*Contribution from the Department of Chemistry,
University College, Belfield, Dublin 4, Ireland*

Electrophilic Substitution Reactions of Tricarbonylarenemetals

D. A. Brown and F. J. Hughes

Received September 15, 1967

Attempted kinetic studies of the acetylation of tricarbonylbenzenechromium are reported. It is shown that the Lewis acid, aluminium trichloride, reacts directly at the chromium atom to give $Cr^{II}(Al_2Cl_6)(CS_2)_2$; consequently no theoretical conclusions on relative reactivities of free arene and π-bonded arenes can be drawn from this system. It is suggested that additional electrophilic substitution at the metal atom may occur on Friedel Crafts reactions of all metal-organic systems.

Introduction

The electrophilic substitution reactions of the metallocenes have been studied extensively.[1] Relative rate data for Friedel-Crafts acetylation in the presence of aluminium chloride as Lewis acid show that ferrocene is approximately 10^6 times more reactive than benzene. In the case of the tricarbonylarenechromiums, it was originally reported[2] that only nucleophilic substitution occurred readily and that no acetylation proceeded under the above conditions; however, this was subsequently shown by two groups independently to be incorrect.[3,4] It has also been observed that acetylation of tricarbonyltoluenechromium[5] proceeds apparently with more difficulty than toluene and yields an isomer distribution of o, 39%; m, 46%; p, 15% compared to o, 9.5%; m, 1,5%; p, 89% for toluene ; similarly , tricarbonylalkylbenzenechromiums give unusual isomer distributions.[6] Application of simple molecular-orbital theory to both nucleophilic and electrophilic substitution reactions of tricarbonylbenzenechromium[7] showed that for all reasonable values of the theoretical parameters employed, nucleophilic substitution should be enhanced relative to the free arene. This prediction was subsequently verified by a detailed kinetic study of the nucleophilic substitution of tricarbonylchlorobenzenechromium and tricarbonylfluorobenzenechromium by methoxide ion with the formation of the corresponding anisole π-complex.[8]

$$\pi\text{-}XC_6H_5Cr(CO)_3 \xrightarrow[\text{MeOH}]{\text{MeO}^-} \pi\text{-}MeOC_6H_5Cr(CO)_3$$

To date no kinetic studies of electrophilic substitution of these compounds have been reported and the enhanced rate of deuteration of tricarbonylbenzenechromium relative to benzene by deuterated alcohols and amines in the presence of alkali[9] is undoubtedly an example of nucleophilic rather than electrophilic substitution. We have reported previously, however, that tricarbonylbenzenechromium gives about 30% yield of the acetophenone complex on acetylation in carbon disulphide at 0°C whereas under the same conditions benzene gives negligible yields of acetophenone. In view of this rather confusing situation we have attempted to study the kinetics of the acetylation of tricarbonylbenzenechromium and report the results below.

Experimental Section

Tricarbonylbenzenechromium was prepared as in the literature.[2] Aluminium trichloride was purified by a modification of the method of Brown and coworkers.[10] Aluminium trichloride, covered by a 1.5 cm layer of aluminium, was placed in a sublimation apparatus and heated to just below the sublimation temperature for several hours at 1.0 mm. to decompose any hydrated aluminium chloride present. 50 mm. of dry nitrogen was introduced into the system, and the temperature raised until the aluminium chloride slowly sublimed. This process was repeated at least three times. All solvents and reactants were purified, dried and deoxygenated and manipulations carried out in an inert dry atmosphere. The infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer. The electronic spectra were recorded on a Unican S.P. 500 spectrophotometer with a reflectance attachment which could be flushed with dry nitrogen. Magnetic susceptibility was determined at room temperature by a Gouy balance. Analytical data for chromium and aluminium was obtained by colorimetric methods.[11] Chlorine was determined by pontentiometric titration with silver nitrate. Carbon analysis was carried out by the microanalytical laboratory, U.C.D.

Kinetic Experiments. Acetylation of tricarbonylbenzenechromium at 0°C. Tricarbonylbenzenechromium (1.079 g) was dissolved in 25 mls ethylene

---

(1) M. Rosenblum, «Chemistry of the Iron Group Metallocenes», John Wiley & Sons, New York, Chap. 4 (1965).

(2) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(3) R. Riemschneider, O. Becker and K. Franz., *Monatsh.*, *90*, 571 (1959).

(4) E. Ercoli, F. Calderazzo and E. Mantica, *Chimica e Industria*, *41*, 404 (1959).

(5) G. E. Herberich and E. O. Fischer, *Chem. Ber.*, *95*, 2803 (1963).

(6) W. R. Jackson and W. B. Jennings, *Chem. Comm.*, *22*, 842 (1966).

