Spectroscopic Studies of the Complexes of Acrylonitrile and Acetonitrile with the Carbonyls of Chromium, Molybdenum, and Tungsten

By BONNIE L. ROSS, JEANETTE G. GRASSELLI, WILLIAM M. RITCHEY, AND HERBERT D. KAESZ

Infrared and proton magnetic resonance spectroscopic studies of acrylonitrile complexes of the carbonyls of Cr, Mo, and W are used to assign the geometrical isomerism and manner of attachment of the ligand in these derivatives. Similar studies are also reported for the acetonitrile derivatives, from which the acrylonitrile complexes have been obtained. Evidence is presented for attachment of acrylonitrile through the nitrogen lone-pair in $(CH_2CHCN)M(CO)_5$ (M = W) and $(CH_2CHCN)_2M(CO)_4$ (M = Cr, Mo, and W), which are among the first well characterized examples of this type of bonding for this ligand (heretofore assumed to attach to transition metals principally through the olefinic carbon–carbon bond). The trisubstituted complexes $(CH_2CHCN)_3M(CO)_3$ (M = Mo and W) appear to have the C_{2v} (*trans*) geometry, even though they were prepared by displacement of the ligand from C_{3v} (*cis*) acetonitrile complexes. The acrylonitrile is attached through the olefinic carbon–carbon bond in these derivatives.

Introduction

Acrylonitrile is an interesting ligand for substitution into the carbonyls as it affords a multiplicity of bonding possibilities with the transition metal. One obvious possibility, that of displacement of one carbonyl group and attachment through the nitrogen lone pair (as occurs with saturated nitriles) has not until recently proved favorable.[1] The displacement of one carbonyl group and attachment of acrylonitrile perpendicular to the carbon–carbon double bond has proved more favored, as in the complex $(CH_2CHCN)Fe(CO)_4$,[2] whose structure has been determined,[3] and the complex $(C_6H_5CH=CC_6H_5-C\equiv N)_2Mo(CO)_4$,[4] in which similar attachment is believed to occur. Attachment perpendicular to the CN multiple bond, as once reported for $(CH_3CN)_2Pt(NH_3)_4^{+2}$, is not well characterized, and has been refuted for the one case mentioned.[5] Finally, it is also possible for acrylonitrile to displace the equivalent of two carbonyl groups such as in $(CH_2CHCN)_2Mo(CO)_2$[6] or the complexes of that ligand with Ni.[7]

Direct substitution of acrylonitrile into the group VIB metal carbonyls has not proved feasible for preparation of most of the complexes since the vigor of the reaction needed to induce substitution is often greater than can be withstood by the ligand or its complexes. The series $(CH_2CHCN)_nM(CO)_{6-n}$ (n = 1, 2, or 3; M = Cr, Mo, and W) are best prepared by displacement of the ligand under mild conditions from the corresponding acetonitrile complexes,[8] which are ob-

tained by the usual means.[9] The acrylonitrile complexes and those of acetonitrile from which they were obtained are studied here. Stereoisomerism and the nature of attachment of the ligand are ascertained by infrared spectroscopy and proton magnetic resonance.

Experimental

Acetonitrile complexes of Cr, Mo, and W were prepared by refluxing the metal hexacarbonyls in acetonitrile with controlled carbon monoxide evolution.[8b,9a] The corresponding acrylonitrile complexes were obtained by replacement of the ligand in the appropriate acetonitrile complexes.[8a]

The infrared spectra were recorded on a Perkin-Elmer-221 double-beam infrared spectrophotometer with a prism-grating interchange. The compounds were examined in halocarbon oil–Nujol (hco–Nujol) split mulls in the region 3950–650 cm.$^{-1}$ and in hydrocarbon solution (if possible) or in acetone in the range 2500–1700 cm.$^{-1}$ for optimum resolution of the metal C≡O and C≡N stretching absorptions. Spectra of the compounds in solution were recorded with an expanded abscissa (12.5 cm.$^{-1}$/cm.) in cells of 0.203 and 1 mm. thicknesses, with compensation of solvent absorption. Calibration of chart paper for the metal C≡O and C≡N stretching regions was made with the 1847.8 cm.$^{-1}$ band of atmospheric water vapor.[10] Bands are reproducible within 1 cm.$^{-1}$ on calibrated paper and within 3 cm.$^{-1}$ without calibration.

The di- and trisubstituted acetonitrile and acrylonitrile carbonyl complexes are unstable in air and samples for spectral study were handled under N_2. The disubstituted complexes appeared to be slightly more stable than the trisubstituted. Only the monosubstituted complexes $(CH_3CN)Cr(CO)_5$, $(CH_3CN)W(CO)_5$, and $(CH_2CHCN)W(CO)_5$ appeared to be sufficiently air-stable for normal sampling techniques. Solvents were chosen according to the solubility and stability of the respective compounds. All the acetonitrile and acrylonitrile complexes of the group VIB metal carbonyls are soluble in acetone, and this solvent was used in most cases, although some exchange is suspected with acrylonitrile ligands in $(CH_2CHCN)_3W(CO)_3$ (see below). Only in the case of the monosubstituted complexes is solubility in more

(1) (a) A. G. Massey, *J. Inorg. Nucl. Chem.*, **24**, 1172 (1962); for further discussion, *cf.* (b) L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, New York, N. Y., 1960, pp. 135–138.

(2) S. F. A. Kettle and L. E. Orgel, *Chem. Ind.* (London), 49 (1960).

(3) A. R. Luxmoore and M. R. Truter, *Acta Cryst.*, **15**, 1117 (1962).

(4) G. N. Schrauzer and S. Eichler, *Chem. Ind.* (London), 1270 (1961).

(5) (a) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 801 (1962); (b) Yu. Ya. Kharitonov, Ni Tszya-Tzan, and A. V. Babaeva, *Dokl. Akad. Nauk SSSR*, **141**, 645 (1961); Engl. translation, p. 1185.

(6) A. G. Massey and L. E. Orgel, *Chem. Ind.* (London), 436 (1961).

(7) *cf.* H. P. Fritz and G. N. Schrauzer, *Chem. Ber.*, **94**, 650 (1961), and references cited therein.

