Proton 3 (Figure 4) in manganese complexes of **3** (isomer A) has a chemical shift at higher field than analogous complexes of **1** reflecting the inductive effect of the *tert*-butyl group. Both sets of complexes have the chemical shifts of proton 3 in the order Cl > Br > I (highest field). Isomers B of 3 have this order reversed. The nmr spectra of complexes of **1** show proton 3 (axial) is at higher field than proton 4 (equatorial). The chloride complex has a chemical shift of 0.48 ppm between protons 3 and 4 which is about the difference usually observed between axial and equatorial protons in cyclohexane systems.[35,36]

Nmr spectra of group VIb complexes of **3** have the chemical shift of proton 1 (axial) at higher field (0.9-1.0 ppm) than proton 2 (equatorial)[2] and similar results are observed for isomers B of the manganese halide complexes. In contrast, the manganese halide complexes of **1** and **3** that have been assigned structure (a) (Figure 4) have chemical shifts for proton 1 at unusually low fields, and this similarity of chemical shifts provides additional support for our assignment of structure (a) to isomers A. As mentioned above, the X-ray diffraction study[33] that showed the Mn-Cl bond is bent toward the chelate ring provides some evidence for an attractive interaction between the halide atom and the chelate ring, which could account for the low-field shifts. However, it is possible that the protons occupy a paramagnetically deshielded region of these metal carbonyl complexes.

Acknowledgments. We wish to thank Mr. R. B. Malcolm for his assistance in solving the ABCD spectra. This work was supported by the National Research Council of Canada in the form of operating grants (to W. R. C. and L. D. H.) and Postdoctoral fellowships (to J. T. P. and G. S.).

Registry No. $ClMn(CO)_3As(CH_3)_2CH_2CH_2As(CH_3)_2$, 41660-26-8; $BrMn(CO)_3As(CH_3)_2CH_2CH_2CH_2As(CH_3)_2$, 51652-94-9; $IMn(CO)_3As(CH_3)_2CH_2CH_2CH_2As(CH_3)_2$, 51652-95-0; $ClMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CH_2As(CH_3)_2$, 51652-96-1; $BrMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CH_2As(CH_3)_2$, 51652-97-2; $IMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CH_2As(CH_3)_2$, 51652-98-3; $ClMn(CO)_3As(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$, 51743-86-3; $BrMn(CO)_3As(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$, 51743-87-4; $IMn(CO)_3As(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$, 51743-88-5; $IMn(CO)_3As(CH_3)_2CD_2CH_2CD_2As(CH_3)_2$, 51652-99-4; $ClMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ (A), 51743-89-6; $BrMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ (A), 51743-90-9; $IMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ (A), 51743-91-0; $ClMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ (B), 51743-92-1; $BrMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ (B), 51743-93-2; $IMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ (B), 51743-94-3.

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Detailed Analysis of the Carbonyl Stretching Vibrations in Axial and Equatorial Substituted Iron Carbonyl Compounds. Absolute Infrared Intensities and Force Constants of the Carbonyl Ligands

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Force constant calculations employing a restricted force field of CO stretching vibrations have been carried out for axially mono- and disubstituted phosphine, phosphite, and carbene and equatorially monosubstituted olefin derivatives of iron pentacarbonyl. The computations were made possible with the aid of frequency data obtained from ^{13}CO photochemically enriched species. For the axially substituted $LFe(CO)_4$ species the force constant for the CO ligand opposite L (phosphines, phosphites, or carbene) was found to be greater than those cis to L by approximately 0.50 mdyn/Å. For the equatorially substituted (olefin)$Fe(CO)_4$ derivatives the two CO groups opposite the olefin ligand exhibited somewhat larger force constants as compared with the two CO ligands trans to one another. The calculated force constants for the equatorially substituted (olefin)$Fe(CO)_4$ species were all significantly larger than the corresponding values in the axially substituted $LFe(CO)_4$ derivatives. Absolute infrared intensities of ν_{CO} were determined and used to calculate characteristic MCO group dipole moment derivatives in these complexes. The results of the intensity studies are discussed in terms of vibrational coupling and geometrical and electronic properties of the CO ligands as well as the substituent ligands. In addition, a combination of ν_{CO} force constants and dipole moment derivatives have been employed in understanding and comparing the electron distributions in the metal carbonyl framework of the two isomeric forms of monosubstituted iron pentacarbonyl derivatives. These studies provide as well some criteria for distinguishing between the two types of infrared spectra commonly observed in the isomeric forms of monosubstituted iron pentacarbonyl species.

Introduction

The measurement of infrared intensities of the CO stretching vibrations along with an appropriate normal-coordinate analysis can lead to assignment of relative dipole moment derivatives, μ'_{MCO}.[3-13] These quantities are very reliable

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indicators of M-CO π bonding. Therefore, from a study of μ'_{MCO} for a series of substituted metal carbonyl compounds it is possible to determine the electronic effect of the substituent on the carbonyl ligands.

We have previously discussed infrared intensities in a few $LM(CO)_4$ (M = Co, Fe) compounds containing axial L ligands,[3] *i.e.*, compounds having C_{3v} symmetry with respect to the $M(CO)_4$ fragment. Presently, we wish to present an extensive compilation and interpretation of absolute infrared intensity data for phosphine-, phosphite-, and carbene-substituted iron carbonyl derivatives of the types $LFe(CO)_4$ (C_{3v}) and $L_2Fe(CO)_3$ (D_{3h}), as well as for (olefin)$Fe(CO)_4$ (C_{2v}) compounds.

In strict C_{3v} symmetry (axially substituted), $LFe(CO)_4$ compounds possess three bands in the ν_{CO} stretching region ($2\ A_1 + E$), whereas in strict C_{2v} symmetry (equatorially substituted), $LFe(CO)_4$ compounds exhibit four infrared bands ($2\ A_1 + B_1 + B_2$). It is quite often the case in complexes involving axially substituted $LFe(CO)_4$ compounds that the E mode ν_{CO} vibration will be split, thereby yielding four bands in the infrared spectra in the ν_{CO} region for these compounds. It therefore becomes difficult to distinguish between axially substituted and equatorially substituted $LFe(CO)_4$ compounds on the basis of the number of bands in the CO stretching region. Analysis of infrared intensities in $LFe(CO)_4$ complexes should greatly aid in distinquishing between the two possible geometries.

In addition force constants in $LFe(CO)_4$ molecules are of considerable interest as reactivity indices[14,15] and as bonding parameters.[16-18] Therefore, ^{13}CO photochemically enriched samples were prepared in order to provide ^{13}CO stretching frequencies for more accurate estimates of the carbon monoxide ligand force constants in these iron carbonyl derivatives. Solvent effects on the CO stretching frequencies and absolute intensities were also investigated.

Experimental Section

Materials. Iron pentacarbonyl was used as purchased from Pressure Chemical Co. The following ligands were gifts of the sources cited and were used as received: $(n\text{-}C_4H_9)_3P$, $(C_6H_5)_3P$, and $(CH_3)_2(C_6H_5)P$ (M & T Chemical Co.); $(CH_3O)_3P$ (Mobil Chemical Co.); $(CH_3O)(C_6H_5)_2P$ (Arapahoe Chemical Co.). Acrylic acid and $(C_6H_5O)_3P$ were obtained from Aldrich Chemicals. ^{13}CO (20% enriched) was purchased from Monsanto Research Corp., Miamisburg, Ohio. Hexane was purified by distillation over CaH_2 and tetrahydrofuran (THF) was distilled over sodium benzophenone dianion under nitrogen.

Preparation of Compounds. The compounds $LFe(CO)_4$ and $L_2Fe(CO)_3$ were all prepared and purified by the method described by Conder and Darensbourg.[19]

^{13}CO Enrichment of $LFe(CO)_4$ Compounds. The apparatus for photochemically enriching the axially substituted $LFe(CO)_4$ samples consisted of a water-jacketed 25-ml Pyrex cell as shown in Figure 1. The ^{13}CO atmosphere was continuously recirculated within the closed system by a variable-speed Masterflex tubing pump (Cole-Parmer Co.). Either a 100- or 450-W Hanovia Mercury lamp was used for irradiation, the higher output lamp being employed for the photochemically more stable species.

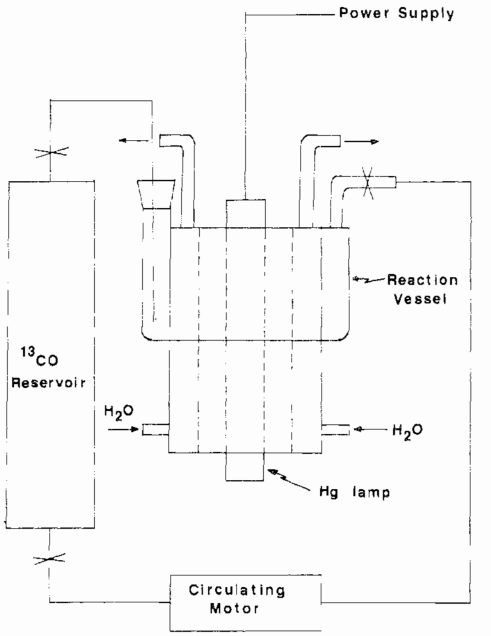

Figure 1. Reaction vessel for ^{13}CO photochemical enrichment studies.

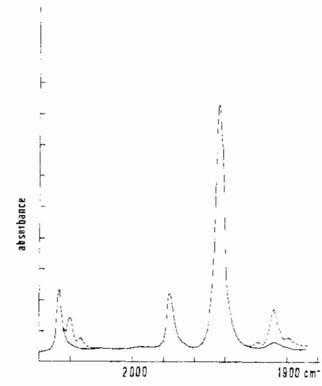

Figure 2. ^{13}CO-enriched spectrum of $(C_6H_5)_3PFe(CO)_4$ in hexane: ——, natural abundance spectrum; - - - -, enriched spectrum.

The course of the enrichment reaction was followed by withdrawing samples with a hypodermic syringe at approximately 5-min time intervals. Infrared spectral measurements were used to follow the extent of enrichment. Figure 2 illustrates a typical ^{13}CO-enriched spectrum of an axially substituted $LFe(CO)_4$ species.

