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Infrared Studies of Amine, Pyridine, and Phosphine Derivatives of Tungsten Hexacarbonyl

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Seventeen complexes, $LW(CO)_5$, where L = amine, pyridine, or phosphine, have been prepared and examined in the C–O stretching region of their infrared spectra. The C–O stretching frequencies and force constants in the amine, pyridine, and phosphine series decrease as the basicity of L increases, and the magnitude of this decrease is virtually the same for all three groups of ligands. The results suggest that W–L π bonding, even for the phosphines, need not be invoked to explain the C–O stretching frequency shifts in these metal carbonyl complexes.

Recent infrared studies[2] of C–O stretching frequencies in *cis*-$Mn(CO)_3(L)_2Br$ suggest that it is the σ-bonding ability of the ligand L, and not its π-bonding capacity, which determines the C–O stretching frequencies of the complex. Prior to this time, C–O stretching frequency shifts in substituted metal carbonyl complexes were almost universally interpreted in terms of the π-bonding ability of L.[3] Also C–O force constants obtained for a variety of substituted metal carbonyl complexes[4] have been discussed from this viewpoint. Since the π-bonding ability of a given L presumably parallels its σ-bonding ability, it is very difficult unequivocally to attribute C–O frequency shifts to the π- or σ-bonding properties of L. The current investigation was undertaken in order to examine the effect on C–O stretching frequencies of ligands which do not have a π-bonding capability but whose σ-bonding properties do vary. Thus we have examined the C–O stretching frequencies of $LW(CO)_5$ complexes containing amines, L, of different basicities (as measured by their pK_a values). These frequency shifts as a function of the basicity of L are then compared with frequency shifts as a function of the basicity of L groups which are potentially capable of π-bonding with the tungsten. Thus if there is no π-bonding between L groups such as pyridines or phosphines and tungsten, the C–O frequencies will depend on the pK_a of L to the same extent as noted in the case of the non-π-bonding amines. On the other hand, if the pyridines and phosphines π bond in addition to σ bonding, the C–O stretching frequencies should depend on the pK_a to an extent which is greater than that observed in cases where only σ bonding is involved.

The results obtained in this study suggest that only σ bonding between tungsten and L determines the C–O stretching frequencies. Changes in C–O force constants with changes in the basicity of L likewise suggest that if the pyridines and phosphines do π bond to the metal, this is not reflected in the force constants of the C–O bonds.

Experimental Section

Preparation of (amine)W(CO)$_5$.—A solution of 0.65 g of $W(CO)_6$ and a three- to fivefold excess of the amine in 25 ml of tetrahydrofuran under a nitrogen atmosphere was irradiated for 2 hr with an ultraviolet lamp, following the general method of Strohmeier.[5] Isolation of the complex from the solution depended upon the nature of the amine.

(a) **$(C_6H_5NH_2)W(CO)_5$.**—The addition of 50 ml of ice water to the tetrahydrofuran solution yielded a yellow precipitate. After filtering and drying, unreacted $W(CO)_6$ was removed by sublimation at 50° under high vacuum, leaving the yellow product. *Anal.* Calcd for $(C_6H_5NH_2)W(CO)_5$: C, 31.6; H, 1.7; N, 3.35. Found: C, 29.9; H, 1.7; N, 3.36.

(b) **(p-$BrC_6H_4NH_2$)W(CO)$_5$.**—The yellow irradiated solution was evaporated to dryness at room temperature under water aspirator vacuum. The resulting yellow solid was dissolved in a minimum of a 1:1 acetone–ethanol solution. The solution was then filtered to remove undissolved material. Upon adding 30 ml of cold water to the filtrate, fine yellow crystals formed. After filtration the solid was dried at room temperature under high vacuum, and the unreacted $W(CO)_6$ was removed at 50° by sublimation. The product was identified from its infrared spectrum.

(c) **(p-$CH_3OC_6H_4NH_2$)W(CO)$_5$.**—This complex was purified as indicated under (b). It was identified from its infrared spectrum.

(d) **$[(CH_3)_2CHNH_2]W(CO)_5$.**—This complex was isolated according to the procedure in (b) and identified from its infrared spectrum.

