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674. *Cycloheptatriene- and Tropylium–Metal Complexes. Part I. The "Normal" Reaction of Tricarbonyltropyliumchromium Salts with Anions.*

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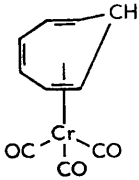
Conversion of tricarbonylcycloheptatrienechromium into tricarbonyltropyliumchromium perchlorate is described. The latter reacts with most anions to give 7-substituted tricarbonylcycloheptatrienechromiums. Numerous examples of this, the "normal" mode of reaction, are given and the analogous behaviour of the corresponding molybdenum compounds is demonstrated.

AT the outset of the present work the reaction of cycloheptatriene with chromium and molybdenum hexacarbonyls had been shown to give tricarbonylcycloheptatriene-chromium (I) and -molybdenum, respectively,[1] and the latter had been converted into the tricarbonyltropylium-molybdenum cation.[2] We now report on the reactions of the latter and more particularly of the analogous tricarbonyltropyliumchromium cation (II) with various anions. *A priori*, this cation may be expected to react with anions in one of two ways.

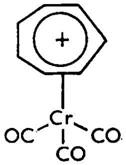
$$\text{Mode 1: } [C_7H_7Cr(CO)_3]^+ + X^- \longrightarrow XC_7H_7Cr(CO)_3$$

$$\text{Mode 2: } [C_7H_7Cr(CO)_3]^+ + X^- \longrightarrow C_7H_7Cr(CO)_2X + CO$$

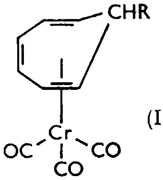
Mode 1 assumes that the positive charge resides largely on the seven-membered ring and that anions can add to this ring as they do to free tropylium ions. It is in fact the mode of reaction most frequently observed by us and is therefore referred to in the present paper as the "normal" reaction.



(I)



(II)



(III)

Mode 2 assumes that sufficient of the charge is located on the metal atom for anionic attack at this point and is based on the analogy with the behaviour[3] of the tricarbonylbenzenemanganese cation with cyanide:

$$[C_6H_6Mn(CO)_3]^+ + CN^- \longrightarrow C_6H_6Mn(CO)_2{\cdot}CN + CO$$

Our investigation was prompted by the hope that reaction of cyclopentadienide ion by essentially this mode might lead to cycloheptatrienylcyclopentadienylchromium, isomeric with dibenzenechromium. This expectation was not realised, but the interesting rearrangement observed with cyclopentadienide ions is reported in detail in the following paper. It is possible, however, that the "abnormal" base reaction described in Part III is initiated by a step, essentially following mode 2.

The starting material (II) may be obtained as the fluoroborate from the cycloheptatriene complex (I) in the same manner as its molybdenum analogue, but is more conveniently prepared as the perchlorate by using triphenylmethyl perchlorate. Owing to the difficulties in analysing either of these salts, the reineckate and tri-iodide were employed for more complete characterisation. Tricarbonylmethyltropyliumchromium perchlorate and the corresponding tri-iodide were prepared similarly. Although tricarbonyltropyliummolybdenum perchlorate may be prepared by the same method, it, unlike the chromium analogue, is rather explosive.

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[1] Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.
[2] Dauben and Honnen, *J. Amer. Chem. Soc.*, 1958, **80**, 5570.
[3] Coffield and Closson, Abs. 134th Amer. Chem. Soc. Meeting, 1958, 58P.

In the present paper we describe the " normal " reaction of the tricarbonyltropylium-chromium perchlorate with the hydride, methoxide, hydrogen sulphide, t-butylcyclopentadienide and diethyl methylmalonate ions. These lead to the products [III; R = H, OMe, SH, $C_5H_4{\cdot}CMe_3$, $CMe(CO_2Et)_2$] in which the substituent R can be on the same (*cis*) or the opposite side (*trans*) of the ring from the chromium atom. Attempts to decide between these alternative stereochemical formulations are in progress. All the products obtained were crystalline and possessed sharp melting points and are therefore undoubtedly pure and probably all of the same configuration.