(8) (a) D. P. Tate, A. Buss, and J. M. Augl, *Inorg. Chem.*, **2**, 427 (1963); (b) D. P. Tate, A. Buss, and J. M. Augl, in manuscript.

(9) (a) D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, **1**, 433 (1962); (b) these complexes may also be formed photochemically, *cf.* G. R. Dobson, M. F. A. El-Sayed, I. W. Stolz, and R. K. Sheline, *ibid.*, **1**, 526 (1962), and references cited therein, particularly to Strohmeier and co-workers; (c) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **2**, 323 (1963).

(10) E. K. Plyer, A. Danti, L. R. Blaine, and E. D. Tidewell, *J. Res. Natl. Bur. Std.*, **64A**, 29 (1960).

suitable solvents (*n*-hexane, cyclohexane) sufficient to obtain spectra of optimal resolution of the metal carbonyl absorptions.

Proton magnetic resonances were observed with a fully equipped Varian DP-60 spectrometer. Samples were examined as saturated solutions (5–10 wt. %) in acetone-d_6 with $(CH_3)_4Si$ as internal reference. Radiofrequency power was held well below saturation intensity and a sweep rate of approximately 1.0 c.p.s./sec. was employed. The sample temperature was $25.0 \pm 0.5°$ in all cases, and the samples were handled under dry N_2 to minimize decomposition. The spectra were calibrated by the usual side-band technique and line positions were reproducible to ± 0.01 p.p.m. or better.

Results

The results of infrared spectral measurements are summarized in Table I. Typical spectra for the complexes studied are given in Fig. 1–3. The proton magnetic resonance spectra of some selected acrylonitrile complexes are shown in Fig. 4a and 4b. Bands due to the media and impurities are cross-hatched.

Discussion

I. Acetonitrile Complexes.—For the monosubstituted carbonyls $(CH_3CN)M(CO)_5$ (M = Cr and W), three bands are observed in the metal $C≡O$ stretching region (see Table I), indicating a C_{4v} local symmetry for an octahedral structure.[9c,11,12] An additional band between 1982 and 1992 cm.$^{-1}$ of varying relative intensity is most likely due to $M(CO)_6$, which was very difficult to remove from the samples. A representative spectrum for the carbonyl absorptions has been published by Dobson, *et al.*,[9b] and their positions for the absorption maxima are more or less in agreement with ours. We have assigned (Table I) these absorptions to the expected symmetry modes, following previous work.[12] The A_1^{1a} (notation in Fig. 2 of Orgel[12a]) mode is of lower energy than the E mode, which is symptomatic of a ligand of lower π-bonding ability than the carbonyl group.[12c]

A typical spectrum of acetonitrile ligand vibrations is that for the bis-acetonitrile complex (Fig. 2a). In the monosubstituted complex (as in the others), the nitrile stretching absorption is shifted to higher frequency from that in the free ligand by 20–30 cm.$^{-1}$, indicating metal to ligand bonding by way of the lone pair of the nitrogen.[13] Absorption in this region does not agree entirely with data reported by Stolz, *et al.*,[9c] but is consistent for both Cr and W in KBr, Nujol, and solution. The weak band at 1030 cm.$^{-1}$ is most likely the degenerate CH_3 rocking vibration of the ligand.[14] The band appeared consistently in spectra

of all the acetonitrile complexes and proved useful in verifying the presence of the ligand. No spectrum was obtained of $(CH_3CN)Mo(CO)_5$, which, in contrast to the Cr and W complexes, appeared to be extremely unstable.

For the disubstituted carbonyls, $(CH_3CN)_2M(CO)_4$ (M = Cr, Mo, W), four bands are observed in the metal carbonyl stretching region. A representative spectrum is given in Fig. 2a. Due to the low solubility of these complexes in hydrocarbons, optimum resolution of the carbonyl absorptions was not possible. Three of the four carbonyl bands are broad; nevertheless, this pattern strongly resembles that expected for *cis*-disubstituted octahedral carbonyls.[11] No separate absorption was seen which could be attributed to the presence of a *trans*-disubstituted isomer (expected to have only one absorption band), nor did we observe any change in relative intensities of the absorption bands present upon chromatographic purification, which would have occurred if the absorption of the *trans* isomer were hidden under the observed pattern. If such an isomer were present, it could only be in minimal quantities. We have assigned the absorptions to the expected modes (see Table I).

As found for the monosubstituted complexes, the $C≡N$ stretching absorption appears at higher frequencies in the disubstituted complexes than in the free ligand, *i.e.*, for $(CH_3CN)_2W(CO)_4$ at 2282 cm.$^{-1}$ in Nujol (or 2258 cm.$^{-1}$ in acetone solution). This is a consequence of bonding of the ligand to the metal through the lone pair on nitrogen. A weak band or shoulder on the high frequency side of the nitrile stretching band, which appears in Nujol mulls of these complexes, could be the second $C≡N$ absorption of the two expected for a *cis*-$(RC≡N)_2M(CO)_4$[9c] (see discussion for $(CH_2CHCN)_2W(CO)_4$, below). However, without more detailed spectroscopic studies, it is not possible to rule out entirely some alternate assignment, such as the possibility that the weak absorption could be due to a combination of the symmetric CH_3 deformation and symmetric $C–C$ stretching modes[14] which appear as very weak bands in the range of 1350–1370 and 930–940 cm.$^{-1}$, respectively, since not all of the complexes with more than one nitrile ligand showed additional absorptions for the $C≡N$ group when these were expected by considerations of symmetry.