(e) **$(C_6H_{11}NH_2)W(CO)_5$.**—The irradiated solution was evaporated on a water aspirator until all of the tetrahydrofuran had been removed. The yellow crystals present in the excess amine were filtered off and dissolved in pentane; the product crystallized from solution on cooling to −80°. The yellow product was freed from $W(CO)_6$ by subliming at 50° under high vacuum. Its infrared spectrum in the C–O stretching region was the same as that reported in the literature.[6]

(f) **(morpholine)W(CO)$_5$.**—The solution was evaporated to dryness at 50° under vacuum to remove excess morpholine. The yellow residue was washed six times with 5-ml portions of pentane. After filtering, these washings were cooled to −80° whereupon yellow crystals precipitated. Unreacted $W(CO)_6$ was removed by sublimation under high vacuum at 50°. The yellow complex, $(C_4H_9NO)W(CO)_5$, was identified from its infrared spectrum by comparison with its previously published spectrum.[7]

(g) **$[(CH_3)_2NH]W(CO)_5$.**—The compound was purified as

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[1] NSF High School Teacher Research Participant.

[2] R. J. Angelici, *J. Inorg. Nucl. Chem.*, **28**, 2627 (1966).

[3] W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963), and references therein.

[4] F. A. Cotton, *ibid.*, **3**, 702 (1964).

[5] (a) W. Strohmeier, K. Gerlach, and G. Matthias, *Z. Naturforsch.*, **15b**, 621 (1960); (b) W. Strohmeier, K. Gerlach, and D. von Hobe, *Chem. Ber.*, **94**, 164 (1961).

[6] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

[7] G. W. A. Fowles and D. K. Jenkins, *ibid.*, **3**, 257 (1964).

given under (f). *Anal.* Calcd for $[(CH_3)_2NH]W(CO)_5$: C, 22.8; H, 1.9; N, 3.8. Found: C, 22.9; H, 2.2; N, 4.3.

(h) $[(CH_3)_3N]W(CO)_5$.—Purification was effected according to procedures given in (f). *Anal.* Calcd for $[(CH_3)_3N]W(CO)_5$: C, 25.1; H, 2.4; N, 3.7. Found: C, 25.3; H, 2.4; N, 4.6.

(i) (quinuclidine)$W(CO)_5$.—This compound was a gift of Mr. Arthur Vandenbroucke.

Preparation of (pyridine)$W(CO)_5$.—These complexes were prepared by irradiating a solution of 0.65 g of $W(CO)_6$ and a fivefold excess of the pyridine (C_5H_5N, 3-BrC_5H_4N, or 4-CH_3-C_5H_4N) in 25 ml of tetrahydrofuran. Under high vacuum the solutions were evaporated to dryness. The yellow residue was washed six times with 5-ml portions of pentane. After filtering, the washings were cooled to −80° to give yellow crystals which were filtered and dried under vacuum. Excess $W(CO)_6$ was sublimed off at 50° under vacuum. The infrared spectrum of $(C_5H_5N)W(CO)_5$ was in good agreement with published spectra.[6] *Anal.* Calcd for (3-$BrC_5H_4N)W(CO)_5$: C, 24.8; H, 0.9. Found: C, 24.8; H, 1.8. *Anal.* Calcd for (4-$CH_3C_5H_4N)W(CO)_5$: C, 31.6; H, 1.7; N, 3.4. Found: C, 31.4; H, 2.1; N, 3.4.

Preparation of (phosphine)$W(CO)_5$.—These complexes were prepared by the method of Magee, *et al.*[8] A solution of the phosphine and a slight molar excess of $W(CO)_6$ were refluxed (160–165°) in diglyme (bis-2-methoxyethyl ether) under a nitrogen atmosphere for 4 hr. At the end of the reaction a rapid stream of nitrogen was passed over the solution thereby subliming unreacted $W(CO)_6$ into the condenser.

Complexes of $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, and $(p\text{-}CH_3OC_6H_4)_3P$ were isolated from the above solution by first filtering and then cooling to −80°. The resulting brown crystals were filtered off and undissolved in a minimum of 1:1 $CHCl_3$-C_2H_5OH solution. Cooling to −80° gave a white precipitate which was dried under vacuum. *Anal.* Calcd for $[(C_6H_5)_3P]W(CO)_5$: C, 47.1; H, 2.6. Found: C, 47.2; H, 2.6; mp 143–144°. *Anal.* Calcd for $[(p\text{-}CH_3C_6H_4)_3P]W(CO)_5$: C, 49.7; H, 3.3. Found: C, 49.1; H, 3.5. *Anal.* Calcd for $[(p\text{-}CH_3OC_6H_4)_3P]W(CO)_5$: C, 46.1; H, 3.3. Found: C, 44.8; H, 3.1.

