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PROTONATION OF METAL CARBONYL COMPLEXES

I. AN INFRARED STUDY OF THE ARENECHROMIUM TRICARBONYL AND ARENECHROMIUM DICARBONYL TRIPHENYLPHOSPHINE COMPLEXES

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SUMMARY

Through the use of IR spectroscopy, protonation of arenechromium dicarbonyl triphenylphosphine complexes in trifluoroacetic acid and in mixtures of the latter with methylene chloride, has been shown to occur at the metal atom. No protonation of arenechromium tricarbonyls appears to occur under similar conditions.

The ease of protonation appears to increase with the introduction of increasing electron-releasing substituents into the π-bonded aromatic ring.

INTRODUCTION

We have recently shown[1,2] that compounds of the type $ArCr(CO)_3$ and $ArCr(CO)_2PPh_3$ undergo hydrogen–deuterium exchange in acid media, and it has been assumed that protonation of the carbonyl complex is involved in one of the possible reaction steps. The possibility of protonation in compounds of this type has been verified previously in a number of cases. Thus, using PMR spectroscopy it was shown that arenechromium tricarbonyls and other carbonyl complexes apparently add protons at the metal atom when dissolved in a mixture of trifluoroacetic acid and boron trifluoride hydrate[3]. If protonation of carbonyl complexes does occur at the metal atom, then it may lead to a quantitative method for the determination of the basicity of the metal in the complex.

The use of IR spectroscopy could prove helpful in the study of protonation in carbonyl complexes. Protonation of a metal atom should lead to a decrease in its formal charge, which in turn may lead to a decrease in the $d_\pi(M)$–$p_\pi(CO)$ interaction in the M–C bond and to an increase in the CO stretching frequencies.

These suggestions are supported by the results obtained in other studies. Thus, in the isoelectronic series $C_5H_5M(CO)_3$, a change in the formal charge of one unit led to a shift of more than 100 cm^{-1} in ν(CO). The following values for this frequency have been observed[4]: $C_5H_5Fe(CO)_3^+$ 2120, 2070 cm^{-1}, $C_5H_5Mn(CO)_3$ 2035, 1953 cm^{-1}, $C_5H_5Cr(CO)_3^-$ 1876, 1695 cm^{-1}, $C_5H_5V(CO)_3^{2-}$ 1748, 1645 cm^{-1}. Similar results for the isoelectronic series $M(CO)_4$ provide additional evidence[5]; $Ni(CO)_4$ 2057 cm^{-1}, $Co(CO)_4^-$ 1886 cm^{-1} $Fe(CO)_4^{2-}$ 1786 cm^{-1}.

The use of IR spectra should also enable protonation at the metal atom and interaction of the proton with the carbonyl oxygen to be distinguished. Thus, in the latter case the frequency $\nu(CO)$ for interaction with the carbonyl oxygen should be lower while for the other CO groups the frequency should increase.

The same phenomenon has been observed during the interaction of the carbonyl oxygen with Lewis acids[6]. Kotz and Pedrotty[7] have used IR spectroscopy in the study of protonation. An increase in the CO stretching frequencies (over 130–150 cm^{-1}) in (phosphoniumcyclopentadienyl)chromium tricarbonyl has been observed on replacing an aprotic solvent such as chloroform with an acidic solvent such as trifluoroacetic acid.

In the present work the IR spectra of some arenechromium tricarbonyl and arenechromium dicarbonyl triphenylphosphine complexes with different substituents in the π-bonded benzene ring have been investigated in the spectral region where CO stretching frequencies normally occur.

RESULTS AND DISCUSSION

The IR spectra of the complexes $ArCr(CO)_3$ exhibit two $\nu(CO)$ modes (A_1 and E) according to the local symmetry C_{3v} of the $Cr(CO)_3$ moiety. In addition, with the complexes $ArCr(CO)_2PPh_3$, two further $\nu(CO)$ modes (A' and A'') are observed corresponding to the local symmetry C_s. Carbonyl stretching modes in the neutral solvent (cyclohexane) used in this work are listed in Table 1.