The tris-acetonitrile metal carbonyls $(CH_3CN)_3$-$M(CO)_3$ (M = Cr, Mo, W) have two infrared-active metal carbonyl stretching modes representing predominantly an isomer of all-*cis* (C_{3v}) configuration of ligands about the metal atom.[9c,11,12] A representative spectrum of the carbonyl region has been published by Dobson, *et al.*,[9b] and their observed band maxima differed slightly from ours (due in part to the difference in solvent). We have also assigned our absorptions to the expected modes, guided by previous work in this area.[12]

Ligand vibrations follow those of the bis complex (Fig. 2a). The $C≡N$ stretching frequency is shifted to a higher frequency from that in the free ligand and ap-

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

(12) (a) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962); if we consider the notation in Fig. 2 of this reference to be correct, then the headings A_1^{1a} and A_1^{1b} in Table II of this reference should be interchanged in order to be in agreement with that figure and the discussion in the text; (b) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962); (c) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (d) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

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TABLE I

INFRARED ABSORPTIONS OF ACETONITRILE AND ACRYLONITRILE COMPLEXES OF THE CARBONYLS OF Cr, Mo, AND W (IN CM.$^{-1}$)

| Compound (medium)	C≡N stretch	Metal carbonyl absorptions and symmetry type[c]				Ligand vibrations	
I. Acetonitrile	2259 (s)					2300 (m)	1442 (s)
						1373 (s)	1032 (m)
						920 (m)	750 (w)
$(CH_3CN)M(CO)_5$, C_{4v}[c]		A_1[1b]	E	A_1[1a]			
M = W (*n*-hexane)	2282 (w)	2083 (m)	1948 (s)	1931 (m)			
			(1916[a] (w))				
M = W (hco–Nujol[d])	2292 (w)	2080 (m)	1947 (s)	1868 (sh)		1030 (w)	
M = Cr (hco–Nujol)	2291 (w)	2080 (m)	1952 (s)	1927 (sh)		1368 (w)	1030 (w)
						945 (w)	646 (w)
M = Cr (*n*-hexane)	2285 (w)	2080 (w)	1954 (s)	1930 (m)			
			(1920[a] (w))				
$(CH_3CN)_2M(CO)_4$, C_{2v}[c]		A_1	A_1	B_1	B_2		
M = W (acetone)	2258 (w)	2022 (m)	1919 (s)	1899 (s)	1848 (s)		
M = W (Nujol)	2282 (w)	2022 (m)	1900 (s)	1880 (s)	1839 (s)	2315 (w)	1373 (w)
						1031 (w)	946 (vw)
M = Cr (hco–Nujol)	2287 (w)	2019 (m)	1908 (s)	1882 (s)	1843 (s)	1030 (w)	
M = Mo (hco–Nujol)	2280 (w)	2023 (m)	1912 (s)	1881 (s)	1833 (s)	1030 (w)	
$(CH_3CN)_3M(CO)_3$, C_{3v}[c]		A_1	E				
M = W (acetone)	2257 (w)	1915 (s)	1793 (s)				
M = W (hco–Nujol)	2265 (w)	1885 (s)	1778 (s)			2278 (sh)	1359 (w)
						1030 (w)	938 (w)
M = Cr (Nujol)	2280 (w)	1910 (s)	1782 (s)			2308 (w)	1362 (w)
						1032 (w)	940 (w)
M = Mo (hco–Nujol)	2278 (w)	1915 (s)	1783 (s)			2305 (w)	1360 (w)
						1028 (w)	938 (w)
II. Acrylonitrile	2235 (s)					2290 (w)	1419 (s)
						1100 (m)	975 (vs)
						875 (w)	690 (s)
$(CH_2CHCN)M(CO)_5$, C_{4v}[c]		A_1[1b]	E	A_1[1a]			
M = W (*n*-hexane)	2239 (w)	2079 (m)	1949 (s)	1934 (m)			
			(1919[a] (w))				
M = W (hco–Nujol)	2252 (w)	2079 (m)	1951 (s)	1930 (sh)		1602 (w)	1410 (w)
						1287 (w)	962 (m)
$(CH_2CHCN)_2M(CO)_4$, C_{2v}[c]		A_1	A_1	B_1	B_2		
M = W (acetone)	2232 (w)	2011 (m)	1939 (sh)	1918 (s)	1848 (s)		
M = W (hco–Nujol)[b]	2235 (sh)	2024 (m)	1900 (s)	1870 (s)	1834 (s)	1600 (w)	1402 (w)
	2220 (w)					1279 (w)	953 (m)
M = Cr (Nujol)	2249 (w)	2028 (m)	1910 (s)	1878 (s)	1839 (s)		
M = Mo (hco–Nujol)	2240 (w)	2023 (m)	1905 (s)	1870 (s)	1831 (s)		
$(CH_2CHCN)_3M(CO)_3$, C_{2v}[c]		A_1[1b]	B_1	A_1[1a]			
M = W (acetone)	2222 (m)	2012 (sh)	1980 (s)	1911 (s)	1842 (s)		
M = W (Nujol)	2221 (m)	2014 (sh)	1979 (s)	1901 (s)	1833 (s)	1440 (w)	1401 (w)
						1344 (w)	1280 (w)
						1174 (m)	1087 (w)
						960 (m)	
M = Mo (hco–Nujol)	2225 (m)		1975 (s)	1900 (s)	1832 (s)	1456 (w)	1406 (w)
						1356 (w)	1280 (w)
						1197 (m)	1095 (w)
						962 (m)	

[a] This very weak band is the ^{13}C mode of the most intense metal carbonyl absorption.   [b] Weak bands were also observed at 2080 (w) and 1947 (sh), assigned to a trace of $(CH_2=CHCN)W(CO)_5$.   [c] Assignment follows those in the articles cited in ref. 12, and also, see text.   [d] Abbreviation for halocarbon oil–Nujol.

pears at 2265 cm.$^{-1}$ in Nujol for $(CH_3CN)_3W(CO)_3$ (2257 cm.$^{-1}$ in acetone solution) in keeping with attachment of ligand to metal by way of the nitrogen lone pair. A weak band on the high frequency side of the C≡N stretching band appears in the spectra of these complexes in Nujol mulls. This could be the second C≡N stretching frequency expected for this complex, or a combination band, as discussed under the bis-acetonitrile complexes. The band reported at 2215 cm.$^{-1}$ by Stolz, *et al.*,[9c] is most probably due to an impurity. The samples were difficult to obtain pure and very weak metal carbonyl bands which are not listed

appeared in various positions, in the 1950 to 2100 cm.$^{-1}$ range. A common impurity is $(CH_3CN)_2M(CO)_4$, identified by its carbonyl absorption at higher frequency.

