ELECTRONIC EFFECTS IN GROUP VIB ARENE-METAL CARBONYL COMPLEXES AND RELATED SPECIES

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INTRODUCTION

The study of the electronic effects in metal–arene complexes is of some theoretical interest in view of the nature of the bonding involved in attachment of the ligand to the metal in these compounds. It is generally accepted that the metal–ligand bonding may be divided into two parts, the forward coordination in which the ligand donates electrons to the metal and the back-donation whereby filled metal *d* orbitals interact with vacant (usually antibonding) orbitals of the ligand[1].

It is of interest to determine how the chemical properties of the arene ligand may be discussed in terms of these two types of orbital interaction. In the case of substituted benzenechromium tricarbonyls there is a considerable amount of evidence to show that the π-complexed $Cr(CO)_3$ group exerts a net electron withdrawing effect on the ring. Various p*K* measurements have shown that anilinechromium tricarbonyl is a weaker base than aniline and that benzoic-acid-chromium tricarbonyl and phenylacetic-acid-chromium tricarbonyl are both stronger than the corresponding uncomplexed acids[2,3]. Also, chlorobenzenechromium tricarbonyl undergoes ready nucleophilic substitution, sodium methoxide giving the corresponding anisole complex in high yield at moderate temperatures[2]. The high dipole moment (5.08 D) of benzenechromium tricarbonyl, in which the benzene ring forms the positive end of the dipole, is also fairly indicative of net electron donation from the ligand[4].

If the metal tricarbonyl is taken as a substituent then the forward coordination can be considered to exert a $-R$ effect and although this is an obviously important interaction there seems to be no reason why it should always be dominant. In certain reactions involving chemical change on the arene moiety the back-donation ($+R$ effect) might become more important*. The most likely reactions would be those in which a full or partial positive charge is developed on the ligand during the chemical change.

The present paper deals with attempts to establish the $+R$ effect of the metal-tricarbonyl group in the arene-metal carbonyl complexes. Some evidence for the existence of this back-donation can in fact be found in Whiting's data[2]. Whereas the effect of the π-$Cr(CO)_3$ group on the acidity of phenylacetic acid is almost exactly the same as that of the *p*-NO_2 group, the corresponding electron withdrawing effect of the π-$Cr(CO)_3$ group in the benzoic acid series is much less than that of the *p*-NO_2 group.

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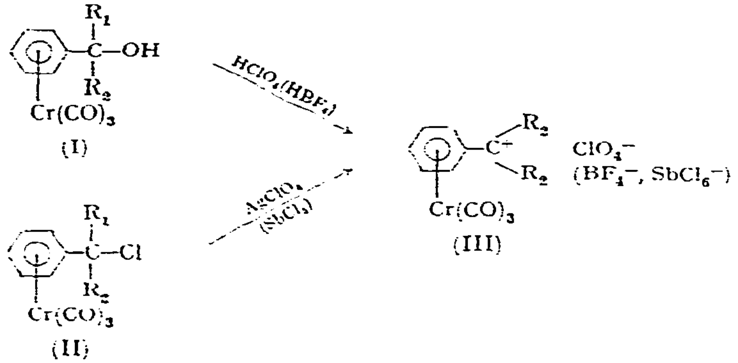
[*] With $\pm R$ electronic effects, π-complexed groups such as $Cr(CO)_3$ are similar, for example, to a nitroso group.

If the Hammett σ value for p-NO_2 is taken as 0.82 in both series[5], the calculated σ values for the π-$Cr(CO)_3$ group are 0.62 in the phenylacetic acid series and 0.81 in the benzoic acid series respectively. Anomalously high σ values are observed in benzoic acid series for $+R$ substituents such as p-Cl and p-OMe which preferentially stabilize the undissociated acid relative to the anion, thus making the observed acidity anomalously low[5,6]. Whiting suggests that the differing effects of the π-$Cr(CO)_3$ group in the benzoic acid and phenylacetic acid series may be due to steric effects; this may be partially true but the above is a valid alternate explanation.

RESULTS AND DISCUSSION

Our first approach was to attempt the synthesis of a stable π-complexed carbonium ion salt. The benzyl cation and its derivatives appeared to be most suited for this purpose as the back-donation from the metal could take place into non-bonding molecular orbitals and thus would not destabilize the internal bonds of the ligand. Accordingly the synthesis of salts of the benzylchromium tricarbonyl cations (III) was attempted by the two schemes shown.