TABLE 1

THE CO STRETCHING FREQUENCIES (cm^{-1}) OF THE COMPLEXES $ArCr(CO)_3$ AND $ArCr(CO)_2PPh_3$ AS MEASURED IN CYCLOHEXANE AND CF_3COOH SOLUTIONS

Compound	*In cyclohexane*	*In CF_3COOH*	
		Non-protonated form	*Protonated form*
$CH_3OOCC_6H_5Cr(CO)_3$	1926, 1991	1939, 1997	
$C_6H_6Cr(CO)_3$	1916, 1984	1917, 1986	
$CH_3C_6H_5Cr(CO)_3$	1910, 1978	1910, 1978	
$CH_3OC_6H_5Cr(CO)_3$	1908, 1977	1907, 1978	
$(CH_3)_3C_6H_3Cr(CO)_3$	1902, 1970	1900, 1968	
$(CH_3)_2NC_6H_5Cr(CO)_3$	1886, 1962	1950, 2009	
$CH_3OOCC_6H_5Cr(CO)_2P(C_6H_5)_3$	1876, 1923	1920	1975, 2014
$C_6H_6Cr(CO)_2P(C_6H_5)_3$	1861, 1911		1968, 2014
$CH_3C_6H_5Cr(CO)_2P(C_6H_5)_3$	1855, 1905		1961, 2013
$CH_3OC_6H_5Cr(CO)_2P(C_6H_5)_3$	1852, 1905		1957, 2002
$(CH_3)_3C_6H_3Cr(CO)_2P(C_6H_5)_3$	1847, 1896		1955, 2000
$(CH_3)_2NC_6H_5Cr(CO)_2P(C_6H_5)_3$	1835, 1889		1920, 1990[a]

[a] The spectrum changes rapidly with time and is reproducible only with difficulty.

From the data in Table 1 it will be seen that a noticeable shift of the CO stretching frequencies occurs upon replacement of the ring substituents. The substitution of strong donor groups (NMe_2) by acceptor groups (COOMe) causes a shift in the ν(CO) frequency of over ca. 40 cm^{-1}. Replacement of the carbonyl ligand by a stronger donor (triphenylphosphine) decreases the value of the ν(CO) frequency by over 50–75 cm^{-1}. Such shifts, which were also reported earlier[8,9] are in good agreement with modern concepts regarding the nature of the M–C bond in carbonyl complexes.

Replacement of the neutral solvent, cyclohexane, by trifluoracetic acid did not significantly change the spectra of $ArCr(CO)_3$ complexes, the shifts in carbonyl frequencies being close to those normally observed when one solvent is replaced by another[10].

From this it follows that there is no specific interaction between the dissolved substance and the solvent, and only in (dimethylaminobenzene)chromium tricarbonyl were the ν(CO) modes shifted to high frequencies presumably through nitrogen protonation and ammonium salt formation. The band positions observed in this instance agree with the properties of the ammonium substituent which is a stronger acceptor in comparison with the carbomethoxy group[11].

In CF_3COOH solution, however, the frequencies of both the symmetric and antisymmetric CO modes of the triphenylphosphine derivatives increase by over ca. 100 cm^{-1}, *i.e.* protonation of the molecule may be assumed to occur under these conditions. The fact that these two bands are shifted simultaneously eliminates the possibility of protonation at the carbonyl oxygen, and from the observed value of the shift it must be concluded that protonation occurs at the metal atom. If protonation occurred in the aromatic ring then the bands would be shifted in the same direction but to a lesser extent. Data obtained from PMR spectroscopy support protonation at the metal atom and do not agree with protonation at the aromatic ring or carbonyl ligand.

Although no protonation of $ArCr(CO)_3$ complexes was observed in trifluoroacetic acid by IR spectroscopy, replacing the solvent by the stronger acid $BF_3 \cdot H_2O$ gives rise to PMR signals corresponding to protonation at the metal atom in the high field region ($\delta \approx -4$)[3]. Substituting one carbonyl group by a triphenylphosphine ligand increases the metal basicity and leads to protonation by the weaker trifluoroacetic acid. PMR spectra of $ArCr(CO)_2PPh_3$ complexes [$Ar = CH_3C_6H_5$, $(CH_3)_3C_6H_3$, $CH_3OC_6H_5$] exhibit doublet signals in the high field region $\delta = -4.27$, -4.08 and -4.56; $J(H\text{-}Cr\text{-}^{31}P) = 63$, 67 and 69 Hz respectively, corresponding to direct protonation of the chromium atom. From the values of the chemical shifts and the spin–spin coupling constant with ^{31}P, such protonation of the metal is quite favourable. The PMR data will be discussed in detail in Part II of this series.

In acetic acid, which is even weaker than trifluoroacetic acid, no protonation occurs even with triphenylphosphine-substituted compounds, the measured spectra being, in fact, similar to those in a neutral solvent. Triphenylphosphine-substituted complexes are virtually completely protonated in CF_3COOH where no bands corresponding to a non-protonated form were revealed in the spectra.

The only exception to this rule is the carbomethoxy derivative. This complex shows a weak absorption at 1920 cm^{-1} (non-protonated form) in addition to bands for a protonated compound. The second band of the non-protonated form could not be detected because of its overlap with the strong solvent absorption.