II. Acrylonitrile Complexes.—For $(CH_2CHCN)W(CO)_5$, three bands are observed in the metal carbonyl region, indicating C_{4v} symmetry for an octahedral structure.[11,12] $W(CO)_6$ was difficult to remove from the samples and appeared as a band of varying intensity at 1987 cm.$^{-1}$ in *n*-hexane and 1985 cm.$^{-1}$ in cyclohexane (at 1988 cm.$^{-1}$ in halocarbon oil). A representative spectrum is given in Fig. 1a. Figure 1b shows

WAVELENGTH (MICRONS)
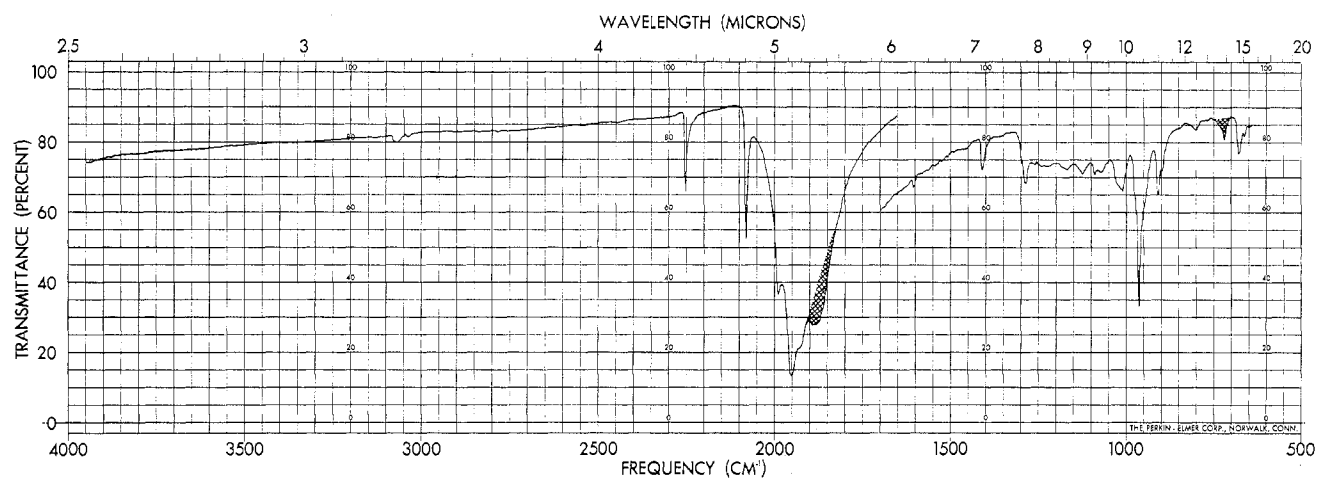
Fig. 1a.—Infrared spectrum of (CH₂CHCN)W(CO)₅, C₄ᵥ, in hco-Nujol.

FREQUENCY (CM⁻¹)
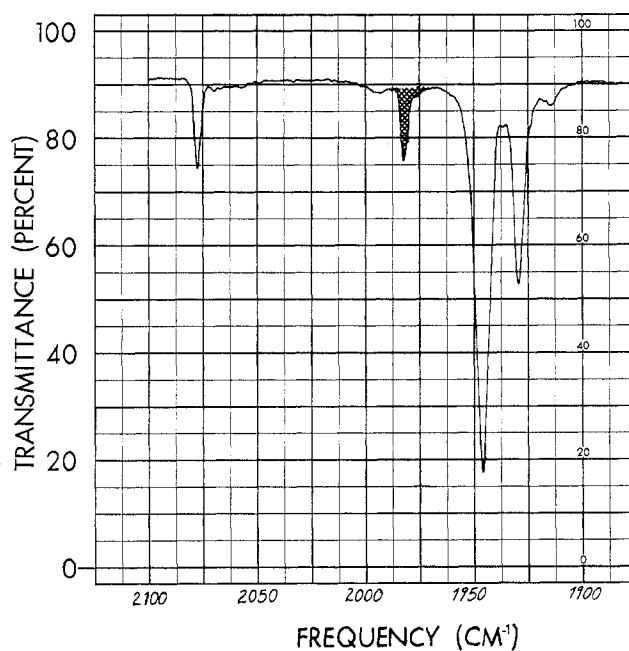
Fig. 1b.—Infrared spectrum of (CH₂CHCN)W(CO)₅, C₄ᵥ, in cyclohexane, 0.203 mm. compensated, expanded abscissa.