Infrared Spectral Measurements. Ir spectra were recorded on a Perkin-Elmer 521 spectrophotometer. Spectra were calibrated against a water vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. The spectral slit width of the instrument was set at 1.5 cm^{-1} and spectra were measured on an expanded abscissa scale with a scan speed of 15 cm^{-1} min^{-1}.

Sample concentrations were in the range 10^{-3}-10^{-4} *M*. Solutions were prepared by weighing out the solid or liquid samples on a Cahn electrobalance to ±0.01 mg. Linear Beer's law plots were obtained for the ν_{CO} frequencies over the absorbance range studied. One-millimeter and 0.1-mm matched sodium chloride cells, calibrated by the interference fringe method, were used for the measurements in hexane and tetrahydrofuran, respectively.

Spectra for intensity measurements were recorded in absorbance and the areas under the bands were determined with a planimeter. Intensities were determined at a number of concentrations and extrapolated to zero concentration in order to correct for instrumen-

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tal slit width effects. Data were analyzed by the linear least-squares method.

Machine Calculations. Trial force constants for the CO stretching vibrations for the axially substituted LFe(CO)$_4$ species were calculated using a modified Cotton–Kraihanzel approach employing the three observed frequencies (A$_1^{(2)}$, A$_1^{(1)}$, and E). The force constants (k_1, k_2, k_c, and k_c') were calculated assuming a ratio of k_c'/k_c. The ratio was varied between 1.00 and 1.60 in intervals of 0.10. It then becomes a problem of deciding which set of force constants is the correct one out of the several sets generated by this procedure. Dalton, *et al.*,[20] have suggested a procedure for determining the ratio of k_c' to k_c (generally a value of k_c'/k_c of about 1.0-1.1 was employed by these authors[21]) and therefore a procedure for calculating the CO stretching force constants from only the three observed frequencies. We have found that calculations employing the procedure of Dalton, *et al.*,[20] led to a choice of force constants which mispredicts some of the ^{13}CO band positions. In addition the resulting L_{ij} matrix elements suggest too large a coupling between the two A$_1$ symmetry modes. We have found in our work that a value of k_c'/k_c of about 1.40 results in a set of constants which accurately predicts all of the ^{12}CO and ^{13}CO band positions. These calculations were performed with an iterative computer program in which the trial force constants were those calculated using a k_c'/k_c ratio of 1.40. The observed frequencies for all the ^{12}CO species and the observed vibrations for the monosubstituted and, in some cases, disubstituted ^{13}CO species were used as input in these computations. The program, based on the work of Schachtschneider and Snyder,[22] adjusts a set of force constants common to a group of related molecules. Table I shows comparative data for a typical complex, $(C_6H_5)_3PFe(CO)_4$.

It should be noted that the ratio of k_c'/k_c greatly influences the values of the CO stretching force constants k_1 and k_2, with k_1 being more drastically affected. The ^{13}CO bands which the procedure of Dalton, *et al.*,[20] calculates most incorrectly are those corresponding to the monosubstituted axial ^{13}CO molecule. Dalton's procedure calculates the high-frequency band at 2034 cm^{-1} for an axial monosubstituted ^{13}CO molecule. This band is not observed and is indeed some 9 cm^{-1} lower in frequency than the corresponding vibration observed and calculated for the equatorial monosubstituted ^{13}CO molecule (see Table II). This latter vibration should be more affected by ^{13}CO substitution since it is ascribed to predominantly equatorial CO stretching motion. Bor's procedure[23] yields a set of constants which accurately predicts all the ^{13}CO and C^{18}O data which have been observed in $(C_6H_5)_3PFe(CO)_4$ by Noack and Ruch.[24]

Therefore, if one has to resort to force constant calculations in the LFe(CO)$_4$ system in the absence of ^{13}CO or C^{18}O frequency data, a ratio of k_c'/k_c of about 1.40 ± 0.05 would be a much better approximation than that previously proposed.[20]

Force constants for the equatorially substituted (CH$_2$=CHCOOH)-Fe(CO)$_4$ and related molecules were determined as described previously for other C_{2v} M(CO)$_4$ molecules.[13]

Dipole moment derivatives for the A$_1^{(2)}$ vibrations, $\mu'_{\text{MCO}}{}^{A_1^{(2)}}$, were calculated as a function of the angle θ and the ρ parameter using the procedure in ref 3 and employing a computer program which gives printed output as well as plots of these derivatives as a function of θ and ρ. For a given value of ρ, θ was changed by intervals of 0.05°. Illustrative plots of these data are shown in Figure 3.

Machine calculations were performed on an IBM 7044 at the Tulane University Computer Center.

Results and Discussion

Carbonyl Stretching Force Constants. Table II contains the observed and calculated ^{12}CO and ^{13}CO stretching frequencies for LFe(CO)$_4$ species whereas the calculated force constants for these molecules are listed in Table III. ^{13}CO was incorporated into the LFe(CO)$_4$ species by photochemically activating the LFe(CO)$_4$ compounds in hexane solution in the presence of ^{13}CO. It would be expected that there would be no stereospecific enrichment of one CO position over the other since ^{13}C nmr has suggested that axial and equatorial CO positions are undergoing rapid intramolec-

Table I. Comparative CO Stretching Force Constant Data for $(C_6H_5)_3PFe(CO)_4$

Force constants[a]				L_{ij} matrix elements	
k_1	k_2	k_c'	k_c	L_{11}	L_{12}
16.35	15.66	0.37_8	0.32_8[b]	0.27693	0.26297
16.18 ± 0.08	15.75 ± 0.03	0.44_7	0.31_4[c]		
16.15	15.71	0.44_7	0.31_7[d]	0.31741	0.21236

[a] k_1, k_2, k_c', and k_c refer to the axial, equatorial, equatorial-equatorial, and axial–equatorial constants, respectively. [b] Reference 20. [c] G. Bor, *Inorg. Chim. Acta*, 1, 81 (1967). [d] This work.

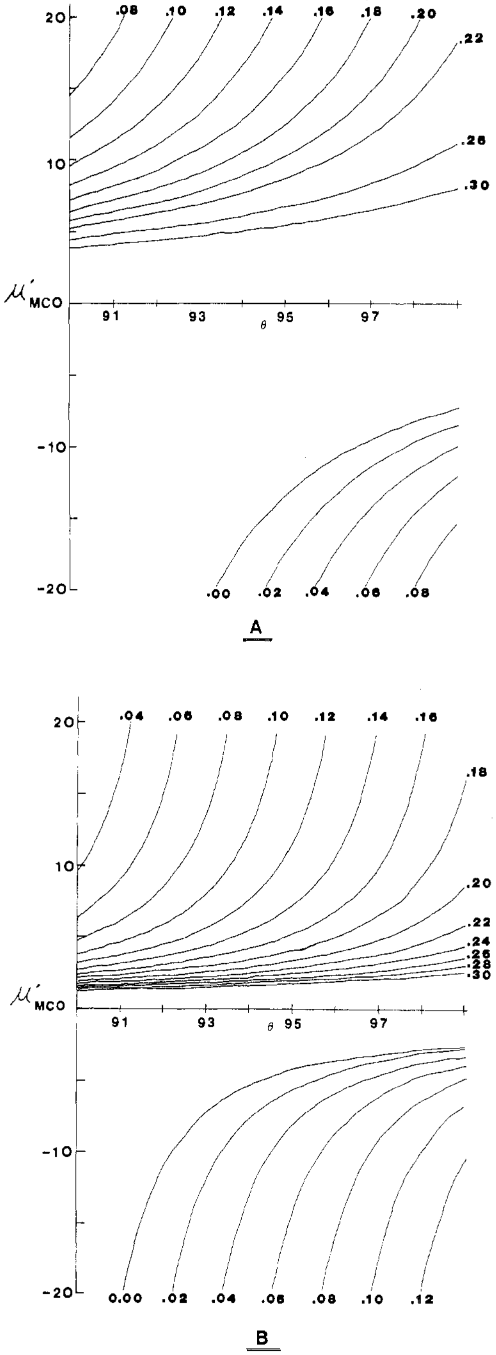

Figure 3. Plots of $\mu'_{\text{MCO}}{}^{(2)}$ *vs.* θ and ρ for axially substituted LFe-(CO)$_4$ complexes: A, $(C_4H_9)_3PFe(CO)_4$; B, $(C_6H_5O)_3PFe(CO)_4$.

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Table II. Observed and Calculated ^{12}CO and ^{13}CO Stretching Vibrations ($\nu(CO)$) in Axially Substituted $LFe(CO)_4$ Compounds[a]