Complexes of $(C_6H_5)(C_2H_5)_2P$ and $(n\text{-}C_4H_9)_3P$ were separated from the diglyme solution by first filtering and then chromatographing the solution on an alumina column using pentane as eluent. The pentane was removed under vacuum leaving a light yellow oil. The complexes were further purified by chromatographing them a second time. *Anal.* Calcd for $[(C_6H_5)(C_2H_5)_2P]W(CO)_5$: C, 36.7; H, 3.1. Found: C, 36.3; H, 3.3. *Anal.* Calcd for $[(n\text{-}C_4H_9)_3P]W(CO)_5$: C, 38.8; H, 5.1. Found: C, 38.8; H, 5.5.

Infrared Spectra.—All infrared spectral measurements were made on a Beckman IR-12 grating spectrophotometer, calibrated with a polystyrene standard. To minimize errors, frequency measurements were made on a series of compounds (such as the amines, pyridines, or phosphines) during a single sitting. Frequencies are reproducible to ±0.5 cm^{-1}. Cyclohexane was used as solvent and NaCl cells of 1-mm thickness were required to obtain sufficiently intense absorptions.

Results

The infrared spectra of the $LW(CO)_5$ molecules in the C–O stretching region are characterized by three absorptions having weak, very strong, and strong intensities (Figures 1 and 2). These absorptions have been assigned by several workers to the $A_1^{(2)}$, E, and $A_1^{(1)}$ vibrational modes, respectively. These assignments have been verified by approximate force constant calculations and Raman data for several metal carbonyl complexes having C_{4v} symmetry.[4,6,9,10] The frequency assignments given in Table I were made in accordance with this previous work. The $A_1^{(2)}$ and E modes are associated with the four equivalent CO groups, and the $A_1^{(1)}$ mode is that of the CO *trans* to L.

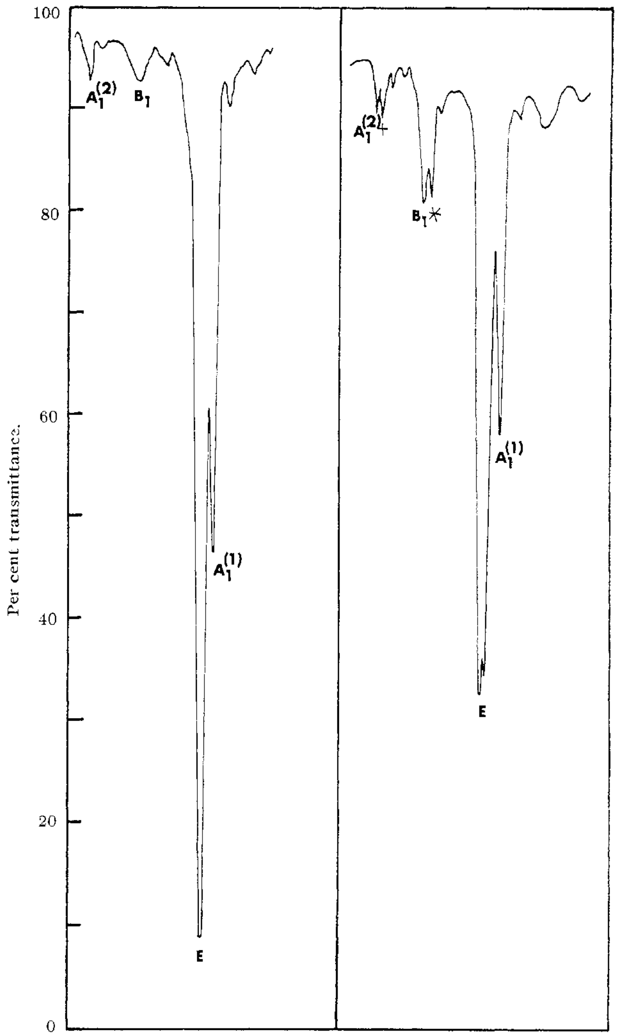

Figure 1.—Infrared spectra in cyclohexane: left, $(C_6H_{11}NH_2)$-$W(CO)_5$; right, $(p\text{-}CH_3C_6H_4NH_2)W(CO)_5$; *, $W(CO)_6$; +, unknown impurity, see text.