The tricarbonyltropylium-molybdenum ion is much less stable under the reaction conditions employed in the chromium series, but at least the reactions with borohydride and diethyl sodiomalonate have been shown to proceed in the same manner.

Since phenyl-lithium did not react with the tropyliumchromium ion (cf. Part III, below) according to the " normal " mode of reaction, we attempted to obtain tricarbonylphenylcycloheptatrienechromium by the method of Abel *et al.*[1] from phenylcycloheptatriene. These authors give no physical properties or analyses for their product. Even after careful chromatography we failed to obtain a pure compound. The main fraction gave correct analyses but melted over a wide temperature range and was presumably a mixture of stereo- and/or position isomers. Contrary to the impression given by the earlier workers, it was accompanied by material, which from its infrared spectrum was clearly tricarbonylcycloheptatrienylbenzenechromium; this likewise was only obtained as a gummy mixture of isomers. The proportions of these two types of product may well depend on the reaction time, since we were readily able to displace cycloheptatriene from its tricarbonylchromium complex with, for example, mesitylene. This is in harmony with the ready displacement of cycloheptatriene from this complex by phosphines,[1,4] amines,[4] sulphides,[5] etc., and of one arene by another in tricarbonylbenzene-chromium derivatives.[6]

EXPERIMENTAL

M. p.s were determined in sealed, evacuated capillaries. Ligroin refers to the solvent of b. p. 60—80°. Alumina employed for chromatography was Spence's " grade H " which had been partially deactivated by exposure to air for 6 hr. All reactions were carried out under nitrogen.

Tricarbonylcycloheptatrienechromium (I).—Cycloheptatriene (6 g., 0·065 mole) and chromium hexacarbonyl (5 g., 0·023 mole) were refluxed in diethylene glycol dimethyl ether (25 ml.) for 14 hr. After the removal of solvent under reduced pressure, the product (3·16 g., 64%) was crystallised from ligroin. Tricarbonylcycloheptatrienechromium formed deep red needles, m. p. 129—130° (lit.,[1] m. p. 128—130°), soluble in all common organic solvents (Found: C, 52·6; H, 3·6; O, 20·7. Calc. for $C_{10}H_8CrO_3$: C, 52·6; H, 3·5; O, 21·0%).

Conversion into Tricarbonylmesitylenechromium.—Tricarbonylcycloheptatrienechromium (1 g., 0·0044 mole) and mesitylene (10 ml.) were refluxed for 24 hr. The excess of mesitylene was removed *in vacuo* and the yellow residue (0·93 g.) dissolved in ligroin and chromatographed on alumina (40 g.). Elution with ligroin gave unchanged tricarbonylcycloheptatrienechromium (14·1 mg.). This was closely followed by a second band, which yielded tricarbonylmesitylene-chromium (0·74 g., 66%) as yellow needles, m. p 168—169° (lit.,[7] m. p. 172—174°), soluble in all common organic solvents (Found: C, 56·2; H, 4·9. Calc. for $C_{12}H_{12}CrO_3$: C, 56·2; H, 4·7%).

Tricarbonyltropyliumchromium Salts (II).—Tricarbonylcycloheptatrienechromium (0·4 g., 0·00175 mole) was dissolved in methylene chloride (10 ml.) and triphenylmethyl fluroroborate[8] (0·67 g., 0·002 mole) in the same solvent (15 ml.) was added. The product was precipitated (0·53 g., 99%) and recrystallised from acetone as orange needles, which darken above 230° but do not melt below 300° (Found: C, 39·3; H, 2·5. $C_{10}H_7BCrF_4O_3$ requires C, 38·3; H, 2·3%).

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[4] Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

[5] Cotton and Zingales, *Chem. and Ind.*, 1960, 1219.

[6] Natta, Ercoli, Calderazzo, and Santambrogio, *Chimica e Industria*, 1958, **40**, 1003.

[7] Jackson, Nicholls, and Whiting, *J.*, 1960, 469.

[8] Dauben, Honnen, and Harmon, *J. Org. Chem.*, 1960, **25**, 1442.

Tricarbonyltropyliumchromium tetrafluoroborate is soluble in water, very slightly soluble in methylene chloride, and insoluble in ligroin, benzene, or ether.