	All ^{12}CO			Mono $^{13}CO(eq)$			Mono $^{13}CO(ax.)$			Di $^{13}CO(eq)$	
	Obsd	Calcd		Obsd	Calcd		Obsd	Calcd		Obsd	Calcd
L = $P(C_6H_5)_3$											
$A_1^{(2)}$	2050.5	2050.3	A'	2042.5	2042.6	$A_1^{(2)}$	*b*	2040.8			
$A_1^{(1)}$	1977.3	1977.3	A'		1974.8	$A_1^{(1)}$		1942.3			
E	1945.2	1944.5	A''	1945.2	1944.5	E	1945.2	1944.5			
			A'	1910.0	1910.8						
L = $P(OCH_3)(C_6H_5)_2$											
$A_1^{(2)}$	2054.0	2056.3	A'	2047.5	2048.4	$A_1^{(2)}$	*b*	2047.1	A'	2041.0	2039.1
$A_1^{(1)}$	1983.0	1982.8	A'		1980.2	$A_1^{(1)}$		1947.4	A'		1975.7
E	1946.7[c]	1947.4	A''	1946.7	1947.4	E	1946.7	1947.4	A'	1923.5	1926.2
			A'	1912.8	1913.9				A''	1904 sh	1904.1
L = $P(OCH_3)_3$											
$A_1^{(2)}$	2062.7 (2058.0)	2063.4	A'	2055.7	2055.9	$A_1^{(2)}$	*b*	2052.9			
$A_1^{(1)}$	1990.7 (1983.3)	1990.5	A'		1987.7	$A_1^{(1)}$		1956.1			
E	1955.5[d] (1946.3)[e]	1954.3	A''	1955.5	1954.3	E	1955.5	1954.3			
			A'	1918.7[d]	1920.5						
L = $P(CH_3)_2(C_6H_5)$											
$A_1^{(2)}$	2050.5	2050.8	A'	2043.0	2043.5	$A_1^{(2)}$	*b*	2040.0			
$A_1^{(1)}$	1977.0	1976.9	A'		1973.9	$A_1^{(1)}$		1943.2			
E	1939.5	1938.2	A''	1939.5	1938.2	E	1939.5	1938.2			
			A'	1904.3	1904.8						
L = $P(n\text{-}C_4H_9)_3$											
$A_1^{(2)}$	2046.7 (2041.7)	2048.3	A'	2040.5	2040.5	$A_1^{(2)}$	*b*	2038.4	A'	2031.5	2032.3
$A_1^{(1)}$	1974.0 (1964.8)	1973.7	A'		1970.9	$A_1^{(1)}$		1939.1	A'		1965.9
E	1935.0 (1930.1)	1933.3	A''	1935.0	1933.3	E	1935.0	1933.3	A'		1912.6
			A'	1900.3	1900.2				A''	1889 sh	1890.2
L = $P(OC_6H_5)_3$											
$A_1^{(2)}$	2064.7 (2063.0)	2066.0	A'	2058.8	2058.7	$A_1^{(2)}$	*b*	2055.0			
$A_1^{(1)}$	1995.5 (1990.3)	1995.2	A'		1992.1	$A_1^{(1)}$		1961.2			
E	1959.5[c] (1958.3)	1957.7	A''	1959.5	1957.7	E	1959.5	1957.7			
			A'	1924.3	1923.8						

[a] Spectra were recorded in hexane solution, except where duplicate frequencies listed in parentheses were determined in tetrahydrofuran. [b] This band is buried beneath the mono-^{13}CO equatorially substituted band. [c] There was only a slight splitting of the E mode vibration in this case. See ref 15. [d] This calculation was carried out using an average frequency for the split E mode. See discussion in text concerning this procedure. [e] There is also a shoulder on this band at approximately 1953 cm^{-1}.

Table III. Calculated Force Constants in Axially Substituted $LFe(CO)_4$ Compounds[a]

L	Force const, mdyn/Å			
	k_1	k_2	k_c'	k_c
$(C_6H_5)_3P$	16.15	15.71	0.44_7	0.31_7
$(CH_3O)(C_6H_5)_2P$	16.23	15.78	0.46_7	0.31_7
$(CH_3O)_3P$	16.40	15.88	0.45_7	0.32_5
$(C_6H_5)(CH_3)_2P$	16.20	15.63	0.46_6	0.33_0
$(n\text{-}C_4H_9)_3P$	16.11	15.58	0.48_9	0.32_5
$(C_6H_5O)_3P$	16.48	15.92	0.45_0	0.32_0

[a] Determined from frequency data obtained in hexane solution.

ular exchange.[25] This is analogous to the rapid intramolecular exchange of CO ligands in $Fe(CO)_5$.[26] A modification of the Berry mechanism[27] which is undoubtedly operative in $Fe(CO)_5$ is probably necessary in light of the presence of large phosphine ligands in the $LFe(CO)_4$ molecules.

However, since the positions of the ^{13}CO vibrational bands for the axially enriched species are all buried beneath bands due to the all ^{12}CO or equatorially enriched ^{13}CO species (see Table II), it has not been possible to observe the presence of the axially substituted ^{13}CO species directly by infrared methods.

The infrared spectra of $LFe(CO)_4$ compounds in the CO stretching region consist of three bands ($2\ A_1 + E$) (Figure 4) for the axially substituted species and four bands ($2\ A_1 + B_1 + B_2$) (Figure 4) for the equatorially substituted species. The symmetry coordinates for these two symmetry species are shown pictorially in Figure 5 along with their designations. In several axially substituted species the E vibrational mode is split into two bands of near-equal intensities. This is particularly true for carbene–iron tetracarbonyl derivatives (Figure 6).[28,29] Figure 7 illustrates the similarity between the four-band pattern in an axially substituted derivative (*e.g.*, $(CH_3O)_3PFe(CO)_4$) as compared with that of an equatorially substituted derivative (*e.g.*, $(CH_2{=}CHCOOH)Fe(CO)_4$).

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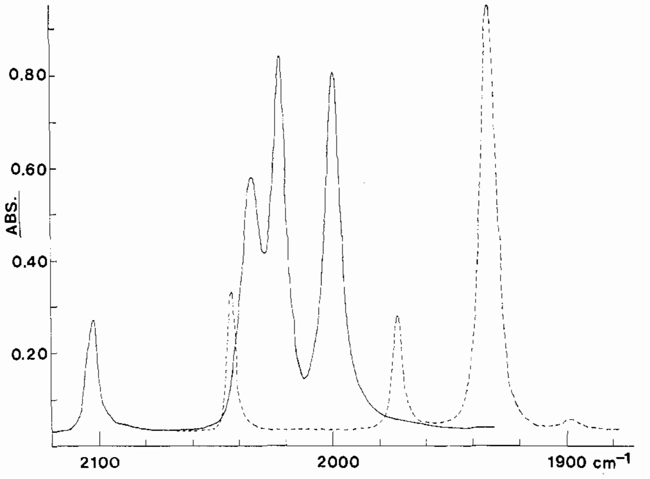

Figure 4. Comparison of the three-band ν(CO) infrared spectrum in a typical axially substituted derivative *vs.* the four-band pattern in an equatorially substituted derivative: ----, $(C_6H_5)_3PFe(CO)_4$; ——, $(CH_2{=}CHCOOH)Fe(CO)_4$.

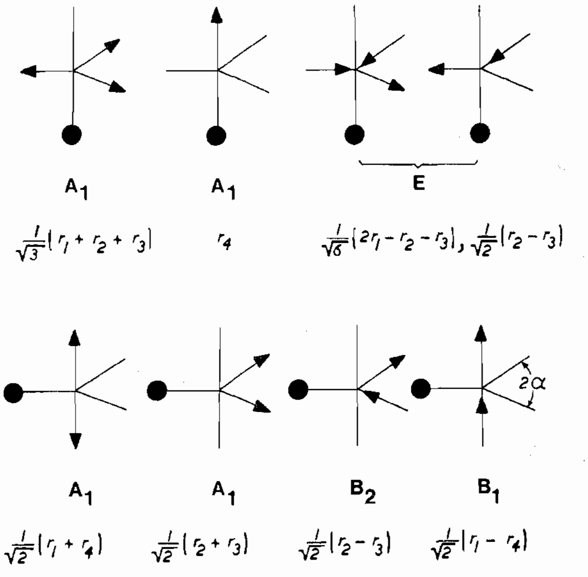

Figure 5. Symmetry coordinates for axial and equatorial monosubstituted derivatives of iron pentacarbonyl.

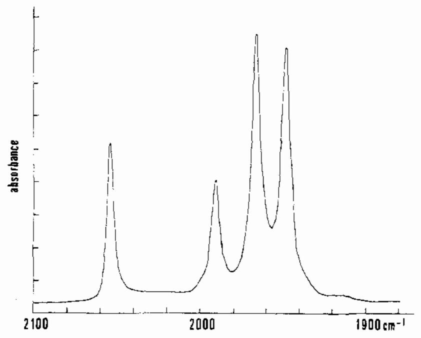

Figure 6. Infrared spectrum in the ν(CO) region of $(C_6H_5)(C_2H_5O)CFe(CO)_4$ in hexane: 2055.0, 1991.0, 1967.0, and 1949.0 cm⁻¹. The calculated force constants using a k_c'/k_c of 1.40 were k_1 = 16.38, k_2 = 15.87, k_c' = 0.405, k_c = 0.289.

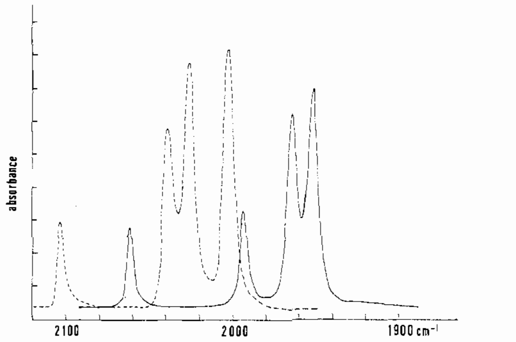

Figure 7. Four-band pattern for ν(CO) in an axial $LFe(CO)_4$ derivative ($L = (CH_3O)_3P$) as compared with that in an equatorial derivative ($L = CH_2{=}CHCOOH$): ——, $(CH_3O)_3PFe(CO)_4$; ----, $(CH_2{=}CHCOOH)Fe(CO)_4$.

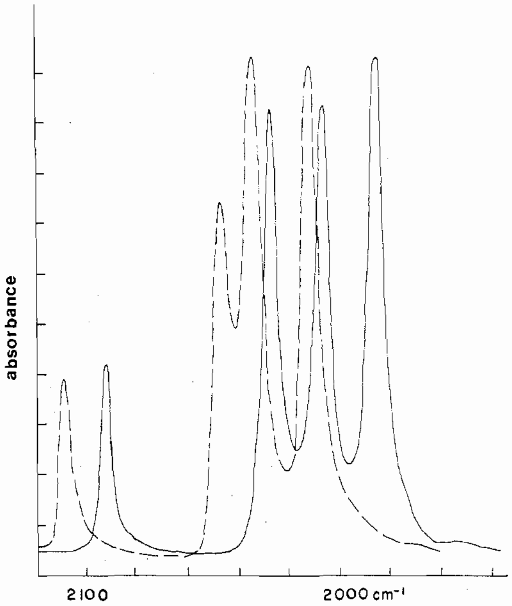

Figure 8. Infrared spectra in ν(CO) of equatorially substituted olefinic iron tetracarbonyl derivatives; ----, $(CH_2{=}CHCOCl)Fe(CO)_4$; ——, $(CH_2{=}CHCONC_5H_{10})Fe(CO)_4$.