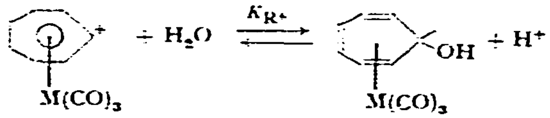


Benzyl-alcohol-chromium tricarbonyl (I, $R_1 = R_2 = H$) when treated with strong acids underwent very rapid reaction but no stable salts could be isolated. In all cases rapid decomposition occurred and carbon monoxide was evolved. No greater success was attained in these experiments using complexes in which the non-complexed ligand itself was known to form stable carbonium ions under similar reaction conditions. These alcohol complexes (I, $R_1 = H$, $R_2 = Ph$; $R_1 = R_2 = Ph$; $R_1 = Ph$, R_2 = 2-thienyl[7]), as well as the corresponding chloro complexes, each underwent decomposition with liberation of carbon monoxide when treated in the manner indicated.

Hydride ion abstraction from 9,10-dihydroanthracenechromium tricarbonyl using $SbCl_5$ was also tried but again decomposition with evolution of carbon monoxide occurred. The uncomplexed hydrocarbon readily forms the anthracenium cation under these conditions[8].

The failure to isolate salts of the complexed cations cannot be taken as evidence against a $+R$ effect operating by the metal. In fact the most ready explanation for the facile decarbonylation which occurred would be that electron density was transferred to the cationic ligand at the expense of back-donation to the carbonyl groups with consequent weakening of the metal–CO linkages.

Because of the facile decarbonylation of the complexed benzylic cations attention was directed to a study of the stability of tropylium-metal tricarbonyl salts. These salts were already known[9–11] and can be conveniently made by hydride ion abstraction from the corresponding tropylidene complexes[12]. These complex cations, in the form of fluoroborate salts, were found to be sufficiently stable to allow the positions of the equilibria



to be measured. The results are as shown.

	K_{R^+}	pK_{R^+}
$C_7H_7^+BF_4^{-\,a}$	1.8×10^{-5}	4.7
$C_7H_7Mo(CO)_3^+BF_4^-$	6.7×10^{-7}	6.2
$C_7H_7Cr(CO)_3^+BF_4^-$	4.9×10^{-7}	6.3
$C_7H_7W(CO)_3^+BF_4^-$	$\sim 10^{-6}$	~ 6

[a] Von Doering and Knox[13] report $K_{R^+} = 1.8 \times 10^{-5}$ at 25°.

These data clearly indicate that the attachment of the $M(CO)_3$ grouping to the seven-membered ring has the effect of stabilizing the cation relative to the conjugate base. A ready explanation for the reduced electrophilicity of the tropylium cation when attached to the metal tricarbonyl is seen if one invokes the concept of increased back-donation in the cationic complex relative to the neutral alcohol complex.

The following infrared data* for the $\nu_{C\equiv O}$ stretching bands of the complexed tropylium cations and the corresponding neutral tropylidene complexes are also consistent with this electronic shift.

	$\nu_{C\equiv O}$ (cm^{-1})		
$C_7H_8Mo(CO)_3$	1908	1925	1994
$C_7H_7Mo(CO)_3^+BF_4^-$	2003	2032	2077
$C_7H_8Cr(CO)_3$	1905	1927	1985
$C_7H_7Cr(CO)_3^+BF_4^-$	1989	2022	2065

In the salts the $\nu_{C\equiv O}$ absorptions are displaced 80–100 cm^{-1} to higher frequencies. Back-donation into the antibonding orbitals of the CO groups is reduced because of the demands of the tropylium ligand, the C≡O force constants and stretching frequencies are therefore correspondingly raised. This argument is not conclusive however because a reduction of the forward coordination by the C_7 moiety in the cations,

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* Honnen[14] measured in nujol. We have also measured the spectra with very similar results.

as compared to that in the tropylidene complexes, might be expected and this too would have the effect of increasing the carbonyl stretching frequencies in the cations.

