more electronegative atom or substitution in the *para* position should both result in an enhanced

TABLE 2

CORRELATION BETWEEN THE CHARACTERISTIC CO FREQUENCY AND THE σ-DONOR CAPACITY OF THE LIGAND

R	σ	$\Sigma\sigma$	$\Sigma\sigma_{HK}$	ν(CO)		
				$R_3PNi(CO)_3$	$R_3AsNi(CO)_3$	$R_3SbNi(CO)_3$
C_6H_5	0.000	0.000	−1.443	2069.8	2072.7	2073.8
$4\text{-}FC_6H_4$	0.062	0.186		2072.8	2075.8	2076.3
$4\text{-}ClC_6H_4$	0.227	0.681	−0.876	2073.7	2076.6	2077.3
$3\text{-}FC_6H_4$	0.337	1.011		2075.3	2077.7	2078.2
$3\text{-}ClC_6H_4$	0.373	1.119	−0.657	2076.3	2077.6	2078.5

σ-donating capacity for the ligand. Nevertheless, these anomalies may be explained if it is assumed that the aryl groups attached to the P, As or Sb atom make a mesomeric contribution.

Since a very good correlation is also found between the σ_T parameters and the CO stretching frequencies, it must also be concluded that the ν(CO) shifts in $LNi(CO)_3$ compounds mainly depend on the σ-donating capacity of the ligand. The trends obtained, however, also demonstrate that both the inductive and mesomeric effects in the ring may influence the total σ-donor ability of the ligand as a whole.

III. Metal-ligand bonding in $LCr(CO)_5$ compounds

It has been demonstrated in a previous paper [1] that a correlation between the CO band positions for $LCr(CO)_5$ derivatives and the bonding abilities of the ligand is not particularly meaningful, since a corresponding correlation between the σ_T parameters and the CO frequencies for these compounds resulted in the following sequence for the σ-donating capacity: (3) Sb > P > As, a sequence which is in complete disagreement with that found in the $LNi(CO)_3$ complexes studied here. For this reason it is possible that sequence (3) may suggest some degree of π back-bonding accompanying σ donation in the chromium—ligand bond.

TABLE 3

CO FORCE CONSTANTS FOR $LCr(CO)_5$ COMPOUNDS[a]

L in $LCr(CO)_5$	CO Force constants (mdynes/Å)				
	K_1	K_2	K_c	K_c'	K_t
$(C_6H_5)_3P$	15.46_3	15.82_9	0.2779_0	0.3083_4	0.5862_4
$(4\text{-}FC_6H_4)_3P$	15.64_5	15.84_7	0.2727_2	0.3093_6	0.5820_8
$(3\text{-}FC_6H_4)_3P$	15.68_5	15.87_4	0.2668_0	0.3128_7	0.5796_7
$(4\text{-}ClC_6H_4)_3P$	15.67_0	15.86_4	0.2693_6	0.3095_6	0.5789_2
$(3\text{-}ClC_6H_4)_3P$	15.69_7	15.88_8	0.2654_7	0.3106_3	0.5761_1
$(C_6H_5)_3As$	15.48_4	15.86_0	0.2835_3	0.2990_7	0.5826_0
$(4\text{-}FC_6H_4)_3As$	15.60_4	15.87_8	0.2779_0	0.3024_7	0.5803_7
$(3\text{-}FC_6H_4)_3As$	15.53_7	15.90_5	0.2784_3	0.3035_2	0.5819_5
$(4\text{-}ClC_6H_4)_3As$	15.61_4	15.88_6	0.2763_7	0.3041_5	0.5805_2
$(3\text{-}ClC_6H_4)_3As$	15.62_7	15.90_7	0.2729_3	0.3051_9	0.5781_2
$(C_6H_5)_3Sb$	15.48_4	15.84_9	0.2755_5	0.2926_9	0.5682_4
$(4\text{-}FC_6H_4)_3Sb$	15.67_9	15.87_4	0.2656_2	0.2962_0	0.5618_2
$(3\text{-}FC_6H_4)_3Sb$	15.69_8	15.89_8	0.2672_9	0.2924_0	0.5597_3
$(4\text{-}ClC_6H_4)_3Sb$	15.68_5	15.88_3	0.2762_5	0.2818_9	0.5581_4
$(3\text{-}ClC_6H_4)_3Sb$	15.69_4	15.90_9	0.2705_9	0.2853_6	0.5559_4

[a] For assignments see ref. 1.

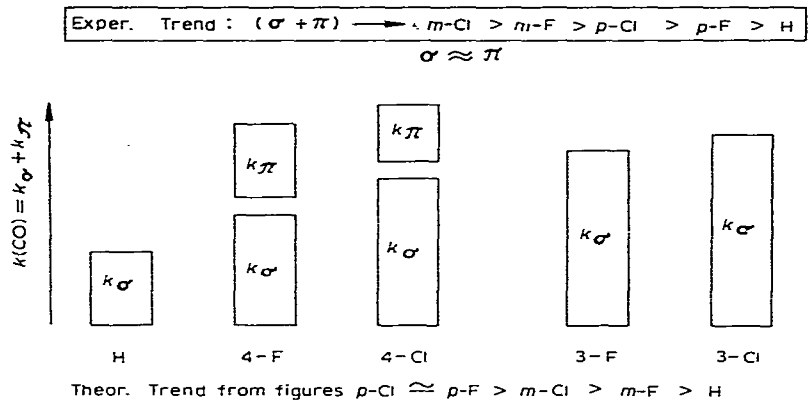


Fig. 1. Comparison of experimental and theoretical CO force constant sequences, assuming nearly equivalent σ- and π-bonding contributions.