Complexes of the latter type have been shown by X-ray crystallographic techniques to be of C_{2v} symmetry with respect to the $Fe(CO)_4$ moiety.[30] Table IV contains our assignment of CO stretching frequencies and calculated force constants in some typical olefinic iron tetracarbonyl species.[31] We have observed the infrared spectra of a variety of these species and they all have similar spectra in the CO stretching region (see Figure 8) with only some slight but distinctive changes in the relative band intensities. As noted in Table IV the assignment for one of these species ($(CH_2{=}CHCOOH)Fe(CO)_4$) was confirmed by the good agreement between observed and calculated ^{13}CO frequency data.

In the axially substituted cases where a split E mode occurred an average value of the two frequencies was employed in calculating the force constants. This is a reasonable approximation since the complexes studied which showed a split E mode exhibited only a slight frequency separation with the lone exception of $(CH_3O)_3PFe(CO)_4$ (Figure 7). An attempt was made to test the effect of this approximation on the calculated force constants and L_{ij} matrix elements for this particular complex. The approach taken was to allow one of the equatorial CO ligands to be slightly different from the other two. This would of course destroy

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(30) (a) C. Pedone and A. Sirigu, *Inorg. Chem.*, 7, 2614 (1968); (b) A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962); (c) D. Bright and O. S. Mills, *J. Chem. Soc. A*, 1979 (1971).

(31) F. W. Grevels, E. Koerner von Gustorf, and G. Bor, Proceedings of the 3rd International Symposium of Inorganica Chimica Acta, Venice, Italy, 1970, No. E4: (b) F. W. Grevels and E. Koerner von Gustorf, *Justus Liebigs Ann. Chem.*, 1821 (1973).

Table IV. Carbonyl Stretching Frequencies and Calculated Force Constants in Equatorially Substituted Olefinic Iron Tetracarbonyl Derivatives

Olefin	ν(CO), cm^{-1}				Force const,[a] mdyn/Å				
	$A_1^{(2)}$	$A_1^{(1)}$	B_2	B_1	k_1	k_2	k_t	$k_{c'}$	k_c
$CH_2=CHCOCl$	2106.0	2043.7	2031.3	2008.6	17.00	16.87	0.57$_4$	0.33$_9$	0.26$_1$
$CH_2=CHCOOH$[b]	2101.4	2037.2	2024.3	2000.6	16.85	16.79	0.62$_7$	0.30$_1$	0.25$_6$
$CH_2=CHCONC_5H_{10}$	2095.0	2029.9	2008.5	1987.8	16.65	16.65	0.69$_8$	0.36$_2$	0.25$_9$
$CH_2=CHCN$[c]	2105.0	2042.5	2029.5	2008.5	16.98	16.87	0.57	0.34	0.26

[a] These are defined as follows: k_1, cis carbonyls, *i.e.*, in the equatorial plane; k_2, trans carbonyls; $k_{c'}$, cis–cis interaction; k_c, trans–cis interaction; k_t, trans–trans interaction. [b] Additional ^{13}CO frequency data were obtained on the monosubstituted (^{13}CO) natural-abundance sample of this derivative at high concentrations. The observed frequencies along with their calculated positions: $^{13}CO_{eq}$: obsd, 2087 and 1972 cm^{-1}; calcd, 2090 and 1971 cm^{-1}. $^{13}CO_{ax}$: obsd, 1988 sh; calcd, 1989 cm^{-1}. [c] Taken from ref 31a.

Table V. Carbonyl Stretching Frequencies and Force Constants for *trans*-$L_2Fe(CO)_3$ Compounds

Compd	ν(CO),[a] cm^{-1}	Force const,[b] mdyn/Å	
		k_2	$k_{c'}$
$[(n\text{-}C_4H_9)_3P]_2Fe(CO)_3$	1872.3 (1865.3)	14.63	0.49
$[(CH_3O)_3P]_2Fe(CO)_3$	1921.3, 1911.8	15.29	0.46
$[(C_6H_5O)_3P]_2Fe(CO)_3$	1933 sh, 1924.8 (1924 br)	15.47	0.45
$[(C_6H_5)_3P]Fe(CO)_3C(OC_2H_5)C_6H_5$	1912.5, 1899.0	15.11	0.45

[a] Frequencies were recorded in hexane solvent, except for those in parentheses which were recorded in THF solvent. [b] The stretching force constants were calculated from the E mode frequency (or the average value of the split E mode frequencies) and the equation $\lambda_E = \mu(k_2 - k_{c'})$, where $k_{c'}$ was taken to be the same as that observed in the corresponding $LFe(CO)_4$ derivatives.

the C_{3v} symmetry of the molecule, reducing it to C_s which leads to the expected four-band pattern (3 A′ + A″) which was observed. In addition this results in an expansion of the CO force field from four independent constants to seven. It was possible with the aid of ^{13}CO isotopically enriched samples to observe a total of eight or nine CO stretching frequencies in $(CH_3O)_3PFe(CO)_4$. The result was to yield a force field which calculated all the observed bands to within ±2 cm^{-1}. The axial force constant was found to be essentially identical with that calculated employing the approximate method ($k_1 = 16.39$), whereas the equatorial constants were found to be slightly different (16.00 and 15.81) as compared with 15.88 obtained by the approximate method.

The slight mixing of the high-frequency component (A′) of the split E mode with the other two A′ modes (previously designated A_1 modes in C_{3v}) is evident by a small decrease in the intensity of this component relative to the A″ component (see Figure 7). Only a small change in the L_{ij} matrix elements which indicate the extent of mixing between the two highest frequency A′ modes (formerly A_1 modes) was observed with a concomitantly small added contribution from the A′ component of the split E mode.

Table V contains the observed CO stretching frequencies and calculated force constants for the axially disubstituted iron tricarbonyl species.

It is seen in Table III that in axially substituted $LFe(CO)_4$ derivatives, k_1, the axial CO stretching force constant, is significantly larger than k_2, the equatorial CO stretching force constant, in all complexes studied, the difference being 0.57–0.42 mdyn/Å. At the same time these constants are all significantly lower than those observed in $Fe(CO)_5$ (CO_{ax}, 16.95; CO_{eq}, 16.59).[32] It is also noteworthy that both k_1 and k_2 decrease as the donor ability increases and/or the π-acceptor ability decreases for the substituted phosphine or phosphite. These results are therefore consistent with our reactivity studies involving nucleophilic attack at the carbonyl carbon atom in $Fe(CO)_5$ and its axially monosubstituted derivatives.[14,15]

An additional decrease in the equatorial carbonyl force constant, k_2, in the trans-disubstituted $L_2Fe(CO)_3$ derivatives as compared with that in $LFe(CO)_4$ derivatives further indicates the increasing donor abilities and/or decreasing π-acceptor abilities of the substituted phosphine, phosphite, or *carbene* ligands as compared with the CO ligand.

Table IV illustrates the effects on the CO force constants of substitution at an equatorial position in $Fe(CO)_5$ with an electron-withdrawing olefinic ligand. The carbonyl ligands in the equatorial plane were found to have force constants, k_1, larger than the corresponding constant in $Fe(CO)_5$ (16.59),[32] with the olefinic ligands containing more strongly electron-withdrawing substituents having significantly larger force constants, *i.e.*, for the $CH_2=CHC(O)Cl$, $CH_2=CHCOOH$, and $CH_2=CHCN$ derivatives. At the same time the trans CO groups have force constants very similar to the corresponding constant in $Fe(CO)_5$ (16.95) but somewhat smaller. These results are in part in contrast to those reported by Dessy, *et al.*,[33] on related olefinic complexes of iron tetracarbonyl. Although these workers found k_1 larger than that in $Fe(CO)_5$, k_2 was calculated to be grossly smaller than k_2 in $Fe(CO)_5$ (*e.g.*, they found in (acrylamide)$Fe(CO)_4$, $k_1 = 17.35$ and $k_2 = 16.05$). This discrepancy is a direct result of their reversal in the relative order of the assignments of the $A_1^{(1)}$ and B_2 vibrational modes, as well as being due to the restrictions these workers imposed on the interaction force constants. We feel however that our assignments are correct as evidenced by the good agreement with ^{13}CO frequency data and arguments based on quantitative relative intensity measurements.

Absolute Infrared Intensities. The measured absolute infrared intensities of the various symmetry-adapted CO stretching vibrations in axially substituted $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ derivatives, as well as for the equatorially substituted $(CH_2=CHCOOH)Fe(CO)_4$ derivative, may be found in Table VI.[34-36] The L_{ij} matrix elements, which

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(32) G. Bor, *Inorg. Chim. Acta*, **3**, 191 (1969).

(33) R. E. Dessy, J. C. Charkoudian, T. P. Abeles, and A. L. Rheingold, *J. Amer. Chem. Soc.*, **92**, 3947 (1970).

(34) The absolute intensities of ν(CO) in $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ (where L = $P(C_2H_5)_3$ and $P(OCH_3)_3$)[35] and the complex $Fe(CO)_4(CH_2=CHCH=CH_2)$[36] have been reported. However, no separation of the intensities of the three low-frequency bands in the latter complex was given. In addition, ref 31b contains absolute intensity data for several equatorially substituted olefinic iron tetracarbonyls.