WAVELENGTH (MICRONS)
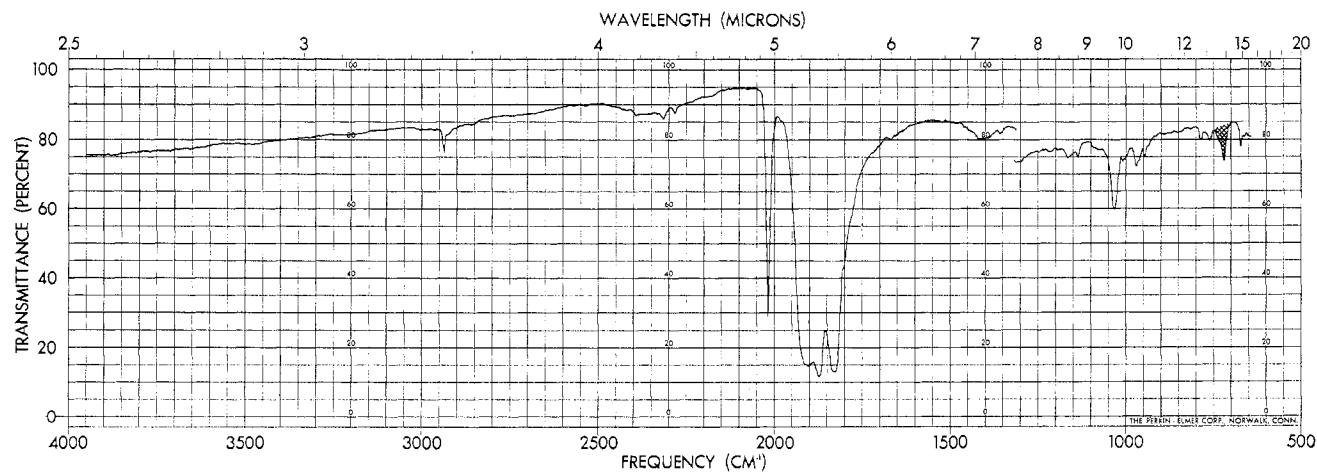
Fig. 2a.—Infrared spectrum of (CH₃CN)₂W(CO)₄, C₂ᵥ (*cis*), in hco-Nujol.
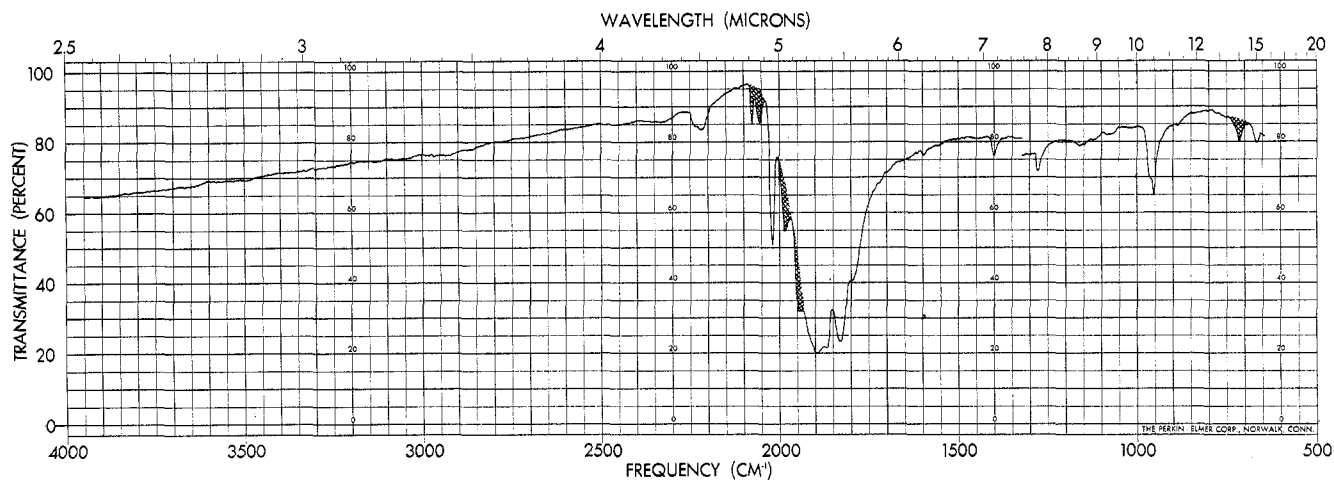
Fig. 2b.—Infrared spectrum of $(CH_2CHCN)_2W(CO)_4$, C_{2v} (*cis*), in hco–Nujol
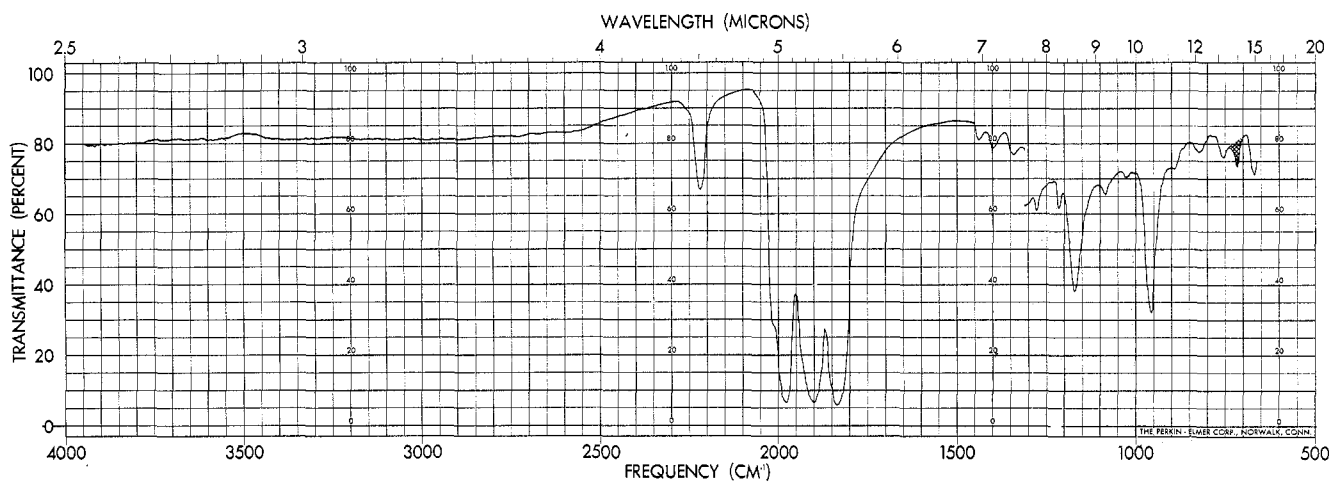
Fig. 3.—Infrared spectrum of $(CH_2CHCN)_3W(CO)_3$, C_{2v} (*trans*), in hco–Nujol.
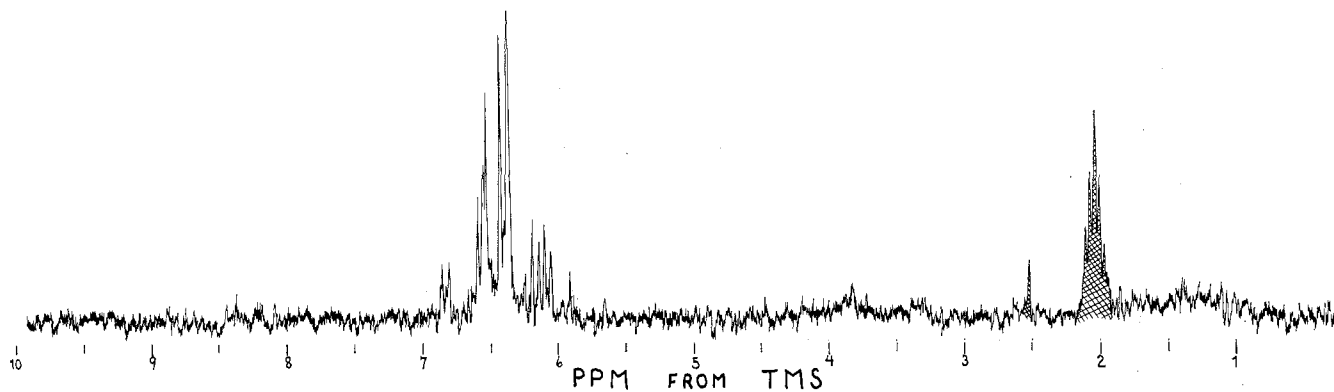
Fig. 4a.—Proton magnetic resonance spectrum of $(CH_2CHCN)W(CO)_5$, C_{4v}, in acetone-d_6.
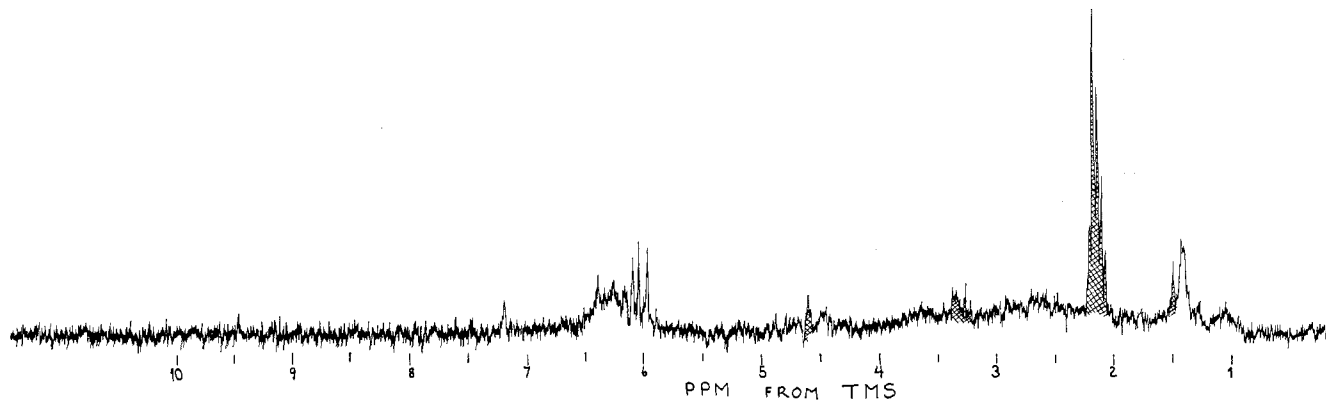
Fig. 4b.—Proton magnetic resonance spectrum of $(CH_2CHCN)_3W(CO)_3$, C_{2v} (*trans*), in acetone-d_6.