Tricarbonyltropyliumchromium perchlorate (1·25 g., 97%) was prepared similarly by using triphenylmethyl perchlorate in place of the fluoroborate. It crystallised from acetone, forming red needles which darken above 270° but do not melt below 300°. It exploded violently during attempted carbon–hydrogen analysis and is readily detonated by friction. The compound is soluble in water, very sparingly soluble in methylene chloride, ether, and tetrahydrofuran, and insoluble in ligroin or benzene.

An aqueous solution of the perchlorate on treatment with a saturated solution of Reinecke's salt quantitatively precipitated the *reineckate*, which formed orange needles from acetone (Found: C, 29·7; H, 2·7; O, 9·3; N, 15·6. $C_{14}H_{13}Cr_2N_6O_3S_4$ requires C, 30·8; H, 2·4; O, 8·8; N, 15·4%). Tricarbonyltropyliumchromium reineckate decomposes above 280°, but does not melt below 320°; it is slightly soluble in alcohol and insoluble in non-polar solvents.

The *tri-iodide* was quantitatively precipitated when an aqueous solution of the perchlorate was treated with an excess of a solution of potassium tri-iodide. Tricarbonyltropyliumchromium tri-iodide forms brown needles (from acetone) which decompose above 150° (Found: C, 19·7; H, 1·2; O, 7·8; I, 62·9. $C_{10}H_7CrI_3O_3$ requires C, 19·7; H, 1·2; O, 7·9; I, 62·4%). It is insoluble in non-polar solvents and slightly soluble in alcohol.

Tricarbonylmethyltropyliumchromium Perchlorate.—Tricarbonylmethylcycloheptatrienechromium [1] (1 g., 0·0041 mole) in methylene chloride (8 ml.) was treated with triphenylmethyl perchlorate (2 g., 0·0058 mole) in the same solvent (25 ml.). Tricarbonylmethyltropyliumchromium perchlorate was quantitatively precipitated and formed red needles (from acetone) which darken above 270° but do not melt below 300°. It is soluble in water, very sparingly soluble in methylene chloride, ether, and tetrahydrofuran and insoluble in ligroin or benzene. For characterisation, an aqueous solution of the perchlorate was treated with aqueous potassium tri-iodide in excess. The precipitated *tricarbonylmethyltropyliumchromium tri-iodide* crystallised from acetone as brown needles, which decomposed from 150° but did not melt below 320° (Found: C, 21·5; H, 1·6. $C_{11}H_9CrI_3O_3$ requires C, 21·2; H, 1·5%).

Tricarbonyltropylium-molybdenum Salts.—Tricarbonylcycloheptatrienemolybdenum [1] (1 g., 0·0037 mole) was treated with triphenylmethyl perchlorate (1·5 g., 0·0044 mole) in methylene chloride (50 ml.). A precipitate of *tricarbonyltropylium-molybdenum perchlorate* (1·29 g., 95%) was obtained immediately. Recrystallisation from acetone gave orange needles, which decompose explosively at ~80°, are soluble in water, sparingly so in methylene chloride, ether, and tetrahydrofuran, and insoluble in ligroin or benzene. The compound is readily detonated by heat and friction.

An aqueous solution of the perchlorate was treated with an excess of a solution of Reinecke's salt and a quantitative yield of the *reineckate* was obtained. Recrystallisation from acetone gave orange plates, which decompose above 170° but do not melt below 300° (Found: C, 28·7; H, 2·2; N, 14·1. $C_{14}H_{13}CrMoN_6O_3S_4$ requires C, 28·5; H, 2·2; N, 14·3%). The compound is insoluble in water and only slightly soluble in alcohol or methylene chloride.

The *tri-iodide* was quantitatively precipitated when an aqueous solution of the perchlorate was treated with an excess of potassium tri-iodide. The crystals were washed with carbon tetrachloride to remove free iodine and recrystallised from acetone as brown plates, which decompose from 100° but do not melt below 320° (Found: C, 18·5; H, 1·2. $C_{10}H_7I_3MoO_3$ requires C, 18·8; H, 1·1%). It is insoluble in water, but slightly soluble in alcohol or methylene chloride.