This last observation indicates that the presence of an electron-attracting substituent in the aromatic ring decreases the basicity of the metal and hinders its protonation. From the data presented it will be seen that an equilibrium of the type $ArCr(CO)_2L + H^+ \rightleftharpoons [ArCr(CO)_2LH]^+$ is set up in the system, the position of equilibrium depending upon the acidity of the medium, the nature of ligands at the metal atom and of the substituents in the aromatic ring.

To obtain more detailed information regarding this dependence, the IR spectra of triphenylphosphine derivatives have been investigated in various mixtures of trifluoroacetic acid and methylene chloride. The CO stretching frequencies, obtained at the molar ratios of CF_3COOH/CH_2Cl_2 equal to 1/4 and 1/10 are recorded in Table 2. It can be seen that at a value of 1/4 all compounds, with the exception of the $COOCH_3$ derivative, are completely protonated. At the ratio 1/10, the mesitylene and anisole derivatives are completely protonated, the carbomethoxy derivative is non-protonated while the benzene and toluene derivatives exhibit the presence of both forms, displaying four ν(CO) bands in the spectra.

TABLE 2

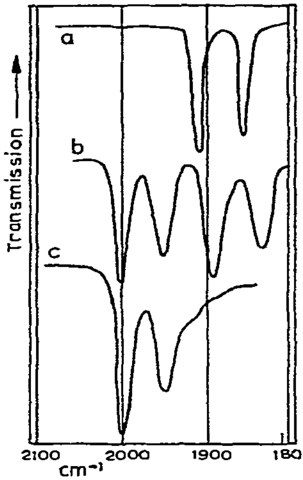
THE CO STRETCHING FREQUENCIES (cm^{-1}) OF $ArCr(CO)_2P(C_6H_5)_3$ IN CF_3COOH/CH_2Cl_2 MIXTURES

Ar	*In CF_3COOH/CH_2Cl_2*			
	1/4		1/10	
	Non-protonated form	*Protonated form*	*Non-protonated form*	*Protonated form*
$CH_3OOCC_6H_5$	1865, 1917		1870, 1915	
C_6H_6		1952, 2001	1835, 1891	1948, 2000
$CH_3C_6H_5$		1947, 1997	1885	1947, 1996
$CH_3OC_6H_5$		1950, 1995		1947, 1995
$(CH_3)_3C_6H_3$		1942, 1987		1940, 1987

The spectra of $C_6H_6Cr(CO)_2PPh_3$ in cyclohexane and in 1/4 and 1/10 mixtures of CF_3COOH and CH_2Cl_2 are shown in Fig. 1.

No quantitative information is at present available regarding the acidity functions H_0 of CF_3COOH solutions in CH_2Cl_2. Thus, it is not possible to estimate quantitatively the equilibrium constants for the protonation reactions. However a qualitative measure of these constants may be obtained from a study of the effects of ring substitutents on the ability of complexes to undergo protonation. For this purpose, the spectrum of each compound was measured at concentrations of CF_3COOH sufficient to allow the presence of both protonated and non-protonated forms in the system.

The ratio of the band optical densities for the protonated and non-protonated forms *versus* the molar concentration of CF_3COOH in methylene chloride is shown in Fig. 2. Since a low-frequency band for the non-protonated form overlaps the solvent absorption band, the ratios were measured only for the high-frequency bands



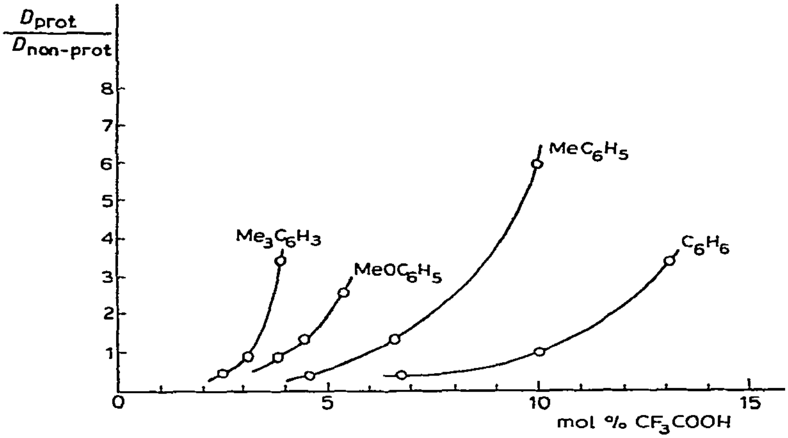


Fig. 1. IR spectra of $C_6H_6Cr(CO)_2P(C_6H_5)_3$ in (a) cyclohexane, (b) in a 1/10 mixture of CF_3COOH/CH_2Cl_2 and (c) in a 1/4 mixture of CF_3COOH/CH_2Cl_2.