(7) D. A. Brown, *J. Chem. Soc.*, 4389 (1963).

(8) D. A. Brown and J. R. Raju, *J. Chem. Soc.*, (A), 40 (1966).

(9) V. N. Setkina, N. K. Barnetskava, K. N. Anisimov and D. N. Kursanov, *Izvest. Akad. Nauk. SSSR*, *10*, 1873 (1964).

(10) H. C. Brown and F. R. Jensen, *J. Amer. Chem. Soc.*, *80*, 2291 (1958).

(11) Saltzmann, *Anal. Chem.*, *24*, 1016 (1952). Snell and Snell, Colorimetric methods of analysis, Vol. II, 3rd ed., published by D. Van Nostrand Co. Inc. (1949).

dichloride; aluminium trichloride (0.6675 g) and acetyl chloride (0.4075 g) were also dissolved in 25 mls ethylene dichloride. Both solutions were stirred for two hours at 0°C and on mixing a dark brown colour developed instantly. 3 ml Samples were removed by means of a hypodermic syringe and hydrolysed with ice-water and the organic layer dried over sodium sulphate. The tricarbonylacetophenonechromium was determined by the appearance of the ketonic carbonyl band at 1692 cm^{-1}, a Beers law plot for this band being linear for the concentrations used. To determine the applicability of this method to the acetylation experiment, the kinetic work of Brown and co-workers[12] was repeated and our results are in good agreement with their published results.

Reaction of tricarbonylbenzene with aluminium trichloride in nitromethane. 0.4 g Tricarbonylbenzenechromium in 15 mls nitromethane and 0.470 g ($2 \times M$) aluminium trichloride in 15 mls nitromethane were mixed together at room temperature in a nitrogen atmosphere. A dark red-brown colour developed immediately and CO was rapidly evolved as evidenced by the disappearance of the metal-carbonyl bands in the infrared spectrum of the mixture after five minutes of reaection. The reaction mixture was stirred for five hours and the solvent removed at 30°C and 0.2 mm pressure. The examination of this solution by G.L.C. established the quantitative release of benzene from the tricarbonylbenzenechromium. After sublimation of unreacted material, a reddish-brown solid was obtained which x-ray powder methods and stereoscopic microscopic examination showed to be a glass, with inconsistent analysis although the ratio Cr:2Al:6Cl was established.

Reaction of tricarbonylbenzenechromium with aluminium trichloride in carbon disulphide. Tricarbonylbenzenechromium (0.4 g) was added to a suspension of aluminium trichloride (0.47 g) in 30 mls carbon disulphide with stirring under nitrogen. After 45 minutes a brown colour developed and after 24 hours the mixture was filtered. The solid was washed with carbon disulphide and unreacted aluminium trichloride removed by sublimation to give a brown product.

Anal. Calc. for $CrAl_2Cl_6(CS_2)_2$; Cr, 11.05; Al, 11.46; Cl, 45.2; C, 5.1. Found: Cr, 10.99; Al, 11.50; Cl, 44.9; C, 6.4. The compound is easily oxidised to green Cr^{III} by both air and water.

The infrared spectrum was obtained by grinding a sample in chloroform and filtering the solution. Peak positions (cm^{-1}): 1490 (s), 1140 (sh), 1090 (s), 1015 (m), 872 (m), 580 (s) (very broad).

Results and Discussion

Kinetic Studies. These studies were made under identical conditions to those reported previously for the acetylation of benzene.[12] A solution of tricarbonylbenzenechromium in ethylene dichloride was treated with an equimolar solution of aluminium chloride and acetyl chloride in the same solvent. The rate of reaction was measured by means of the ketonic ν(C–O) I.R. frequency as described in the experimental section and the reaction was assumed to be first-order in substrate and first-order in $AlCl_3$-acetyl chloride complex as found in analogous studies of the free arenes. Free ketone and π-complexed ketone are not distinguished by this method but the above competition experiments show that production of free ketone is negligible. The results are given in Table I.

Table I. Kinetics of Acetylation of Tricarbonylbenzenechromium. Solvent Ethylene dichloride. Temp. 0°C. $[C_6H_6Cr(CO)_3] = [AlCl_3 . CH_3COCl] = 0.100\ M$

Time (mins)	% Reaction	$K_2 \times 10^3$ l/M. sec.
15.5	7.0	0.820
30	11.5	0.710
80.5	14.5	0.352
120.5	24.0	0.462
165	23.5	0.348
240	24.5	0.225
367	25.0	0.151

For benzene at 0°C, $K_2 \times 10^3 = 0.349$ l/m. sec. (12).