In addition to these three absorptions, the spectra contain a weak to very weak absorption in the approximate range of 1900–1910 cm^{-1}, roughly 35 cm^{-1} lower than the strong E absorption. The position and intensity of this band is consistent with assigning it to a ^{13}CO satellite of the E band.[11] Since the derivatives of $LW(CO)_5$ where L = amine underwent measurable decomposition to form $W(CO)_6$ during the infrared measurements, a band of varying intensity at 1984 cm^{-1} was always present. This was also true of the pyridine derivatives but to a lesser extent. Because of this decomposition it was impossible to locate accurately the forbidden B_1 mode which is frequently found in this region. It was obvious from the spectra however that there was some absorption in the 1980–2000-cm^{-1} region.[4,6,9]

Lastly, an anomalous absorption of weak or very

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(9) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

(10) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

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TABLE I

C–O STRETCHING FREQUENCIES (CM^{-1}) AND FORCE CONSTANTS (MDYNES/A) OBTAINED FOR $LW(CO)_5$ MOLECULES IN CYCLOHEXANE SOLVENT

L	pK_a	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i
Amines							
4-$BrC_6H_4NH_2$	3.9	2078.0	1939.0 1933.0	1923.5	15.15	15.83	0.35
$C_6H_5NH_2$	4.6	2076.0	1937.5 1933.0	1921.0	15.11	15.82	0.34
4-$CH_3OC_6H_4NH_2$	5.3	2075.0	1936.5 1932.0	1918.5	15.07	15.80	0.34
$(CH_3)_2CHNH_2$	10.6	2072.0	1931.5	1918.5	15.07	15.75	0.34
$C_6H_{11}NH_2$	10.7	2072.0	1931.5	1918.5	15.07	15.75	0.34
C_4H_9NO	8.3	2073.5	1932.5	1921.5	15.12	15.77	0.34
$(CH_3)_3N$	9.8	2073.0	1931.5	1919.5	15.08	15.76	0.35
$(CH_3)_2NH$	10.7	2072.0	1930.5	1920.5	15.11	15.74	0.35
$HC(CH_2CH_2)_3N$	10.9	2071.5	1929.0	1917.0	15.05	15.72	0.35
Pyridines							
3-BrC_5H_4N	2.8	2077.0	1938.0	1924.5	15.16	15.85	0.34
C_5H_5N	5.2	2073.0	1935.0	1921.0	15.11	15.80	0.34
4-$CH_3C_5H_4N$	6.0	2072.0	1933.0	1918.5	15.07	15.77	0.34
Phosphines							
$(C_6H_5)_3P$	2.7	2073.0	1944.0	...	15.47 15.57	15.89 15.89	0.31[a] 0.31[b]
$(p\text{-}CH_3C_6H_4)_3P$	4.0[c]	2071.5	1942.5	...	15.45 15.54	15.87 15.86	0.31[a] 0.31[b]
$(p\text{-}CH_3OC_6H_4)_3P$	4.5	2070.5	1941.5	...	15.43 15.53	15.85 15.85	0.31[a] 0.31[b]
$(C_6H_5)(C_2H_5)_2P$	6.3	2070.5	1939.0	1945.5	15.51	15.82	0.32
$(n\text{-}C_4H_9)_3P$	8.4	2068.5	1936.0	1943.0	15.47	15.78	0.32

[a] These k values were calculated assuming that the frequency of the $A_1^{(1)}$ mode was the same as that of the E mode. [b] These k values were calculated on the basis of estimated values for $A_1^{(1)}$. For $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, and $(p\text{-}CH_3OC_6H_4)_3P$, these estimates were 1949.5, 1948.0, and 1947.0, respectively; see text. [c] Estimated from the pK_a values for the other phosphines and the corresponding anilines.

weak intensity frequently appeared at 2066 cm^{-1} in the amine and pyridine complex preparations. From one preparation to another its intensity varied greatly. The presence of this band is shown in Figure 1 and is presumably caused by an unidentified impurity.

Approximate force constant calculations were carried out on the frequencies given in Table I using the method of Cotton and Kraihanzel.[10] The values of k_2, k_1, and k_i obtained from these calculations refer to the C–O stretching force constants of the four equivalent CO groups, the CO group *trans* to L, and the interaction constant between the CO groups, respectively. In the case of the aniline derivatives where the E mode was split (to be discussed later), an average frequency was used.[12] For the triphenylphosphine derivatives which exhibited only two absorptions in their spectra (Figure 2), force constants were calculated on the basis of two different approximations. The first trial was made on the assumption that the E and $A_1^{(1)}$ modes had the same frequency. This method gives a k_1 value for the $P(C_6H_5)_3$ complex which is less than that of the $P(n\text{-}C_4H_9)_3$ analog. This is unreasonable and we have therefore not used these k_1 values for subsequent purposes. A more reasonable assumption is that the observed very strong absorption is the E band and that the $A_1^{(1)}$ frequency can be estimated from the known position of the $A_1^{(1)}$ band in the $P(C_2H_5)_2(C_6H_5)$ and $P(n\text{-}C_4H_9)_3$ complexes (Figure 2). Since the $A_1^{(1)}$ frequency shifts by about the same amount as the $A_1^{(2)}$ and E frequencies in the latter two complexes, this has been assumed to be true for the $A_1^{(1)}$ band of the triphenylphosphine derivatives as well. These estimated frequencies are given in footnote *b* of Table I and should be very close to the real values. Force constants calculated on the basis of these assumptions are also given in Table I. All subsequent discussion will be based on these latter estimated frequencies and force constants.