Table VI. Infrared Intensities of the Carbonyl Stretching Vibrations in $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ Compounds

Compd	Intens × 10^{-4},[a] M^{-1} cm^{-2}			
	$A_1^{(2)}$	$A_1^{(1)}$	E	
$(C_6H_5)_3PFe(CO)_4$[b]	5.98	4.72	26.2	
$(C_6H_5)_2(CH_3O)PFe(CO)_4$	5.53 ± 0.12	4.71 ± 0.08	26.3 ± 0.1	
$(CH_3O)_3PFe(CO)_4$[c]	3.29 ± 0.14	4.92 ± 0.07	28.8 ± 0.2	
	(3.33 ± 0.11)	(5.06 ± 0.17)	(26.0 ± 0.3)	
$(C_6H_5)(CH_3)_2PFe(CO)_4$	4.90 ± 0.24	4.38 ± 0.31	26.1 ± 0.4	
$(n\text{-}C_4H_9)_3PFe(CO)_4$	5.54 ± 0.05	4.32 ± 0.11	26.5 ± 0.4	
	(4.36 ± 0.08)	(4.59 ± 0.09)	(25.3 ± 0.1)	
$(C_6H_5O)_3PFe(CO)_4$[c]	3.66 ± 0.11	4.69 ± 0.12	21.9 ± 0.3	
	(3.21 ± 0.15)	(5.52 ± 0.25)	(22.4 ± 0.4)	
	$A_1^{(2)}$	$A_1^{(1)}$	B_2	B_1
$(CH_2{=}CHCOOH)Fe(CO)_4$	2.60 ± 0.05	6.20 ± 0.1	10.5 ± 0.1	9.50 ± 0.1
		E		
$[(CH_3O)_3P]_2Fe(CO)_3$		32.0 ± 0.2		
$[(n\text{-}C_4H_9)_3P]_2Fe(CO)_3$		27.4 ± 0.3 (26.0 ± 0.1)		
$[(C_6H_5O)_3P]_2Fe(CO)_3$		24.4 ± 0.2 (25.7 ± 0.3)		
$[C_6H_5(OC_2H_5)C](C_6H_5)_3PFe(CO)_3$		23.0 ± 0.4		

[a] Errors listed are standard deviations from a least-squares plot of intensity *vs.* molar concentration. Values listed in parentheses were obtained in tetrahydrofuran, whereas other values were determined in hexane solvent. [b] Data take from ref 3. [c] The E modes in these species are split in hexane solvent and the intensity values listed are for the total intensity of the split modes.

Table VII. Calculated Values of the L_{ij} Matrix Elements for $LFe(CO)_4$ Compounds[a]

L	L_{12}	L_{11}	L	L_{12}	L_{11}
$(C_6H_5)_3P$	0.21236	0.31741	$(C_4H_9)_3P$	0.21448	0.31598
$(CH_3O)_3P$	0.22102	0.31144	$(C_6H_5O)_3P$	0.22689	0.30719
$(CH_3)_2(C_6H_5)P$	0.22467	0.30882	$(C_2H_5O)C_6H_6C–$	0.22801	0.30636
$(CH_3O)(C_6H_5)_2P$	0.20869	0.31983	$(CH_2{=}CHCOOH)$[b]	0.23554	0.30206

[a] $L_{12} = -L_{21}$ and $L_{11} = L_{22}$. [b] This derivative is an equatorially substituted species, whereas all others are axially substituted derivatives.

quantitatively assess the extent of coupling of the two totally symmetrical CO stretching vibrations in the $LFe(CO)_4$ species, were obtained from the above described vibrational analyses and are listed in Table VII.

We will first consider an analysis of the infrared intensities in the axially substituted $LFe(CO)_4$ derivatives. Previously we have developed the equations for the calculation of the MCO group dipole moment derivatives for the three symmetry vibrations ($2\ A_1 + E$) in $LM(CO)_4$ species.[3] These equations are again listed here (eq 1-3) and they take into account the three ways in which the high-frequency (equatorial) $A_1^{(2)}$ vibrational mode gains intensity. The three ways are (a) coupling with the $A_1^{(1)}$ vibrational mode, (b) the C_{ax}-M-C_{eq} angle (θ) deviating from 90°, and (c) electronic migration along the threefold axis during the $A_1^{(2)}$ stretching motion (contained in the ρ parameter). I_1, I_2,

$$I_1 = (\mu'_{MCO}{}^{(1)}L_{11} + \sqrt{3}(\cos\theta + \rho)\mu'_{MCO}{}^{(2)}L_{21})^2 \tag{1}$$

$$I_2 = (\mu'_{MCO}{}^{(1)}L_{12} + \sqrt{3}(\cos\theta + \rho)\mu'_{MCO}{}^{(2)}L_{22})^2 \tag{2}$$

$$I_3 = G_{tt}(\mu'_{MCO}{}^{(3)})^2\ 3\sin^2\theta \tag{3}$$

and I_3 are the measured integrated intensities for the $A_1^{(1)}$, $A_1^{(2)}$, and E CO vibrational modes, respectively; and $\mu'_{MCO}{}^{(1)}$, $\mu'_{MCO}{}^{(2)}$, and $\mu'_{MCO}{}^{(3)}$ are the corresponding group dipole moment derivatives for these symmetry vibrations.

The importance of factor (a) can be adequately examined inasmuch as if coupling of the two A_1 vibrations is the only means by which the $A_1^{(2)}$ mode can gain intensity, the square of the ratio of the L_{ij} matrix elements $(L_{12}/L_{22})^2$ would be directly proportional to the observed ratio of the $A_1^{(2)}$ to $A_1^{(1)}$ intensities. Table VIII lists the calculated (using the restricted CO force field) *vs.* observed $A_1^{(2)}$ to $A_1^{(1)}$ intensity ratios. It is clear from these comparisons that for all the compounds studied mixing of the two A_1 vibrational modes cannot alone account for the observed intensity of the $A_1^{(2)}$ vibration. The observed $A_1^{(2)}$ intensity is noted to be considerably more intense than predicted by coupling alone. It is therefore of utmost importance to give strong considerations to the other two parameters, θ and ρ. Although the main usefulness of the Cotton-Kraihanzel (C-K) force field is to obtain relative values of the primary CO stretching force constants,[37] particularly among molecules of the same symmetry, this approach has as well often been used to calculate eigenvectors for coupled CO stretching vibrations.[38] It is however important at this point to consider whether or not this approach does lead to a reliable estimate of the coupling between CO vibrations of the same symmetry.[39,40] Certainly any corrections to the L_{ij} matrix elements which would result from a more com-

Table VIII. Intensity Ratios Calculated from a Mixing of the A_1 Vibrational Modes Only

Compd	$(L_{12}/L_{22})^2$	$(I_2/I_1)_{obsd}$[a]
$(C_6H_5)_3PFe(CO)_4$	0.448	1.27
$(CH_3O)_3PFe(CO)_4$	0.504	0.669 (0.658)
$(CH_3)_2(C_6H_5)PFe(CO)_4$	0.529	1.12
$(CH_3O)(C_6H_5)_2PFe(CO)_4$	0.425	1.17
$(n\text{-}C_4H_9)_3PFe(CO)_4$	0.461	1.28 (0.950)
$(C_6H_5O)_3PFe(CO)_4$	0.546	0.780 (0.582)
$(C_2H_5O)(C_6H_5)CFe(CO)_4$	0.554	1.03

[a] Intensities observed in hexane solvent; values in parentheses were observed in tetrahydrofuran.

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(35) M. Bigorgne and D. Benlian, *Bull. Soc. Chim. Fr.*, 4100 (1967).

(36) K. Noack, *Helv. Chim. Acta*, 45, 1847 (1962).

(37) F. A. Cotton, *Inorg. Chem.*, 7, 1683 (1968).

(38) S. F. A. Kettle and I. Paul, *Advan. Organometal. Chem.*, 10, 199 (1972), and references contained within.

Table IX. Values of μ'_{MCO}, the MCO Group Dipole Moment Derivatives, in $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ Derivatives[a]

Compd	$\mu'_{\mathrm{MCO}}{}^{(1)}$	$\mu'_{\mathrm{MCO}}{}^{(3)b}$	Compd	$\mu'_{\mathrm{MCO}}{}^{(1)}$	$\mu'_{\mathrm{MCO}}{}^{(3)b}$
$(C_6H_5)_3PFe(CO)_4$	8.29	7.74	$(CH_3O)_3PFe(CO)_4$	7.48	8.11
$(CH_3O)(C_6H_5)_2PFe(CO)_4$	8.12	7.75	$[(CH_3O)_3P]_2Fe(CO)_4$		8.55
$(CH_3)_2(C_6H_5)PFe(CO)_4$	7.84	7.72	$(C_6H_5O)_3PFe(CO)_4$	7.54	7.07
$(n\text{-}C_4H_9)_3PFe(CO)_4$	7.96	7.78	$[(C_6H_5O)_3P]_2Fe(CO)_3$		7.47
$[(n\text{-}C_4H_9)_3P]_2Fe(CO)_3$		7.91	$[(C_6H_5)_3P]Fe(CO)_3C(OC_2H_5)C_6H_5$		7.25

[a] The μ'_{MCO}'s are effective group dipole moment derivatives which involve both MC and CO stretching motions. The units employed here are arbitrary; the intensities are expressed in units of 10^4 M^{-1} cm^{-2}, and L and G terms are based on atomic mass units. These were calculated from intensity determinations in hexane solution. [b] Calculated employing a θ value of 90°; a change in θ of ±2° results in only a 0.13% change in $\mu'_{\mathrm{MCO}}{}^{(3)}$.

plete force field computation would be expected to be approximately constant within a series of closely related compounds (*e.g.*, the frequency difference between the two A_1 CO vibrations in $LFe(CO)_4$ derivatives is approximately a constant, ~73 cm^{-1}). Therefore, although the eigenvectors obtained by a C-K approach could involve sizable errors, trends observed in a series of related compounds should be meaningful.

Equations 1 and 2 lead to a solution for $\mu'_{\mathrm{MCO}}{}^{(1)}$ in terms of the L_{ij} matrix elements and the measured intensities of the two A_1 CO vibrations (eq 4).[41] The calculated values

$$\mu'_{\mathrm{MCO}}{}^{(1)} = \frac{L_{22}\sqrt{I_1} - L_{21}\sqrt{I_2}}{L_{11}L_{22} - L_{12}L_{21}} \tag{4}$$

of $\mu'_{\mathrm{MCO}}{}^{(1)}$ and $\mu'_{\mathrm{MCO}}{}^{(3)}$ as a function of the substituted phosphorus ligands (L) are listed in Table IX. In order to test the effect of significantly changing the L_{ij} matrix elements on the calculated values of $\mu'_{\mathrm{MCO}}{}^{(1)}$ we have varied the ratio L_{12}/L_{11} in the two complexes where $L = P(OCH_3)_3$ and $P(n\text{-}C_4H_9)_3$ by ±15%. Due to the near equality of I_1 and I_2 in $LFe(CO)_4$ derivatives, this has little effect on the computed values of $\mu'_{\mathrm{MCO}}{}^{(1)}$ (variations of ±0.1 were observed). Therefore, we conclude that in these axially substituted $LFe(CO)_4$ derivatives, $\mu'_{\mathrm{MCO}}{}^{(1)}$ values are not extremely sensitive to sizable variations in the L_{ij} matrix elements employed.