Some final support for the concept of a $+R$ effect attributable to the metal tricarbonyl group is seen in the following rate studies of the solvolysis of benzylchloride-chromium tricarbonyl and benzhydryl-chloride-chromium tricarbonyl in 80% aqueous acetone at 25°. Fig. 1 shows the data for the solvolysis of benzylchloride-chromium tricarbonyl and also shows the effect of added salts. Generally the solvolyses were found not to be strictly first order, the calculated first order rate constant decreasing as the percentage reaction increased. Most significant is the effect of the common ion salt LiCl which produces a marked decrease in rate. This behavior and the general shape of the curves shown in Fig. 1 are those expected for an S_N1 reaction proceeding via a carbonium ion intermediate[15,16].

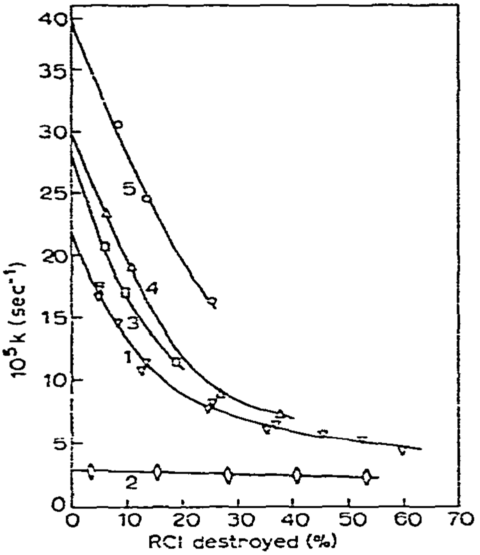

Fig. 1. Solvolysis of benzyl-chloride-chromium tricarbonyl in 80% aqueous acetone: (1) neutral with no added salt; (2) 0.004 M LiCl; (3) 0.0041 M LiClO$_4$; (4) 0.002 M NaOH; (5) 0.0041 M NaOH.

$$\mathrm{RCl} \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \mathrm{R^+ + Cl^-} \xrightarrow{(3)} \text{Products}$$

The effect of addition of LiClO$_4$ produced only a slight increase in reaction rate due to the increase in ionic strength.

In the benzhydryl series similar kinetic behavior and salt effects were observed, in particular the addition of LiCl caused a pronounced decrease in the first order rate constant.

Extrapolation of the rate data measured in the absence of added salts to zero time gave a value of 2.2×10^{-4} sec^{-1} for the initial first order rate of solvolysis of benzyl-chloride-chromium tricarbonyl and 7×10^{-2} sec^{-1} for benzhydryl-chloride-chromium tricarbonyl. The rates for the corresponding uncomplexed chlorides under the same conditions are 1×10^{-9} sec^{-1} and 6.9×10^{-5} sec^{-1} respectively*; the π-$Cr(CO)_3$ group thus increases the rates by factors of $\sim 10^5$ and $\sim 10^3$ respectively. The most reasonable explanation for this rate enhancement is preferential stabilization of the carbonium ion intermediates over that of the starting complexes due to increased back-donation from the chromium atom to the benzylic cation ligand. Thus the kinetic data is consistent with the previous pK_{R^+} data.

A result which is perhaps not in immediate accord with the S_N1 reaction scheme proposed for these solvolyses is the marked increase in rate with added base. This is illustrated in Fig. 1 for the benzyl-chloride-chromium tricarbonyl series. The increase is much greater than that expected solely on the basis of an increase in ionic strength, and furthermore the rate enhancement seems to be proportional to the amount of base added. The effect may be due to concurrent S_N2 reaction or to a special salt effect[18] involving a decrease in return of ion pairs (step 2). Although we have not pursued this further it is of interest to note that a similar situation has been observed in the solvolysis of methylferrocenylmethyl benzoate** by Hill and Richards[19].

EXPERIMENTAL

Benzyl-alcohol-chromium tricarbonyl

This was prepared by the method of Whiting and Nicholls[2]. Treatment with $HClO_4$ and HBF_4 in Ac_2O gave only rapid decomposition.