The pK_a values given in Table I and in the figures for the amines,[13] pyridines,[13] and phosphines[14] are taken from the literature.

Discussion

The three characteristic $A_1^{(2)}$, E, and $A_1^{(1)}$ absorptions predominate in the C–O stretching spectra of the $LW(CO)_5$ molecules. Only in the complexes where L is an aniline is splitting of the E mode observed (Figure 1). Similar splittings have been noted[12] in $C_6H_5C(=O)Mn(CO)_5$ and other $LMn(CO)_5$ derivatives. The larger splittings were associated with the presence of large substituents on the carbon atom of L which was β to the metal. The largest splittings were observed for benzoyl- and perfluorobenzoylmanganese pentacarbonyl. While splitting of the E mode was observed in $(C_6H_5NH_2)W(CO)_5$ and the other aniline com-

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(12) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

(13) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co. Ltd., London, 1965.

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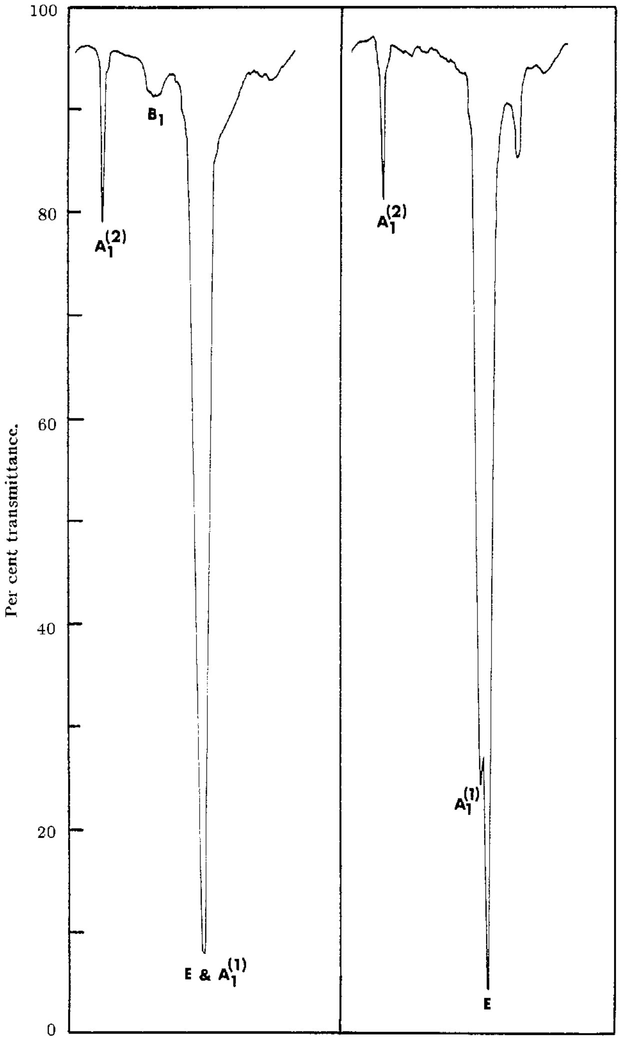

Figure 2.—Infrared spectra in cyclohexane: left, $[(C_6H_5)_3P]W(CO)_5$; right, $[(n\text{-}C_4H_9)_3P]W(CO)_5$.

plexes, complexes such as the cyclohexyl and isopropyl analogs, $(C_6H_{11}NH_2)W(CO)_5$ and $[(CH_3)_2CHNH_2]W(CO)_5$, exhibit no measurable splitting. It is apparently the high electron density of the benzene ring which is primarily responsible for this effect. Perhaps the large size of the tungsten atom has reduced the magnitude of the splitting in these other amines, as was observed for rhenium carbonyl complexes as compared to their manganese analogs.[12] It should be added, however, that no splitting of the E mode has been reported for $C_6H_5CH_2Mn(CO)_5$.[15]