Reduction of Tricarbonyltropyliumchromium Perchlorate by Sodium Borohydride.—Sodium borohydride (0·38 g., 0·01 mole) was added, with stirring, to a solution of tricarbonyltropyliumchromium perchlorate (1 g., 0·0031 mole) in water (250 ml.) at room temperature. The resulting mixture was set aside for 10 min. and then extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated to dryness, leaving a red solid (0·41 g.), which was dissolved in ligroin and chromatographed on alumina (20 g.). Elution with ligroin gave tricarbonylcycloheptatrienechromium (0·39 g., 56%) as deep red needles, m. p. 129—130°, identified by mixed m. p. and infrared comparison with an authentic sample.

Reduction of Tricarbonyltropylium-molybdenum Perchlorate by Sodium Borohydride.—Tricarbonyltropylium-molybdenum perchlorate (0·74 g., 0·002 mole) in water (250 ml.) was stirred with sodium borohydride (0·19 g., 0·005 mole) at room temperature for 10 min. The resulting mixture was extracted with ether, and the dried (Na_2SO_4) extract evaporated to dryness leaving a red solid (0·168 g., 31%). Recrystallisation from ligroin yielded red plates of tricarbonylcycloheptatrienemolybdenum, m. p. and mixed m. p. 100—101°.

*Tricarbonyl-*7*-methoxycyclohepta-*1,3,5*-trienechromium* (III; R = OMe).—Tricarbonyltropyliumchromium perchlorate (1 g., 0·0031 mole), suspended in methanol (20 ml.), was added to a solution from sodium (0·2 g., 0·0087 g.-atom) in methanol (10 ml.). The mixture was stirred for 2 hr., the solvent was removed under reduced pressure, and the residue extracted with ligroin. Evaporation of the ligroin extract yielded *tricarbonyl-*7*-methoxycyclohepta-*1,3,5*-trienechromium* (0·695 g., 88%), crystallising from the same solvent as orange needles, m. p. 107—109° (Found: C, 51·3; H, 4·0; OMe, 11·9. $C_{11}H_{10}CrO_4$ requires C, 51·2; H, 3·9; OMe, 12·0%).

When this compound was treated with triphenylmethyl perchlorate, tricarbonyltropyliumchromium perchlorate was obtained in quantitative yield and was identified by infrared comparison with an authentic specimen and by reduction with sodium borohydride to tricarbonylcycloheptatrienechromium, m. p. and mixed m. p. 129—130°.

*Tricarbonyl-*7*-mercaptocyclohepta-*1,3,5*-trienechromium* (III; R = SH) *and Hexacarbonyl-(ditropyl Disulphide)bischromium.*—Hydrogen sulphide was bubbled through a mixture of tricarbonyltropyliumchromium perchlorate (1 g., 0·0031 mole) in water (200 ml.) and sodium hydrogen sulphide (0·34 g., 0·006 mole) in water (5 ml.) for 8 hr. The precipitated solid (0·52 g.) was then filtered off and dissolved in ether, the solution dried (Na_2SO_4), and the ether evaporated. The red residue (0·395 g.) was dissolved in ligroin–benzene (1 : 1) and chromatographed on alumina (170 g.), giving two bands. Elution with the same solvent gave *hexacarbonyl(ditropyl disulphide)bischromium* (0·27 g., 35%) as orange-red crystals (from ligroin–ether) (Found: C, 46·3; H, 2·9. $C_{20}H_{14}Cr_2O_6S_2$ requires C, 46·3; H, 2·7%). The compound decomposes from about 78° without melting and is soluble in ether, benzene, and acetone and only very slightly soluble in ligroin. The second band decomposed on the column before it could be eluted.

In a second experiment, the red ether extract was concentrated and an orange solid, which decomposed from 60° and melted to a red liquid at 70—71°, was obtained. The existence of a thiol group in this product was shown by the strong infrared absorption at 2658 cm.$^{-1}$. Recrystallisation of tricarbonyl-7-mercaptocyclohepta-1,3,5-trienechromium from ligroin–ether was accompanied by oxidation to the above disulphide.