Benzyl-chloride-chromium tricarbonyl

Benzyl-alcohol-chromium tricarbonyl[2] (2 g) in benzene (50 ml) was shaken with concentrated hydrochloric acid (40 ml) for 10 minutes. The benzene layer was separated washed with water (2 × 50 ml), dried over Na_2SO_4 and evaporated. Recrystallization of the crude product from petroleum ether gave 1.6 g (74 %) yellow needles, m.p. 63-64°. (Found: C, 46.05; H, 2.94; Cl, 13.32. $C_{10}H_7ClCrO_4$ calcd.: C, 45.80; H, 3.05; Cl, 13.51 %.) Treatment with $AgClO_4$, $AgBF_4$, or $SbCl_5$ in nitromethane resulted only in decomposition.

9,10-Dihydroanthracenechromium tricarbonyl

This has been reported previously by Fischer and co-workers[21]; however, by using the preparative method of Whiting and Nicholls[2], the yield was increased to 22 %. Attempted hydride ion abstraction with $SbCl_5$ led to immediate decomposition.

Benzophenonechromium tricarbonyl

Benzophenone (40 g) was refluxed with chromium hexacarbonyl (20 g) in diglyme (150 ml) for 6 hours with mechanical return of the chromium hexacarbonyl. The solution was cooled and ether (100 ml) was added. After filtration the solvent

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* The rate for benzyl chloride was estimated from the data of Swain and co-workers[17] who reported the study in 50 % aqueous acetone at 30° by assuming that change to 80 % has the same relative effect as in benzhydryl chloride solvolysis.

** The enhanced rate of solvolysis of α-metallocenylmethyl acetates, as well as the facile addition of acids to vinylmetallocenes[20], has been interpreted through a direct interaction between the metal atom and the carbonium ion center at the α position, in other words, a neighboring group participation. The enhanced rates of solvolysis observed in the present series of metal carbonyl complexes could possibly involve a similar type of neighboring group effect, but there is no evidence which favors such a description over the one involving enhanced back-donation discussed above.

was removed under reduced pressure to give a mixture of the complex and unreacted benzophenone. The mixture was separated by chromatography over alumina. Successive elution with petroleum ether and benzene gave first unreacted benzophenone and then the complex (orange band). The solvent was removed under reduced pressure and the product was recrystallized from petroleum ether/benzene to give 5.2 g (18 %) of orange-red needles, m.p. 88–89°. (Found: C, 60.75; H, 3.27. $C_{16}H_{10}CrO_4$ calcd.: C, 60.38; H, 3.14 %.)

Diphenylmethanolchromium tricarbonyl

Benzophenonechromium tricarbonyl (0.4 g) in methanol (20 ml) was stirred with sodium borohydride in portions until the characteristic orange color of the complex was completely converted to pale yellow. The mixture was then poured into ice–water and 0.4 g (99 %) pale yellow crystals were obtained. Recrystallization from petroleum ether/benzene gave yellow needles, m.p. 99.5–100.5°. (Found: C, 59.65; H, 4.09. $C_{16}H_{12}CrO_4$ calcd.: C, 60.00; H, 3.75 %.)

Triphenylmethanolchromium tricarbonyl

A solution of phenylmagnesium bromide in ether was carefully added to a stirred solution of benzophenonechromium tricarbonyl (0.5 g) in ether (30 ml) until the orange color had completely disappeared. After an additional 15 minutes the mixture was poured into saturated ammonium chloride. The ethereal layer was separated, dried over magnesium sulfate and evaporated. Recrystallization of the residue from petroleum ether/benzene gave 0.45 g (73 %) yellow crystals, m.p. 139.5–140.5°. (Found: C, 67.05; H, 4.22. $C_{22}H_{16}CrO_4$ calcd.: C, 66.67; H, 4.04 %.)

A cold solution of 0.1 g of complex alcohol in acetic anhydride was treated with a cold solution of perchloric acid in acetic anhydride. A green solution was obtained which gave off a gas slowly, more rapidly at higher temperatures. When poured into ice–water, a white solid was obtained which was identified as triphenylmethanol.

Diphenylthienylmethanolchromium tricarbonyl

An ethereal solution of 2-thienylmagnesium iodide [from 2-iodothiophene (4 g), magnesium (1 g)] was added slowly to a stirred solution of benzophenonechromium tricarbonyl (0.4 g) in ether (20 ml) until the orange color was discharged. The mixture was worked up as previously and gave 0.35 g (71 %) of yellow needles, m.p. 132–133.5°. (Found: C, 59.68; H, 3.35. $C_{20}H_{14}CrO_4S$ calcd.: C, 59.70; H, 3.51 %.) With acids in polar media such as nitromethane only decomposition resulted.