Our approach in determining whether C–O stretching frequencies and force constants are measures of W–L π bonding or not has been a very simple one. The effect of the W–L σ bond on the C–O stretching frequencies was examined by using non-π-bonding amines. In these C_{4v} symmetry molecules,[16] the d_{xz} and d_{yz} orbitals are allowed by symmetry to enter into either σ or π bonding. Thus these orbitals provide a mechanism whereby W–L σ-bond effects can be transmitted to the W–CO π-bonding system. As a relative measure of the W–L σ-bond strength, the pK_a of L has been used. While the pK_a is not an ideal measure of bond strengths in this system, it is the best available; its use in this manner has been discussed previously.[2] With some knowledge of the effect of the pK_a of non-π-bonding L groups on the C–O stretching frequencies, a similar study was made using ligands which were potentially capable of π bonding such as pyridines and phosphines. If the phosphines, for example, do not participate in π bonding, the C–O stretching frequencies should shift much as they did in the case of amine ligands. If there is significant W–P π bonding and the amount of this π bonding decreases from $(C_6H_5)_3P$ to $(n\text{-}C_4H_9)_3P$, the C–O stretching frequencies for the phosphines should decrease much more sharply with changes in pK_a than for the amines.

As expected, the C–O stretching frequencies (Table I) of the amine complexes decrease as the basicity (pK_a) of L increases (Figures 3 and 4). The shifts are small as is true for all of the compounds reported in this paper. There is no question that W–L σ bonding does affect W–C–O π bonding. The fact that at high pK_a values the changes in the $A_1^{(1)}$ frequency with pK_a of the amine become negligible suggests that there is a limit to which electron density can be transferred to the W–CO π bonds. It should be noted that the three amines which lie significantly above the $A_1^{(1)}$ plot (Figure 4) for this group of ligands are secondary and tertiary amines. This suggests that their affinity for $W(CO)_5$ may be lower than that indicated by their pK_a values. The larger bulk of these amines as compared to the primary amines would account for this observation.

The C–O stretching frequencies of the pyridine complexes depend upon the pK_a of the pyridine in much the same way as the amines, at least within the limited pK_a range provided by the pyridines. The C–O stretching frequency trends of the pyridines would not suggest W–py π bonding.

The C–O stretching frequencies of the phosphine derivatives have two interesting features. First, the change of the C–O stretching frequencies (Figures 3 and 4) with a given change in pK_a is not significantly different for the phosphines than for the amines. This indicates that only the pK_a (or the σ-bonding ability) of the phosphine is required to account for the C–O stretching frequency shifts in the (phosphine)$W(CO)_5$ complexes. If W–P π bonding were primarily responsible for C–O stretching frequency shifts, the magnitude of the shifts should be much greater than can be accounted for in terms of the pK_a of the phosphine alone. There is certainly no compelling reason to invoke tungsten–phosphorus π bonding to explain the C–O stretching frequency shifts. Second, the pK_a of the ligand is not the only factor which determines the C–O stretching frequencies since the frequencies of the phosphine complexes lie on lines different from those of the amine complexes (Figures 3 and 4). Although an amine and a phosphine of the same pK_a form complexes whose C–O stretching frequencies differ substantially, this

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(15) R. W. Cattrall and R. J. H. Clark, *J. Organometal. Chem.* (Amsterdam), **6**, 167 (1966).

(16) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963, p 97.

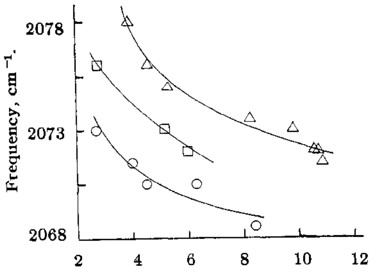

Figure 3.—Plot of $A_1^{(2)}$ frequency of $LW(CO)_5$ *vs.* the pK_a of L: Δ, amines; □, pyridines; O, phosphines.