the metal carbonyl region with optimum resolution for a C_{4v} structure and the least amount of hexacarbonyl impurity. Assignments of the carbonyl absorptions to the expected modes are presented in Table I. The $A_1{}^{1a}$ mode is of lower energy than the E mode, similar to what was found for the mono-acetonitrile complex discussed above. The same reasons may be cited here, as we believe in these two complexes the ligands are attached to the metal in a similar manner, *i.e.*, through the nitrogen lone pair, in contrast to bonding previously reported for acrylonitrile carbonyl complexes of other metals. The nitrile stretching frequency is shifted to a position higher than that in free acrylonitrile, to 2239 cm.$^{-1}$ in *n*-hexane (to 2252 cm.$^{-1}$ in halocarbon oil). Furthermore, the multiple carbon–carbon bond absorption in the spectrum of $(CH_2CHCN)W(CO)_5$ appears at 1601 cm.$^{-1}$, essentially unchanged from its position in free acrylonitrile (1610 cm.$^{-1}$) in agreement with recently published data.[1a] In previous complexes, *e.g.*, $(CH_2CHCN)Fe(CO)_4$,[3] in which acrylonitrile is attached through its olefinic carbon–carbon bond, the C=C stretching vibration is observed to shift to lower frequency,[2] analogous to observations for olefin–metal complexes.[15,16] Our assignment of the mode of attachment of the ligand in $(CH_2CHCN)W(CO)_5$ by infrared analyses is further supported by proton magnetic resonance (see below). Additional infrared absorptions characteristic of the ligand appear in the spectrum: CH deformation at 1410 and 962 cm.$^{-1}$ plus a weak, sharp band at 1287 cm.$^{-1}$. Attempts to prepare the monosubstituted acrylonitrile metal carbonyl complexes of Cr and Mo led to complexes which appeared to be of the type $(CH_2CHCN)_2M(CO)_2$, *cf.* ref. 6.

For the complexes $(CH_2CHCN)_2M(CO)_4$ (M = Cr, Mo, W), four new metal carbonyl bands may be recognized, implying predominance of the *cis* isomer with C_{2v} symmetry of ligands around the central atom.[11,12] The samples were difficult to purify from the hexacarbonyl. Attempted separation of the components by thin-layer chromatography was unsuccessful. The resulting complexes also gave poor infrared spectra. A representative spectrum is given in Fig. 2b. Aside from the poorer resolution due to solvent, the pattern for the carbonyl region approximates that expected for a *cis*-disubstituted complex. Since no separate absorption at lower energy is observed and the lowest energy band of the pattern appeared at normal relative intensity, we conclude that no significant amount of *trans* isomer is present. This is confirmed by comparison of spectra of phosphine complexes known to contain mixtures of isomers (*cf.* Poilblanc and Bigorgne[11]; also independently checked in this laboratory[8b,17]). In these complexes, the single absorption of the *trans*-disubstituted complex changes the appearance of the normal pattern for the *cis* isomer. We believe our conclusions about the acrylonitrile

complexes are valid, since our observed pattern was unchanged after repeated chromatographic purification. The absorptions were assigned to the expected modes of the C_{2v} symmetry.