A better correlation may exist between the type of bonding and the CO force constants, as the latter are related via interaction force constants with all the CO vibrators in the molecule. A correlation study has therefore been undertaken between the CO force constants and the M—L bonding in $LM(CO)_5$ compounds; the force constants for the $LCr(CO)_5$ derivatives summarized in Table 3 have been calculated using the *CK* secular equations in their exact form and employing an improved method published elsewhere [10].

Since the $A_1(1)$ and E modes are unresolved in the CO stretching region of the spectrum of $(3\text{-}FC_6H_4)_3AsCr(CO)_5$, all the above calculated values are approximate to a certain extent and for this reason this compound will not be considered further. In general, however, a trend is observed in all cases for the CO stretching force constant values in R_3E substituted chromium carbonyls.

For R in $R_3ECr(CO)_5$ the corresponding force constants lead to the sequence (4) $3\text{-}ClC_6H_4 \geqslant 3\text{-}FC_6H_4 > 4\text{-}ClC_6H_4 > 4\text{-}FC_6H_4 > C_6H_5$ for both k_1 and k_2 values. On the other hand, for the same aryl group the k_1 values yield the sequence (5) $Sb \approx P > As$ whereas the k_2 values yield (6) $As \approx Sb > P$. Previously such trends were taken as an indication of the $\sigma + \pi$ bonding ability of the ligands.

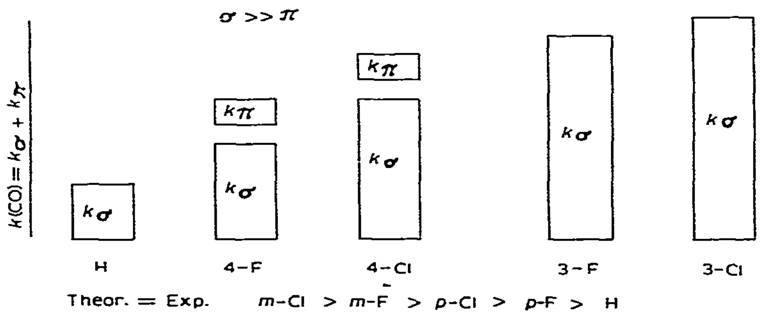
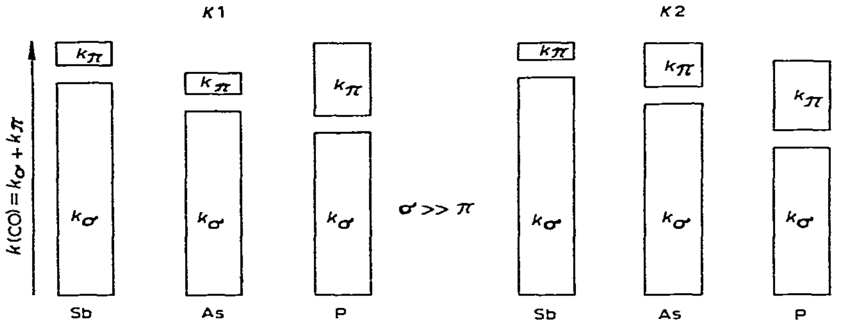


Fig. 2. Comparison of experimental and theoretical CO force constant sequences assuming considerably smaller M—L π bonding.



	K1	K2
Exp. $\sigma+\pi$	Sb ≅ P > As	As ≅ Sb > P
Theor. σ	Sb > As > P	Sb > As > P
Conclusion π	P >> As or Sb (7)	As > Sb (8)

Fig. 3. The M—L σ- and π-bonding contributions in $LCr(CO)_5$ derivatives as derived from CO force constants.

Separation of the σ- and π-bonding contributions in $LM(CO)_5$ has already been achieved by Graham [11]. However, differences in σ and π parameters for the compounds studied here are not so great as those in Graham's series and for this reason will not be analysed further.

However, a consideration of the σ-bonding capacities of the ligands in analogous $LNi(CO)_3$ compounds [1] and the corresponding trend in their CO force constants could lead to a simple pictorial model. Such a model is shown in Fig. 1 and is based on the hypothesis that the contribution of σ- and π-bonding capacities in M—L linkages towards the CO force constants is nearly equivalent and that the π bonding in such linkages should be influenced by mesomeric effects in the aryl groups. The model clearly demonstrates that the observed experimental sequence (4) is not supported by such a hypothesis, but if, on the other hand, a considerably smaller π-bonding contribution towards the CO force constants is assumed the experimental trend is followed as is shown in Fig. 2.

Finally, irrespective of the groups attached to the atoms, the observed force constant sequences (5) and (6) for P, As and Sb may be explained through the use of a similar pictorial model (Fig. 3) again assuming a much lower degree of π bonding in the M—L linkage. In fact the observed sequence (7) and (8) (Fig. 3) for the π contribution towards the CO stretching force constants in M—L linkages is in complete agreement with the σ-donating capacity of the ligand expressed in sequence (2) and closely agrees with the synergic mechanism of the metal—ligand bond.

Hence on the basis of the CO force constants and using a simple pictorial model, it has been shown that for $LCr(CO)_5$ derivatives (i) both σ and π bonding occur in the metal—ligand bonds, (ii) the CO force constants depend principally on the σ-donating abilities of the ligands, (iii) the degree of π bonding in M—L linkages should depend on the mesomeric effects in the aryl groups, and (iv) the metal—ligand bond should be synergic.

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