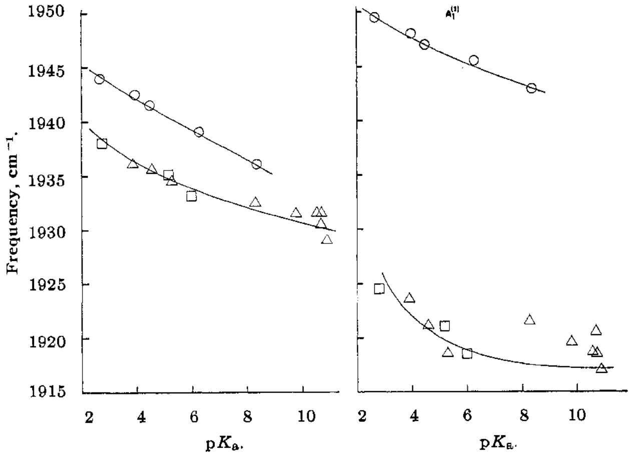

Figure 4.—Plot of E (left) and $A_1^{(1)}$ (right) frequencies of LW-$(CO)_5$ *vs.* the pK_a of L: Δ, amines; □, pyridines; O, phosphines.

difference need not be explained in terms of W–P π bonding as has been done in the past. It is also reasonable to suppose that while these two ligands have the same affinity for a proton (as measured by the pK_a), it is very likely that they will have quite different affinities for the tungsten in these complexes. Such differences in W–N and W–P σ bonding could also account for the observed C–O stretching frequency differences.

Since the C–O stretching force constants are a more reliable measure of the C–O bond strength than the C–O stretching frequencies, force constants for the four CO groups *cis* to L, k_2, and the single CO group *trans* to L, k_1, have been calculated according to the approximate methods of Cotton and Kraihanzel.[10] The results are presented in Table I and are plotted *vs.* the pK_a of L in Figure 5. As anticipated, k_1 and k_2 decrease as the basicity (pK_a) of L increases. The dependence of k_1 on the pK_a of the amines or pyridines at low pK_a appears to be greater than observed for k_2. Since the CO *trans* to L interacts with both the d_{xz} and the d_{yz} tungsten π-bonding orbitals and the CO groups *cis* to L interact with *either* the d_{xz} *or* the d_{yz} orbitals, changes in the pK_a of L should affect the *trans* C–O force constants to a greater extent than the *cis*. This greater dependence of k_1 on pK_a is apparently limited by the inability of the *trans* CO to accept an unlimited amount of π-electron density, as suggested by the leveling off of k_1 at higher pK_a values. Thus the amine and pyridine complexes appear to behave as expected.

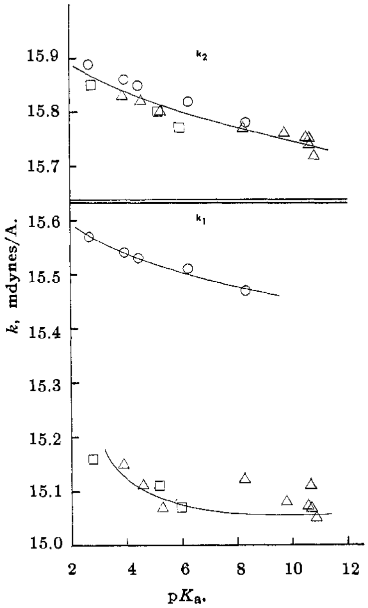

Figure 5.—Plots of the C–O stretching force constants, k_2 (top) and k_1 (bottom), of $LW(CO)_5$ *vs.* the pK_a of L.

That these two types of ligands produce variations in k_1 and k_2 which are virtually identical further suggests that W–N σ bonding, rather than π bonding, is responsible for the changes in C–O bonding. The three amines which lie significantly above the k_1 plot are again either secondary or tertiary amines; perhaps steric effects reduce their effective pK_a toward tungsten as suggested earlier in the discussion of C–O stretching frequencies.

The dependence of the C–O force constants on the pK_a values of the phosphines is of particular interest (Figure 5). The values of k_2 decrease with the pK_a of the phosphines in a manner which is virtually identical with that observed for the amines and pyridines, although there is a hint that the phosphine line lies very slightly above the amine and pyridine line. Thus the values of k_2 can be predicted to a high degree of accuracy solely on the basis of the pK_a of L in $LW(CO)_5$, regardless of whether L is an amine, pyridine, or phosphine. Again this evidence suggests that W–L σ-bonding effects are responsible for changes in the C–O bonds of the carbonyl groups which are *cis* to L.

The behavior of k_1 for the phosphine complexes, however, is notably different from that of the amine complexes. First, the values of k_1 do not level off. Second, the dependence of k_1 on the pK_a of L is not greater than that of k_2, as anticipated from W–C–O π-bonding arguments. Third, the values of k_1 for the phosphines are much higher than those of the amines and pyridines. Thus the phosphines have a notable effect, as compared to the amines and pyridines, on the *trans* CO group, but substantially no corresponding effect on the *cis* CO groups. Considerations of either W–P σ or π bonding would suggest that any changes in the *trans* CO group would be accompanied by changes which were roughly half as large in the *cis* CO groups. Hence the question of why variations in k_1 for the phosphine complexes are not twice as great as variations in k_2 is still unresolved.