It can be seen that reaction ceases after about two hours but the initial rate is greater than that observed for free benzene in accord with our preparative experiments[8] and theoretical prediction.[7] The instantaneous development of a dark-brown colour upon mixing of the above components led us to examine the direct interaction of π-complex and Lewis acid.

Interaction of tricarbonylarenechromiums and Lewis Acids. The reaction of tricarbonylbenzenechromium with aluminium trichloride in nitromethane proceeds with quantitative loss of both the arene and carbonyl ligands of the π-complex, the former being determined by G.L.C. and the latter by I.R. spectroscopy (see experimental section) but no crystalline product was isolated. However, in the case of carbon disulphide as solvent we were able to isolate a crystalline product with reproducible analysis and in this case reaction proceeds slowly with the formation of the compound $Cr^{II}(AlCl_3)_2(CS_2)_2$ which is a brow n solid oxidising immediately on exposure to air to a green Cr^{III} product and insoluble in all common organic solvents. The infrared spectum of a sample ground in chloroform gave a band at 1490 cm^{-1} which we assign to S-bonded carbon disulphide ligands comparable to 1510 cm^{-1} for free CS_2 in chloroform. A similar decrease of 20 cm^{-1} in ν(C–S) has been reported by Wilkinson and co-workers[15] for the complex $RhCl(CS_2)_2(PPh_3)_2$ and interpreted similarly. A broad peak at 580 cm^{-1} is attributable to ν(Al–Cl) and that at 870 cm^{-1} lies close to a combination band ($\nu_3 - \nu_1$) of free CS_2 at 866 cm^{-1}. The electronic spectrum (reflectance) shows maxima at 13,500 cm^{-1} and 19,239 cm^{-1} with a shoulder at 13,986 cm^{-1} which may be compared with 14,000 cm^{-1} and 20,000 cm^{-1} for the known Cr^{II} compound, $KCrF_3$.[13]

---

[12] H. C. Brown, G. Marino, L. M. Stock, *J. Amer. Chem. Soc.*, *81*, 3310 (1959).

[13] A. Earnshaw, L. F. Larkworthy and K. S. Patel, *J. Chem. Soc.*, (A), 363 (1966).

[15] M. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae and G. Wilkinson, *Chem. Comm.*, 92 (1967).

The shoulder could be due to a tetragonal splitting of the $^5T_{2g}$ state as suggested by Earnshaw and co-workers and the position of our bands is consistent with the suggested structure (1) below involving coordination of the Cr^{II} ion by four chlorine and two sulphur atoms. The observed magnetic moment of $\mu_{eff} = 4.51$ B.M. at 293.8°K, is slightly lower than the normal range 4.7-4.9 B.M.) associated with Cr^{II} compounds[13] but the decrease could be due to traces of Cr^{III} being formed on packing of the Gouy tube. We consider that the above results are best explained by a polymeric structure (1) in which the two electrons lost by the zerovalent chromium atom of the arene complex may occupy anti-bonding orbitals of the CS_2 ligands.

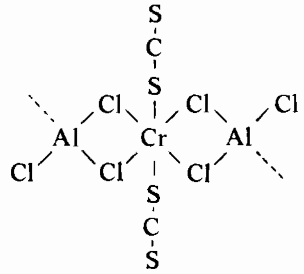
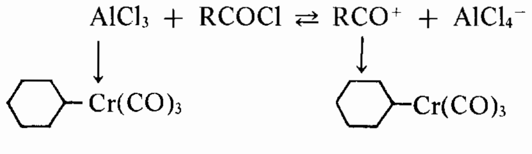


Figure 1.

The formation of a reasonably stable Cr^{II} compound during this reaction by attack of the Lewis Acid at the chromium atom suggests that the small conversion to ketones is the result of two competitive reactions as shown below:



In view of these results we would be very cautious in placing too much theoretical emphasis on observed isomer distributions or relative rate data since in metal-arene complexes we are clearly not dealing with simple acetylation of the arene ring but additional electrophilic attack at the chromium atom. It is interesting to note that reaction of ferrocene with aluminium trichloride in carbon disulphide also produces similar colours and consequently similar interaction may also occur in this system.

Moreover, in view of the similar reactions between ferrocene and aluminium trichloride and the abnormal isomer distribution both for toluene$Cr(CO)_3$,[5] and cyclobutadiene$Fe(CO)_3$,[14] we suggest that all acetylation reactions of metal-ring complexes may involve dual attack at both the ring and the metal atom; consequently isomer ratios and rate data will depend on the relative rates of these two substitution processes.

(14) R. Pettit, Plenary Lecture at 3rd International Symposium on Organometallic Chemistry, Munich (1967).