The dipole moment derivatives for the $A_1{}^{(2)}$ vibration, $\mu'_{\mathrm{MCO}}{}^{(2)}$, were calculated as a function of the remaining two parameters, θ and ρ, where θ was varied from 81 to 99° and ρ from 0 to 0.3. These computations were carried out by solving eq 1 or 2 for $\mu_{\mathrm{MCO}}{}^{(2)}$ as a function of θ and ρ employing the previously determined L_{ij} matrix elements, intensities (I_1 and I_2), and $\mu'_{\mathrm{MCO}}{}^{(1)}$. Graphical analysis was achieved employing a Calcomp routine. Illustrative plots showing the two classes of dependence observed, one for phosphine and one for phosphite derivatives, are seen in Figure 3.

Fortunately there are now available several X-ray crystallographic determinations of axially substituted $LFe(CO)_4$ complexes. For $L = PH(C_6H_5)_2$,[42] asp,[43] $As(C_6H_5)_3$,[44] and $Sb(C_6H_5)_3$,[44] the average C_{ax}-Fe-C_{eq} angles (θ) are all very close to 90°; 91 ± 1° being a representative range. Therefore, since θ appears to vary only slightly if at all with substituent (L) it should be possible from plots such as those seen in Figure 3 to arrive at reasonable values for ρ assuming $\mu'_{\mathrm{MCO}}{}^{(2)}$, the group dipole moment change along the equatorial MCO bond axis during the A_1 vibration, to be similar to the change during the E vibration, $\mu'_{\mathrm{MCO}}{}^{(3)}$.

Infrared intensities of the CO vibrations in metal carbonyls have been shown to be largely determined by π-electronic charge migration in the M–C–O grouping during the CO stretch and thus in turn depend on the demand made for π-electronic change during the various CO symmetry vibrations.[6] From electron demand arguments $\mu'_{\mathrm{MCO}}{}^{(2)}$ should be somewhat smaller than $\mu'_{\mathrm{MCO}}{}^{(3)}$ since there is no net demand made for π-electron density during the E vibrational mode whereas there is a sizable demand made during the A_1 vibration.[3] Nevertheless, $\mu'_{\mathrm{MCO}}{}^{(2)}$ is not expected to be grossly different from $\mu'_{\mathrm{MCO}}{}^{(3)}$.

Using these approximations we arrive at the values listed in Table X for the ρ parameters as a function of the substituent L. As noted in Table IX ρ is considerably larger for phosphine derivatives (~0.18) as compared with phosphite derivatives (~0.07). Physically, ρ times $\mu'_{\mathrm{MCO}}{}^{(2)}$ represents the dipole moment created by electron migration along the threefold axis which arises from π-electron motion in the metal-phosphorus bond. This contribution should be highly dependent on the presence of π-electron density in the metal–phosphorus bond and the ability of the phosphorus ligand to hold onto its electron density, as well as on the demand made for these electrons during the CO stretching vibrations. It therefore follows that the metal–phosphorus π bond is indeed populated and that phosphine ligands are more willing to donate π-electron density to the iron atom upon demand made by the carbonyl ligands than are phosphite ligands. This latter result is undoubtedly due to the greater electron-withdrawing properties of phosphite ligands as compared with phosphine ligands. A similar effect has previously been noted for strongly electron-withdrawing substituents on silicon derivatives of cobalt carbonyls.[3] Again it is important to note the effect of significant errors in the L_{ij} matrix elements on these calculations. As might be anticipated ρ is fairly sensitive to changes in the degree of coupling in the two A_1 vibrations. For example, changes in the ratio L_{12}/L_{11} of ±15% result in variations in ρ values in the complexes where $L = P(OCH_3)_3$ and $(n\text{-}C_4H_9)_3P$ between 0.00–0.10 and 0.12–0.24, respectively. Therefore, although the exact magnitude of the moment produced along the metal–phosphorus bond when the CO groups

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(39) We have not attempted to carry out an extensive vibrational analysis in $LFe(CO)_4$ derivatives due to a lack of experimental vibrational data. However, in group VIb $M(CO)_5L$ derivatives we have transferred the necessary force field from the Jones, *et al.*,[40] calculations and carried out a more complete analysis of these systems in order to note the effect on the L_{ij} matrix elements. These matrix elements were indeed somewhat different from those obtained using the C-K approach and led to variation in the calculated intensity ratio of as much as 10%. In addition, a referee has pointed out that calculations in his laboratory have shown that the intensities calculated from L matrix elements are very different for the C-K approximation compared to the complete vibrational analysis.

(40) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, 8, 2349 (1969).

(41) As previously noted[3] the signs of $I_1{}^{1/2}$ and $I_2{}^{1/2}$ are both taken as being positive.

(42) B. T. Kilbourn, U. A. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969).

(43) F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. A*, 442 (1972); asp = 1-(dimethylarsino)-2-(diphenylphosphino)tetrafluorocyclobutene.

(44) J. J. Legendre, C. Girard, and M. Huber, *Bull. Soc. Chim. Fr.*, 1998 (1971).

Table X. Approximate Values of the ρ Parameters and Net Dipole Moment Changes along the C_3 Axis in $LFe(CO)_4$ Compounds

L	ρ^a	$\rho\mu'_{\mathrm{MCO}}{}^{(2)b}$	L	ρ^a	$\rho\mu'_{\mathrm{MCO}}{}^{(2)b}$
$(C_6H_5)_3P$	0.18 ± 0.02	1.4	$(C_6H_5)(CH_3)_2P$	0.14 ± 0.02	1.1
$(C_6H_5)_2(CH_3O)P$	0.18 ± 0.02	1.4	$(n\text{-}C_4H_9)_3P$	0.18 ± 0.02	1.4
$(CH_3O)_3P$	0.06 ± 0.02	0.49	$(C_6H_5O)_3P$	0.08 ± 0.02	0.57

[a] These values cover the expected range in θ of 91.5 ± 1.5°. [b] $\mu'_{\mathrm{MCO}}{}^{(2)}$ is taken here to be identical with $\mu'_{\mathrm{MCO}}{}^{(3)}$; therefore, these values are slightly higher than the true values.

stretch may not be as listed in Table X, the contribution of the ρ factor to the intensity of the $A_1{}^{(2)}$ vibration is nonetheless observable and trends in a series of related complexes should be meaningful.

Alternatively, an estimate of $\rho\,\mu'_{\mathrm{MCO}}{}^{(2)}$ is possible from a comparison of the *total* A_1 intensity to the E mode intensity. Equation 5 is derived from the ratio of the sum of eq 1

$$\frac{I_1 + I_2}{I_3} = \frac{(\mu'_{\mathrm{MCO}}{}^{(1)})^2 + 3(\cos\theta + \rho)^2(\mu'_{\mathrm{MCO}}{}^{(2)})^2}{(\mu'_{\mathrm{MCO}}{}^{(3)})^2(3\sin^2\theta)} \tag{5}$$

and 2 to eq 3. From the calculated values of $\mu'_{\mathrm{MCO}}{}^{(1)}$, $\mu'_{\mathrm{MCO}}{}^{(3)}$, the ratio of the measured intensities, and a value for θ in the range 91 ± 1°, we can arrive at an estimate for $\rho\mu'_{\mathrm{MCO}}{}^{(2)}$ which is in good agreement with that determined above; *e.g.*, for $(n\text{-}C_4H_9)_3PFe(CO)_4$ and $(C_6H_5O)_3PFe(CO)_4$, $(\cos\theta + \rho)\mu'_{\mathrm{MCO}}{}^{(2)}$ equals 1.18 and 0.357, respectively. Since $\cos\theta$ is negative and of the order of magnitude of 0.01-0.03, $\rho\mu'_{\mathrm{MCO}}{}^{(2)}$ would be very similar to the 1.4 and 0.57 values listed in Table X.

Therefore the perturbing effect of L on the two A_1 vibrational modes can arise from a direct vibronic charge transfer from L to CO during the vibration. This effect is self-contained in our definition of $\mu'_{\mathrm{MCO}}{}^{(1)}$ as evidenced by an increase in the magnitudes of these values over the corresponding E mode derivatives $\mu'_{\mathrm{MCO}}{}^{(3)}$ (Table IX), thereby overcoming the electron demand effect which tends to lower $\mu'_{\mathrm{MCO}}{}^{(1)}$ relative to $\mu'_{(\mathrm{MCO}}{}^{(3)}$. On the other hand the perturbing electronic effect of L on the E mode intensity, which cannot be vibronic due to the polarization of the E mode vibration, can be noted from a comparison of $\mu'_{\mathrm{MCO}}{}^{(3)}$ in $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ derivatives (Table IX). The increase in $\mu'_{\mathrm{MCO}}{}^{(3)}$ with further substitution by L (generally on the order of 4-11% in the observed intensity values) illustrates the net electron-donating effect of phosphine and phosphite ligands as compared with that of the CO ligand. This effect shows up as well in an increase in the magnitude of the ^{57}Fe quadruple coupling parameters, $|\Delta E_q|$, in going from $LFe(CO)_4$ to *trans*-$L_2Fe(CO)_3$.[17] The fact that $\mu'_{\mathrm{MCO}}{}^{(3)}$ increases upon substitution of CO in $LFe(CO)_4$ by an additional L ligand indicates that the Fe-CO π bonding has slightly increased when the axial CO ligand is replaced by phosphines or phosphites.[45,46]

We have begun some initial work on the effects of solvent on the intensities of the CO vibrations in axially substituted iron carbonyl derivatives. The results indicate that the general conclusions reached concerning infrared intensities in hexane solution hold true in tetrahydrofuran solution as well, although there were noticed some small differences in the relative intensities of the two A_1 vibrations. An explanation of this phenomenon will have to await more extensive intensities measurements in a variety of solvents.