The appearance of a C=C stretching band at 1600 cm.$^{-1}$ indicates that the ligand is not attached to the metal through this bond. Proton magnetic resonance spectra unequivocally establish that the ligand is bonded to the metal through the nitrogen lone pair (see below). In the nitrile stretching region for $(CH_2CHCN)_2W(CO)_4$ a doublet is observed, 2220 and 2235 cm.$^{-1}$, in Nujol (a single band, 2232 cm.$^{-1}$, in acetone solution). For a *cis*-disubstituted complex $(R-C\equiv N)_2MX_4$, one would expect to see two nitrile stretching frequencies (C_{2v} symmetry, one A_1 and one B_1 mode, both infrared and Raman active; these would be strictly analogous to the treatment for the carbonyl groups in *cis*-$L_4M(CO)_2$[9c,12]). This second absorption was not seen for the bis-acrylonitrile complexes of Cr and Mo. Ligand bands follow the pattern discussed for $(CH_2CHCN)W(CO)_5$. The very strong 640 cm.$^{-1}$ band in the spectrum of the chromium complex is analogous to a band in the same region of the spectrum of Cr(CO)$_6$ which has tentatively been assigned to a CO bending or a Cr–C stretching vibration.[18]

The tris-acrylonitrile complexes possess three strong metal carbonyl absorptions, as shown in Fig. 3b, and are assigned therefore the *trans*-(C_{2v}) structure. Aside from the tris-phosphite complexes of Poilblanc and Bigorgne,[11] these are the only trisubstituted complexes to show predominance of this isomer. All other tris complexes known possess the all-*cis* (C_{3v}) geometry, including the tris-acetonitrile complex from which the acrylonitrile complexes were synthesized. None of the previous papers dealing with symmetry assignments of carbonyl absorptions has treated the trisubstituted C_{2v} complexes in detail, so it is useful to present some preliminary assignments here. It is possible to arrive at a reasonable vibrational assignment for the expected modes in the trisubstituted C_{2v} complex. From considerations similar to those outlined in previous work,[12] we believe the modes would be arranged in the following order of decreasing energy: $A_1{}^{1b} > B_1 > A_1{}^{1a}$ (see Fig. 5 and Table I). It is not possible, without polarization data on these absorptions (infrared or Raman) to be absolutely certain about the relative positions of the B_1 and the $A_1{}^{1a}$ modes. It is entirely possible that in the presence of a strong π-bonding ligand in the position *trans* to the carbonyl group undergoing vibration in the $A_1{}^{1a}$ mode, it could be shifted to higher energy, and even interchanged with the B_1 mode. This would be reminiscent of the $A_1{}^{1a}$ and the E modes in C_{4v} monosubstituted carbonyls (see Cotton and Kraihanzel,[12c] remembering that the notation of Orgel[12a] is being used in this discussion).

In the tris complexes, $(CH_2CHCN)_3M(CO)_3$, the C=C stretching absorption is shifted to 1440 cm.$^{-1}$

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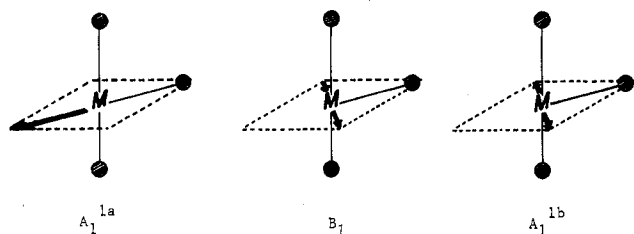
Fig. 5.—The infrared-active CO stretching modes for $L_3M(CO)_3$ molecules, C_{2v} structure: ● represents position occupied by ligand, L; → represents relative phase relation of oscillating local dipole.

$(M = W)$ or 1456 cm.$^{-1}$ $(M = Mo)$ from its position at 1610 cm.$^{-1}$ in the free ligand. On the other hand, the nitrile stretching frequency is found essentially unchanged or shifted only slightly to lower energy, 2222 or 2221 cm.$^{-1}$ $(M = W$, acetone solution or Nujol mull) or 2225 cm.$^{-1}$ $(M = Mo$, Nujol mull) from its position at 2235 cm.$^{-1}$ in the free ligand. These observations imply coordination of the ligand through the olefinic bond, and the slight shift to lower energy of the nitrile frequency reflects electron withdrawal by the $C=C$ bond with which it is conjugated. This interpretation of the infrared data is strongly supported by proton magnetic resonance (see below). The ligand, then, in the tris-acrylonitrile complexes is bonded in a similar manner as found for $(CH_2CHCN)Fe(CO)_4$,[2,3] and in contrast to that found for the mono or bis complexes in this work, as reported above. A gradual growth of the central metal carbonyl band and the shoulder at 2012 cm.$^{-1}$ in acetone solution could represent some ligand exchange with the solvent. The same effect was observed in the spectra of Nujol mulls of the complex recrystallized from acetone, and therefore the final spectral data were obtained from the crude materials. Attempts to prepare $(CH_2CHCN)_3Cr(CO)_3$ gave either $(CH_2CHCN)_2Cr(CO)_4$ or a compound similar to that obtained in the attempted preparation of $(CH_2CHCN)Cr(CO)_5$ (see above).

III. Proton Magnetic Resonance.—$(CH_3CN)Cr(CO)_5$ and $(CH_3CN)W(CO)_5$ both gave rise to a *sharp* singlet shifted downfield 0.41 and 0.59 p.p.m. from the normal location of acetonitrile which clearly indicates that complexes have formed. The two most likely bonding possibilities are either π-complexing through the nitrile group or bonding with the nitrogen through the lone pair of electrons. The latter is favored since a *greater shift* downfield would be expected with π-complexing[19] in these nonolefinic complexes.