Fig. 2. The ratio of band optical densities for the protonated and non-protonated forms of substituted arene chromium dicarbonyl triphenylphosphine complexes ($D_{\text{prot}}/D_{\text{non-prot}}$) in relation to the molar ratio of CF_3COOH in methylene chloride solvent.

(symmetric CO modes). The ratio $D_{\text{prot}}/D_{\text{non-prot}}$ is proportional, but not equal, to the concentration of both forms due to the difference in the absorption coefficients.

As is clearly demonstrated in Fig. 2, the introduction of donor substituents into the benzene ring enhances protonation. Thus, for the mesitylene, anisole, toluene and benzene derivatives when $D_{\text{prot}}/D_{\text{non-prot}} = 1$ the acid concentrations are equal to ca. 2.8, 3.5, 5.6 and 9.5 molar % respectively.

Although no data are included in Fig. 2 for the carbomethoxy derivative, it may be mentioned that even at an acid concentration of ca. 30 molar % its protonated form was still not observable.

From this it follows that the protonation ability of the complexes $ArCr(CO)_2$-PPh_3 decreases in the series Ar $= Me_3C_6H_3 > MeOC_6H_5 > MeC_6H_5 > H > MeO$-$OCC_6H_5$. It is interesting to point out that the ionization potentials of the respective aromatic compounds[12], the CO stretching frequencies of the complexes and the sums of the Hammett constants, σ, of the benzene ring substituents[11] also increase in the same sequence. Thus the presence of substituents in the π-bonded aromatic ring has a considerable influence upon the metal basicity of the complex. Unlike electron attractive groups, donor substituents increase the electron density at the metal atom and facilitate protonation reaction.

It is interesting to compare the results obtained with those of hydrogen–deuterium exchange reactions carried out in acidic media under similar conditions. No protonation of arene chromium tricarbonyl complexes was observed in trifluoroacetic acid and no exchange of the benzene ring hydrogens for deuterium occurred in deuterotrifluoroacetic acid. Under the same conditions, arenechromium dicarbonyl triphenylphosphine complexes (for which the IR spectra indicate protonation) underwent hydrogen–deuterium exchange involving their π-benzene ring hydrogen atoms[1,2]. However, the relationship between the ease of protonation and the rate of exchange is complicated. For example, for compounds with electron-releasing substituents in the series $ArCr(CO)_2PPh_3$, the rate constants for isotopic hydrogen exchange are smaller than the corresponding values for benzenechromium dicarbonyl triphenylphosphine[1,2]. For $Ar=C_6H_6$ and C_6H_5OMe the values of $K \cdot 10^7$ at 27.7° are 5.0 ± 0.5 and 1.9 ± 0.4 sec^{-1} respectively, whilst for $Ar=Me_3C_6H_3$, $K \cdot 10^7$ at 27.7° is equal to 1.9 ± 0.2 sec^{-1}. Thus in the complexes investigated in this study, protonation at the metal atom could be an individual reaction competing with isotopic hydrogen exchange or it could be one of the reaction steps. It is not, however, the slowest and hence rate-determining step.

EXPERIMENTAL

Arenechromium tricarbonyls were synthesized by the method described previously[13]. Arenechromium dicarbonyl triphenylphosphine complexes were obtained from arenechromium tricarbonyls and triphenylphosphine by the use of UV irradiation[14]. Toluenechromium dicarbonyl triphenylphosphine and (dimethylaniline)-chromium dicarbonyl triphenylphosphine were synthesized directly.

Toluene(triphenylphosphine)chromium dicarbonyl

M.p. 157–158° (heptane). (Found: C, 70.15; H, 5.07; P, 6.72. $C_{27}H_{23}CrO_2P$ calcd.: C, 70.13; H, 4.98; P, 6.71%.)

*(Dimethylaniline)(triphenylphosphine)chromium dicarbonyl**

M.p. 189–191° (heptane). (Found: C, 67.98; H, 5.37; P, 6.51; N, 2.81. $C_{28}H_{26}CrNO_2P$ calcd.: C, 68.4; H, 5.30; N, 2.85; P, 6.31%.)

The IR spectra were measured on a Zeiss UR-20 instrument using an LiF prism. A vibrational–rotational spectrum of DCl was used for calibration. Solution preparation and cell filling were performed under an argon atmosphere. Spectra were measured immediately after preparation of the solutions.

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