We wish to turn our attention to equatorially substituted $LFe(CO)_4$ derivatives. Recently we published a detailed explanation of intensity measurements in octahedral $L_2M(CO)_4$ derivatives in which the $-M(CO)_4$ moiety is ideally of C_{2v} symmetry.[13] Basically, equatorially substituted $LFe(CO)_4$ derivatives may be analyzed in an identical manner; however, there are some subtle geometrical differences in the two systems which affect the relative intensities of the four CO stretching vibrations. The equations which we have previously developed for this type system are shown below (eq 6-9), where 2α describes the angle between the CO groups

$$I_{B_1} = 2G_{tt}(\mu'_{\mathrm{MCO}}{}^{B_1})^2 \tag{6}$$

$$I_{B_2} = 2G_{tt}(\sin^2\alpha)(\mu'_{\mathrm{MCO}}{}^{B_2})^2 \tag{7}$$

$$I_{A_1{}^{(2)}} = (\sqrt{2}\mu'_{\mathrm{MCO}}{}^{A_1{}^{(2)}}L_{11} + \sqrt{2}(\cos\alpha)\mu'_{\mathrm{MCO}}{}^{A_1{}^{(1)}}L_{12})^2 \tag{8}$$

$$I_{A_1{}^{(1)}} = (\sqrt{2}\mu'_{\mathrm{MCO}}{}^{A_1{}^{(2)}}L_{21} + \sqrt{2}(\cos\alpha)\mu'_{\mathrm{MCO}}{}^{A_1{}^{(1)}}L_{22})^2 \tag{9}$$

in the equatorial plane (Figure 5). It should again be noted here that although $\mu'_{\mathrm{MCO}}{}^{A_1{}^{(1)}}$, $\mu'_{\mathrm{MCO}}{}^{B_1}$, and $\mu'_{\mathrm{MCO}}{}^{B_2}$ involve a dipole moment change along the M-CO bond axis, $\mu'_{\mathrm{MCO}}{}^{A_1{}^{(2)}}$ represents a dipole moment derivative created by electronic charge motion perpendicular to the bond axis, of the two trans carbonyl ligands.

In the case of the octahedral $L_2M(CO)_4$ derivatives the angle 2α is always very nearly 90°, whereas in the equatorially substituted $LFe(CO)_4$ complexes, which are described as trigonal-bipyramidal species, this angle is ideally 120°. This opening of the OC-Fe-CO angle should result in an increase in the relative intensity of the B_2 vibration to the $A_1{}^{(1)}$ vibration, since these intensities are proportional to the sine and cosine of α, respectively. In equatorially substituted olefinic iron tetracarbonyl molecules where crystal structure data are available (L = fumaric acid,[30a] acrylonitrile,[30b] and tetraphenylbutatriene)[30c] 2α ranges between 100 and 120°, with 100-110° being a more representative span. In addition the angle 2θ between the two trans CO ligands can deviate from 180° by as much as 12°, *e.g.*, in (tetraphenylbutatriene)$Fe(CO)_4$. This latter factor would however only affect the calculated value of $\mu'_{\mathrm{MCO}}{}^{B_1}$ by about 1%.[47]

As shown in eq 8, the $A_1{}^{(2)}$ vibration which involves stretching of trans CO ligands can gain intensity by coupling with the $A_1{}^{(1)}$ vibration. Table VII contains the L_{ij} matrix elements for this mixing in the species $(CH_2{=}CHCOOH)Fe(CO)_4$. On the basis of mixing alone the ratio $I_{A_1{}^{(2)}}/I_{A_1{}^{(1)}}$ is expected to be 0.608. The observed ratio of A_1 intensi-

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(45) The measured intensity of the carbene derivative *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$ is noticeably low relative to the other disubstituted derivatives; *e.g.*, the E mode intensity has decreased by about 12% in going from $(C_6H_5)_3PFe(CO)_4$ to *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$. This would imply that the M-CO π bonding has decreased significantly on replacement of CO by a carbene ligand. At the same time the k_2 value (Table V) (which reflects the CO ligand's σ- as well as π-bonding scheme with the metal) decreases upon carbene formation. Together these two observations would indicate, although somewhat tenuously since data are available for only one complex, that the CO ligands are behaving in this case as poorer π acceptors as well as poorer σ donors as compared with those in $(C_6H_5)_3PFe(CO)_4$. This is probably a result of the carbene ligand's strong σ-donor capacity coupled with its π-acceptor ability. Further evidence of this effect has been noted in the unique labilizing properties of phosphorus ligands by carbene ligands in these complexes.[29,46]

(46) D. J. Darensbourg and H. L. Conder, *Inorg. Chem.*, 13, 374 (1974).

ties is 0.419 (Table VI). Although absolute infrared intensity data have only been obtained for $(CH_2{=}CHCOOH)Fe(CO)_4$, we have observed the relative A_1 intensities in a variety of (olefin)$Fe(CO)_4$ species (see Figures 7 and 8).[48] All of these species have an observed $I_{A_1^{(2)}}/I_{A_1^{(1)}}$ ratio which is very similar, around 0.45.[49-52] Therefore, unlike the axially substituted iron tetracarbonyl derivatives, the observed $A_1^{(2)}$ to $A_1^{(1)}$ intensity ratio is less than that computed from coupling only. The values of $\mu'_{MCO}{}^{A_1^{(1)}}$ and $\mu'_{MCO}{}^{A_1^{(2)}}$ can be calculated from eq 10 and 11 which were derived

$$\mu'_{MCO}{}^{A_1^{(1)}} = \frac{\sqrt{I_{A_1^{(2)}}}L_{21} - \sqrt{I_{A_1^{(1)}}}L_{11}}{(2\cos\alpha)(L_{21}L_{12} - L_{11}L_{22})} \qquad (10)$$

$$\mu'_{MCO}{}^{A_1^{(2)}} = \frac{\sqrt{I_{A_1^{(2)}}}L_{22} - \sqrt{I_{A_1^{(1)}}}L_{12}}{2(L_{11}L_{22} - L_{21}L_{12})} \qquad (11)$$

from eq 8 and 9.[53] Due to the uncertainty in 2α we have calculated $\mu'_{MCO}{}^{A_1^{(1)}}$ and $\mu'_{MCO}{}^{B_2}$ as functions of α from 50 to 60°. Table XI lists the calculated group symmetry dipole moment derivatives in $(CH_2{=}CHCOOH)Fe(CO)_4$.

Figures 7 and 8 illustrate the effect on the relative intensities of the $A_1^{(1)}$ and B_2 vibrational modes of bulky substituents on the olefinic ligand. Olefinic ligands having large steric requirements should lead to a closing of the angle 2α between CO ligands in the equatorial plane.[54] This should in turn lead to an increase in the relative intensity of the $A_1^{(1)}$ CO stretching mode to the B_2 mode. As shown in Figure 8 for the sterically more demanding amide ligand $CH_2{=}CHC(O)NC_5H_{10}$, the $A_1^{(1)}$ vibration has greatly increased in intensity over that of the B_2 vibration. A small decrease in α can alter the intensity ratio of these two vibrational modes drastically; *e.g.*, if α decreases by only 5° from 55 to 50°, the ratio changes by 44%.

The sizable enhancement of $\mu'_{MCO}{}^{A_1^{(1)}}$ and $\mu'_{MCO}{}^{B_2}$ over $\mu'_{MCO}{}^{B_1}$ is due to a vibronic charge transfer from the olefin ligand to the CO ligands transmitted through the metal during the $A_1^{(1)}$ and B_2 vibrations. This vibronic contribution is not possible during the B_1 motion since the vibration is polarized perpendicular to this contributing factor. Since this effect is expected to be a function of the demand made for electron density during the vibration, the $\mu'_{MCO}{}^{A_1^{(1)}}$ is expected to be greater than $\mu'_{MCO}{}^{B_2}$ as is observed. Bor has also reported in complexes of this type that the dipole moment derivative for the CO ligands in the equatorial plane is about 1.3-1.4 times greater than that for the trans CO ligands.[31]

Table XI. Values of μ'_{MCO}, the MCO Group Dipole Moment Derivatives, in $(CH_2{=}CHCOOH)Fe(CO)_4$

$\mu'_{MCO}{}^{A_1^{(1)}}$ [a]	$\mu'_{MCO}{}^{B_2}$ [a]	$\mu'_{MCO}{}^{B_1}$	$\mu'_{MCO}{}^{A_1^{(2)}}$
8.49	7.83	5.71	−0.482
9.51	7.32		
10.91	6.93		

[a] These were computed for α = 50, 55, and 60°, in that order.

The fact that $\mu'_{MCO}{}^{A_1^{(2)}}$ is calculated to be −0.482 follows from the observation that the intensity ratio of the $A_1^{(2)}$ to $A_1^{(1)}$ vibrations is less than anticipated *via* the coupling mechanism alone. However, at this time we do not have an explanation for why this should be so. It is possible that this is indeed due to the procedure we use in obtaining the eigenvectors for the coupled CO vibrations. During the $A_1^{(2)}$ vibration the greatest demand is made upon the metal for π-electron density, since all four CO ligands are stretching simultaneously. Physically the negative $\mu'_{MCO}{}^{A_1^{(2)}}$ value would imply that during the $A_1^{(2)}$ vibration there is a dipole moment change in the direction of the olefinic ligand in (olefin)$Fe(CO)_4$ compounds. At the same time in the $A_1^{(1)}$ and B_2 vibrations the flow of electronic charge from the olefin is in the positive direction, *i.e.*, toward the CO ligands. We are presently carrying out intensity studies on (norbornadiene)$M(CO)_4$ (M = Cr, Mo, W) species in order to see if this is a general phenomenon.

It is important to note that $\mu'_{MCO}{}^{B_1}$ (5.71) in $(CH_2{=}CHCOOH)Fe(CO)_4$ is considerably smaller than a comparable derivative (absence of vibronic contribution) $\mu'_{MCO}{}^{E}$ (~7.75) in the axially substituted phosphine- or phosphite-iron tetracarbonyl species. Therefore, the much larger k_2 value in $(CH_2{=}CHCOOH)Fe(CO)_4$ (16.79) as compared with a k_2 value in a typical axially substituted complex $(C_6H_5)_3PFe(CO)_4$ (15.71) does indeed reflect a much greater Fe-CO π-bond population in these axially substituted iron carbonyl derivatives as compared with olefinic equatorially substituted derivatives.