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Notes

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Equilibrium Studies of Chlorine Pentafluoride

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In the course of our synthesis of chlorine pentafluoride, a new, recently reported interhalogen,[1-3] from chlorine and fluorine, it was found that complete conversion of chlorine to chlorine pentafluoride did not occur, even over extended periods of time and with a tenfold excess of fluorine. The presence of chlorine trifluoride suggested either a very slow reaction or, more probably, that the system was governed by the equilibrium $ClF_3 + F_2 \rightleftarrows ClF_5$, similar to the system $ClF + F_2 \rightleftarrows ClF_3$.[4] A study was undertaken to demonstrate the existence of this equilibrium and to obtain enthalpy and entropy changes for the reaction $ClF_3 + F_2 = ClF_5$.

Experimental Section

Materials.—Fluorine obtained from the Allied Chemical Corporation, chlorine and chlorine trifluoride from the Matheson Company, and chlorine pentafluoride from the Rocketdyne Division of North American Aviation were used in this study. Monel reactors fitted with Monel valves and Ashcroft Monel tube Duragauges were found compatible with the halogens and interhalogens used. Thus, a near equality in the material balance of reactants and products could be assumed. Reactors made from 304 stainless steel proved unsatisfactory in this regard and even the Monel metal was significantly corroded by the fluorine–interhalogen mixtures above 300°, over prolonged periods of time.

Sampling.—A 16-hr period was taken as sufficient to establish equilibrium, temperature control being maintained with the aid of a Wood's metal bath. To sample the equilibrium composition, an isolated small sample was quenched by rapid expansion. Nonuniform composition due to partial condensation in incompletely immersed portions of the apparatus was avoided by maintaining the partial pressure of ClF_3 and ClF_5 below their ambient temperature equilibrium vapor pressures.

Analyses.—The fluorine content of an equilibrium sample was calculated from the difference between the total and condensable gas pressures in a known volume as well as by gas chromatographic separation. The partial pressure of fluorine was calculated from the per cent fluorine and the total equilibrium pressure prior to quenching. Separation was effected with a 20 ft, 0.25 in. column packed with a 50/50 weight ratio of 12-21 halocarbon oil on 30–50 mesh, low-density, Kel-F molding powder.[5] This column was not capable of separating ClF_3 and ClF_5. The chlorine fluorides were separated by vacuum sublimation using −196 and −112° baths. From infrared spectra of the pure components, run under identical conditions, it was possible to estimate the concentration of each fluoride originally present in the equilibrium mixture, with an accuracy within 20%. The spectra were obtained using Monel gas cells fitted with silver chloride windows.

Results and Discussion

The temperature range and equilibration times appropriate for this study were defined by a series of pressure–temperature–time curves for both chlorine trifluoride–fluorine mixtures and chlorine pentafluoride alone. Negative deviations from a Boyle's law behavior, first discernible near 180° for chlorine trifluoride–fluorine mixtures, indicated reaction. Positive deviations during the heating of chlorine pentafluoride were first seen near 200°. Even at 210°, 4 hr was required to ensure that no further pressure changes were taking place. At 217° the rate of dissociation was conveniently rapid; a pressure increase of one-third was observed after 40 min. In the temperature range 211–271° no undesirable side reactions were detected after 16-hr heating periods. Since the rate of formation or dissociation of ClF_5 below 200° was too slow, catalysis of these reactions was investigated. Attempts to catalyze equilibration at lower temperatures with AgF_2, BF_3, or increased surface were unsuccessful.

The equilibrium constant, $K_p = P_{ClF_5}/P_{ClF_3}P_{F_2}$, was calculated from the ratio of the partial pressures of ClF_5 and ClF_3 and from the partial pressure of fluorine under equilibrium conditions. The results of eight determinations at various temperatures are shown in Table I. Determination of the ratio P_{ClF_5}/P_{ClF_3} by infrared analysis[6,7] was affected by certain errors inherent in this technique. The method of determining absorbances was by difference from background on a logarithmic scale. Errors in the estimate of the relative concentrations of ClF_3 and ClF_5 undoubtedly accrued from the variation in cell background and pen response, but it is possible that additional inaccuracy arose from some interaction of the fluorine and fluorides with the less inert parts of the containers, *e.g.*, the

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