Benzhydryl-chloride-chromium tricarbonyl

Anhydrous hydrogen chloride was bubbled into a cooled stirred solution of diphenylmethanolchromium tricarbonyl (1.3 g) in ether (100 ml) for 1 hour. The ether was evaporated and the residue was recrystallized from petroleum ether to give 1.06 g (77 %) yellow needles, m.p. 76.5–77.5° (dec.). (Found: C, 56.77; H, 3.48. $C_{16}H_{11}ClCrO_3$ calcd.: C, 56.73; H, 3.27 %.)

Kinetic studies

The method was essentially that of Hughes, Ingold and co-workers[21]. The reaction was followed by titration with sodium hydroxide using bromothymol blue.

Infinity titres were usually taken at 10 half-lives, and were within 5% of the theoretical in all cases. Instantaneous first order rate constants were calculated from the equation $kt = 2.303 \log [V_\infty/(V_\infty - Vt)]$ (for full details see ref. 23). The results for benzyl chloride chromium tricarbonyl are shown in Fig. 1, the results for benzhydryl-chloride-chromium tricarbonyl are given below.

	Case I (*no salts added*)			*Case II* (*0.008 M in LiCl*)			*Case III* (*0.008 M in KOH*)	
Time (min)	0.5	1	2	0.5	2	3.5	0.5	1
RCl destroyed (%)	48	62	78	24.7	57.9	75	77.2	86.2
$10^3 k$ (sec^{-1})	21.9	16.1	12.8	9.5	8.6	6.6	49.2	32.9

For benzhydryl chloride itself the method gave $k = 6.94 \times 10^{-5}$ sec^{-1} which is in good agreement with the previous reported[24] value 7.24×10^{-5} sec^{-1}.

Product analysis

(*1*) *Benzyl chloride complex.* Benzyl-chloride-chromium tricarbonyl was dissolved in 50% aqueous acetone (100 ml). After 2 hours at 25°, water was added and the solution was extracted with ether (3 ×). The ether extracts were washed with water (2 × 50 ml), 5% sodium carbonate (1 × 50 ml), and dried over magnesium sulfate. Evaporation gave 0.153 g (82%) benzyl-alcohol-chromium tricarbonyl, m.p. 93–94°, undepressed when mixed with an authentic sample.

In 80% aqueous acetone the yield is only 27%; considerable decomposition occurs during the 3-day reaction time.

(*2*) *Benzhydryl chloride complex.* Benzhydryl-chloride-chromium tricarbonyl (0.130 g) was dissolved in 50% aqueous acetone. After 1.25 hours at 25°, the mixture was worked up as above to give 0.139 g (113%) yellow solid, m.p. 89–96°. Recrystallization from petroleum ether gave 0.066 g yellow needles, m.p. 98–100°. A mixed m.p. with authentic benzhydrol complex showed no depression.

pK_{R^+} measurements

The pH's of known concentrations, usually 0.01 *M*, of complexed fluoroborate salts in water was measured at 30.0 ± 0.1° using a Metrohm pH meter. Values of K_{R^+} were then calculated by substitution in the equation $K_{R^+} = [H^+]^2/\{[C_7H_7M(CO)_3^+BF_4^-]_0 - [H^+]\}$. For tropylium itself, the experimental K_{R^+} agreed very well with that reported previously by Doering and Knox[13].

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SUMMARY

Evidence has been sought for the stabilization of aromatic carbonium ions following π complex formation with a metal carbonyl group. Attempts to isolate salts

of the benzylchromium tricarbonyl cation and various members of this class have been unsuccessful due to the rapid decarbonylation of the system. However, the stability of the tropylium-M(CO)$_3$ cations (M = Cr, Mo and W) is found to be greater than that of tropylium itself towards attack by nucleophiles. Further evidence for the stabilization of the cations by the metal is seen in the enhanced rates of solvolysis of benzyl-chloride-chromium tricarbonyl and benzhydryl-chloride-chromium tricarbonyl.

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