Unfortunately, it is not possible to make a comparison of μ'_{MCO} values in the two isomeric forms in the absence of changes in the electronic properties of the substituted ligand since pure isomers of axially and equatorially substituted iron tetracarbonyl complexes containing identical ligands are not available. However, we are currently investigating the infrared intensities of ν(CO) in complexes of the type (diphos)$Fe(CO)_3$,[55] which presumably contain both equatorial and axial phosphine ligands, to assess further this electronic effect.

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Registry No. $(C_6H_5)_3PFe(CO)_4$, 35679-07-3; $(CH_3O)(C_6H_5)_2$-

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[47] Deviations in the angle 2θ can affect the intensity of the $A_1^{(2)}$ vibration as well. However, for a value of 2θ of 168°, the contribution to the $A_1^{(2)}$ intensity is only about 4% of its observed value. This computation was made employing the equation $I_{A_1^{(2)}} = 2G_{tt}(\cos^2\theta)(\mu'_{MCO})^2$, where μ'_{MCO} is the derivative along the M-C-O bond axis and its value is assumed to be similar to $\mu'_{MCO}{}^{B_1}$. There is a misprint of this equation in our previous publication; however, the computations made at that time were indeed done correctly.[13]

[48] Most amide and other olefinic derivatives that are stable enough for intensity measurements tend to be insoluble in hydrocarbon solvents and thereby made the determination of infrared intensities of the quality needed here impossible. Nevertheless, the spectra of the amide species in hexane are possible when the complexes are prepared *in situ* from the highly soluble $(CH_2{=}CHCOCl)Fe(CO)_4$ derivative and amines.[16] In addition to that shown in Figure 8, a large variety of amide derivatives with very similar spectra have been examined.

[49] In the equatorial $PF_3Fe(CO)_4$ derivative, which exists in the presence of the axial $PF_3Fe(CO)_4$ derivative, the relative $A_1^{(2)}$ to $A_1^{(1)}$ intensity is also ~0.47.[50-52] This seemingly general observation further substantiates our assignment of the carbene derivatives of iron tetracarbonyl as axial derivatives (the observed relative $A_1^{(2)}$ to $A_1^{(1)}$ intensity was 1.03 (Table VIII)).

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PFe(CO)$_4$, 51743-95-4; (CH$_3$O)$_3$PFe(CO)$_4$, 51743-96-5; (C$_6$H$_5$)(CH$_3$)$_2$PFe(CO)$_4$, 51743-97-6; (n-C$_4$H$_9$)$_3$PFe(CO)$_4$, 18474-82-3; (C$_6$H$_5$O)$_3$PFe(CO)$_4$, 51653-00-0; (CH$_2$=CHCOCl)Fe(CO)$_4$, 51743-98-7; (CH$_2$=CHCOOH)Fe(CO)$_4$, 51743-99-8; (CH$_2$=CHCONC$_5$H$_{10}$)Fe(CO)$_4$, 51744-00-4; (CH$_2$=CHCN)Fe(CO)$_4$, 51744-01-5; [(n-C$_4$H$_9$)$_3$P]$_2$Fe(CO)$_3$, 51653-01-1; [(CH$_3$O)$_3$P]$_2$Fe(CO)$_3$, 19457-84-2; [(C$_6$H$_5$O)$_3$P]$_2$Fe(CO)$_3$, 20516-74-9; [C$_6$H$_5$(OC$_2$H$_5$)C](C$_6$H$_5$)$_3$PFe(CO)$_3$, 42947-52-4.

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Studies on Interactions of Isocyanides with Transition Metal Complexes. X.[1] Preparation and Reactions of Alkyliron Complexes Containing Isocyanide[2]

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Reactions of π-C$_5$H$_5$Fe(CO)(CNR')X (R' = C$_6$H$_{11}$, (CH$_3$)$_3$C, PhCH$_2$; X = Cl, I) with p-YC$_6$H$_4$MgCl (Y = H, Cl) give the corresponding benzyl derivative π-C$_5$H$_5$Fe(CO)(CNR')CH$_2$C$_6$H$_4$Y-p whereas reactions with other Grignard reagents (*e.g.*, CH$_3$MgI, i-C$_3$H$_7$MgBr, PhMgBr) lead to decomposition. When the latter reactions are run in the presence of CO, π-C$_5$H$_5$-Fe(CO)(CNR')COR complexes (R = CH$_3$, i-C$_3$H$_7$, Ph, p-ClC$_6$H$_4$) are obtained. The former reactions under comparable conditions give both benzyl and phenylacetyl derivatives. The mechanism of these reactions is discussed. Reactions of π-C$_5$H$_5$Fe(CO)(CNR')R (R = PhCH$_2$, p-ClC$_6$H$_4$CH$_2$, p-ClC$_6$H$_4$; R' = C$_6$H$_{11}$, PhCH$_2$) with CO undergo preferentially an isocyanide insertion to afford the corresponding iminoacyl complexes π-C$_5$H$_5$Fe(CO)$_2$[C(R)=NR']. The mass spectra of the isocyanide complexes and the iminoacyl ones are also investigated.

Introduction

Reactions of carbonyl-π-cyclopentadienylalkylmetal complexes π-C$_5$H$_5$M(CO)$_n$R (M = Fe, n = 2; M = Mo, n = 3) with isocyanides proceed with either carbonyl or isocyanide insertion into the metal–carbon σ bonds.[3-5] In some cases the competitive insertion proceeds to give the corresponding metal-acyl and -iminoacyl complexes. It is of particular interest to know whether CO or R'NC is inserted preferentially in some alkylmetal complexes containing both CO and R'NC ligands, when reacted with Lewis bases. Reported here in detail is an extensive investigation on the syntheses and the reactions of carbonyl(isocyanide)-π-cyclopentadienylalkyliron complexes.

Experimental Section

General Procedures and Physical Measurements. All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Yanagimoto Model MP-S2 and a Mitamura capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer or on a Shimazu IR-27G spectrophotometer. Proton magnetic resonance spectra were obtained on JEOL C-60, JEOL C-50HL, and Varian HA-100B spectrometers, using tetramethylsilane as a reference. The mass spectra were measured on a Nippondenshi Type JPS-1S mass spectrometer with a direct-inlet system. The photochemical reactions were carried out with a Usio-Denki 450-W high-pressure mercury lamp (Type UV-453).

Materials. Isocyanides[6] were prepared by procedures described in the literature. π-C$_5$H$_5$Fe(CO)$_2$X (X = Cl,[7] I[8]) were prepared according to published methods.

Preparation of Bis[carbonyl(*tert*-butyl isocyanide)-π-cyclopentadienyliron]. A mixture of [π-C$_5$H$_5$Fe(CO)$_2$]$_2$ (2.0 g, 5.7 mmol) and *tert*-butyl isocyanide (1.0 g, 12.0 mmol) in THF (30 ml) was irradiated at 25°. After 24 hr, the solvent was removed under reduced pressure, and then the residue was chromatographed on alumina. Two bands (dark brown and dark green) were observed. The first band (benzene) afforded a trace of (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$[CNC(CH$_3$)$_3$].[9] The work-up of the second band [benzene–CH$_2$Cl$_2$ (1:1)] gave dark green crystals (1.7 g, 67%) of [π-C$_5$H$_5$Fe(CO)$\{$CNC(CH$_3$)$_3\}$]$_2$, recrystallized from benzene–hexane. *Anal.* Calcd for C$_{11}$H$_{14}$NOFe: C, 56.93; H, 6.08; N, 6.03. Found: C, 56.97; H, 5.92; N, 6.17.

The compound is very stable in the solid state but decomposes in solution, especially in CHCl$_3$. The infrared spectrum (KBr) shows three strong peaks at 2055 and 2093 cm^{-1} assignable to the coordinated isocyanide groups and 1732 cm^{-1} due to the bridged carbonyl groups. This suggests that the complex has a cis structure in the solid state. The proton nmr spectrum in CS$_2$ consists of two singlets at τ 8.27 (CH$_3$) and 5.73 (C$_5$H$_5$).

This nmr behavior could be explained by having a facile, rapid cis $\rightleftarrows$ trans isomerization as well as by related compounds, *e.g.*, [π-C$_5$H$_5$Fe(CO)$_2$]$_2$[10,11] and (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$[CNC(CH$_3$)$_3$].[11] Study on this subject will be reported in the future.

Preparation of Carbonyl(isocyanide)-π-cyclopentadienyliron Halides. Two representative examples are described below. Analytical data and spectroscopic data are summarized in Table I.

(a) π-C$_5$H$_5$Fe(CO)(CNC$_6$H$_{11}$)I. A mixture of π-C$_5$H$_5$Fe(CO)$_2$I (3.1 g, 10.4 mmol) and cyclohexyl isocyanide (1.2 g, 11.0 mmol) in benzene (30 ml) was refluxed for 2 hr. The reaction mixture was then chromatographed on alumina, benzene being used as an eluent. Removal of solvent and crystallization of the residue from benzene–hexane gave π-C$_5$H$_5$Fe(CO)(CNC$_6$H$_{11}$)I (3.2 g, 80%) as dark yellow crystals.

The benzyl and *tert*-butyl isocyanide derivatives were prepared by similar procedures. The chloride complex was prepared at 25°.

(b) π-C$_5$H$_5$Fe(CO)[CNC(CH$_3$)$_3$]I. A solution of iodine (0.7 g, 2.8 mmol) in benzene was added to a solution of [π-C$_5$H$_5$Fe(CO)$\{$CNC(CH$_3$)$_3\}$]$_2$ (1.1 g, 2.4 mmol) in benzene (20 ml) at 25° and stirred for 24 hr. By procedures similar to that described in (a), π-C$_5$H$_5$Fe(CO)[CNC(CH$_3$)$_3$]I (1.1 g, 62%) was obtained.

Reactions of Carbonyl(isocyanide)-π-cyclopentadienyliron Halides with Grignard Reagents. Two representative reactions are described in detail.

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