The proton magnetic resonance of $(CH_2CHCN)W$-$(CO)_5$, $(CH_2CHCN)_2W(CO)_4$, and $(CH_2CHCN)_3W$-$(CO)_3$ clearly demonstrates the difference in bonding between the trisubstituted complex on one hand, and the mono and bis complexes on the other, and are in
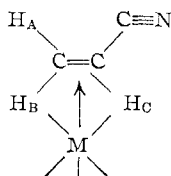
(19) See references such as (a) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961); (b) R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3600 (1961); or (c) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961). A review article covering this general topic is: J. R. Holmes, H. D. Kaesz, and S. L. Stafford, *Advan. Organometallic Chem.*, in press.

complete agreement with the interpretation of the infrared spectra. Pure acrylonitrile yields a 13-line ABC type spectrum[20] and those obtained from the mono and bis complexes are essentially identical (Fig. 4) with it, except that the resonance lines are shifted slightly downfield. These results, by comparison with the acetonitrile system, suggest that the bonding to the metal does not involve π-complexing through the olefinic bond. The mono- and bis-acrylonitrile complexes can be pictured as
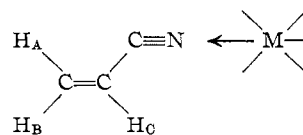
If this is the case, one would expect to find very small, if any, changes in the coupling constants and only the CH proton should show a significant chemical shift. In an attempt to verify this, the spectral parameters for the pure and complexed acrylonitrile were calculated with Castellano's EXAN II program,[21] modified for a 7090 IBM computer. The results for pure acrylonitrile and the bis complex are shown in Table II.

TABLE II
COMPUTED SPECTRAL PARAMETERS FOR BIS-$(CH_2CHCN)_2W(CO)_4$ AND UNCOMPLEXED ACRYLONITRILE

	CH_2CHCN	$(CH_2CHCN)_2$-$W(CO)_4$	Δ
δH_A, p.p.m.	370.37[a]	368.23[a]	+0.04
δH_B, p.p.m.	362.37	360.57	+0.03
δH_C, p.p.m.	339.33	347.06	−0.13
J_{AB}, c.p.s.	0.91	0.90	−0.01
J_{AC}, c.p.s.	17.94	16.84	−1.10
J_{BC}, c.p.s.	11.64	10.46	−1.20

[a] Downfield from tetramethylsilane (TMS).

Essentially identical results were obtained utilizing the Reilly and Swalen program.[22] Indeed, it is seen from these results that the only significant change in chemical shift is that for H_C and that there is no significant change in the coupling constants. The changes in J_{AC} and J_{BC} both involve H_C and this is easily explained as being due to a slight change in the C–H_C bond angle which would be expected. There can be little doubt, then, that the olefinic bond is not perturbed in the mono and bis complexes and therefore is not involved in the metal–ligand bonding.

The trisubstituted complex, on the other hand, shows a greatly perturbed resonance pattern with a new resonance line appearing 4.7 p.p.m. upfield (*i.e.*, 1.3 p.p.m. below TMS) and one downfield by 1.1 p.p.m. (*i.e.*, 7.1 p.p.m. below TMS) from the center of the usual acrylonitrile spectrum where now only a few sharp lines are observed (see Fig. 4b). These shifts are in general agreement with what can be expected for olefin

(20) Varian n.m.r. spectra catalog, Spectrum No. 15.
(21) S. Castellano, private communication.
(22) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

π-complexes of metal carbonyls.[19] In this case, the acrylonitrile complex is pictured as

H_A would be expected to appear at lowest field and H_B would be expected to appear at considerably higher field (3–5 p.p.m.) than in the free ligand. Each proton might be expected to give rise to a quartet here, but the geminal coupling constant J_{AB} may be very small (~ 0) and thus H_A and H_B may appear as poorly resolved doublets. The resonance line appearing at 7.1 p.p.m. below TMS may not have been due to the complex. Due to the limited solubility of this complex a better spectrum was not obtained and hence a more detailed analysis was not possible. However, the large upfield shift of the H_B type protons is expected and in the tris complex there is little doubt that the bonding involves an olefinic π-complex.

Conclusions

It is clear that in the mono- and disubstituted acrylonitrile complexes of the chromium sub-group carbonyls, the attachment of the ligand is through the lone pair on nitrogen, similar to that in saturated nitriles. This differs from what is observed for the tris complexes of these carbonyls, as well as for most other complexes of acrylonitrile (excepting Lewis acid types[18]) in which the ligand is attached through the olefinic carbon–carbon bond. In complexes containing more than one acrylonitrile molecule, we do not observe any evidence that there is a mixture of the two types of bonding for the several ligands.

The mode of attachment of this ligand definitely influences the stereochemistry of the final complex. The bis-acetonitrile and the bis-acrylonitrile complexes, in which the ligand is attached to the metal through the lone pair on nitrogen, are predominantly the *cis* isomers, which is readily explained by consideration of the *trans* effect,[23] where the *trans*-directing ability is in the order $C=C > C\equiv O > R-C\equiv N:\leftarrow$. On the other hand, $(CH_2=CH_2)_2Re(CO)_4{}^+$ has recently been reported[24] as the *cis* isomer. Certainly it is known that strongly π-bonding groups must compete for the same metal d-electrons if they are *trans* to each other, therefore the isolation of this compound as the *cis* isomer is not unreasonable.

The symmetry we observe for the tris-acrylonitrile complex (*trans*-C_{2v}) is unusual since we would expect the thermodynamically favored isomer to be the all-*cis* form. The C_{2v} symmetry is not easily explained on the basis of the *trans* effect.[17] The final stereochemistry may be determined by an unusual thermodynamic effect such as the spatial requirements or repulsions of the ligands, or to a kinetic effect in that the rearrangement to the thermodynamically favored isomer is slow or not allowed. A final answer will probably await detailed mechanistic study, which is currently planned by Dr. D. P. Tate of this laboratory.

Formation of a tris complex of C_{2v} symmetry from a starting material of C_{3v} symmetry affords some interesting possibilities for speculation on the nature of these substitution reactions.[17] Certainly, now that the absorptions of some of the end-products have been identified, it becomes feasible to scan the reaction mixtures directly to see whether any intermediates, and their geometries, can be identified.

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(24) E. O. Fischer and K. Ofele, *Angew. Chem.*, **74**, 76 (1962).