Extraction of the red reaction mixture with dilute aqueous sodium hydroxide gave an orange extract, but attempts to isolate the thiol from this alkaline solution were unsuccessful.

*Tricarbonyl-*7-[1,1*-di(ethoxycarbonyl)ethyl*]*cyclohepta-*1,3,5*-trienechromium* (III; R = $CMe(CO_2Et)_2$].—Tricarbonyltropyliumchromium perchlorate (2 g., 0·0062 mole) and diethyl sodiomethylmalonate (2·36 g., 0·012 mole) [prepared from sodium (0·276 g., 0·012 g.-atom), ethyl alcohol (10 ml.), and diethyl methylmalonate (2·8 g., 0·016 mole)] in tetrahydrofuran (50 ml.) were allowed to react at room temperature overnight. The solvent was distilled off *in vacuo* and the red residue extracted with ligroin. Chromatography on neutralised alumina gave a single red band of *tricarbonyl-*7-[1,1*-di(ethoxycarbonyl)ethyl*]*cyclohepta-*1,3,5*-trienechromium* (1·94 g., 79%), eluted with ligroin–benzene (1 : 1). Recrystallisation from ligroin gave red plates, m. p. 91—92° (Found: C, 54·1; H, 5·0. $C_{18}H_{20}CrO_7$ requires C, 54·0; H, 5·0%). No tricarbonylbenzenechromium could be detected.

When this ester (1·2 g., 0·003 mole) had been refluxed in methanolic 10% potassium hydroxide (30 ml.) for 3 hr., filtration of the mixture gave a yellow potassium salt (0·5 g.), which showed strong absorption at 1996, 1876, and 1653 cm.$^{-1}$ in the carbonyl stretching frequency region and became brown in air. Acidification with 2N-hydrochloric acid (5 ml.) of its aqueous solution (30 ml.), extraction with ether (250 ml.), and evaporation of the dried ($MgSO_4$) ether extract yielded only a yellow liquid (164 mg.), which decomposed in air.

Tricarbonyl - 7 *-* [*di(ethoxycarbonyl)methyl*]*cycloheptatrienemolybdenum* (with G. H. Smith).—Sodium (0·12 g., 0·0052 g.-atom) in ethanol (5 ml.) was added to an excess of diethyl malonate (5 ml.) in tetrahydrofuran. Tricarbonyltropylium-molybdenum fluoroborate (1·83 g. 0·0051 mole) was then added and the mixture shaken for 30 min. After removal of solvents and unchanged diethyl malonate under reduced pressure, the solid residue was extracted with n-pentane (25 ml.). On concentration of the extract, *tricarbonyl-*7-[*di(ethoxycarbonyl)methyl*]*-cycloheptatrienemolybdenum* (0·725 g., 33%) separated as red needles, m. p. 92—93° (Found: C 47·6; H, 4·4. $C_{17}H_{18}MoO_7$ requires C, 47·45; H, 4·2%).

*Tricarbonyl-*7-[5(?)*-t-butyl-*5*-cyclopentadienyl*]*cycloheptatrienechromium* (III; R = Bu^t).—Dimethylfulvene (0·7 g., 0·0066 mole) in ether (10 ml.) was added dropwise to methyl-lithium [prepared from methyl iodide (1 g., 0·007 mole) and lithium metal (0·11 g., 0·016 g.-atom) in ether (7 ml.)] with cooling. Tricarbonyltropyliumchromium perchlorate (0·43 g., 0·0013 mole) was then added, resulting in the immediate formation of a deep red colour and the liberation of heat. The mixture was left overnight, the solvent removed under reduced pressure, and the red residue extracted with ligroin. Chromatography of this extract on alumina (40 g.) and elution with the same solvent afforded three bands. One yielded only a trace of a yellow oil and the second a trace of a red gum. From the third band, *tricarbonyl-t-butylcyclopentadienylcycloheptatrienechromium* (63 mg., 14·4%) was obtained, crystallising from ligroin as red needles, m. p. 129—130° (Found: C, 65·4; H, 6·1. $C_{19}H_{20}CrO_3$ requires C, 65·5; H, 5·9%). It is soluble in all common organic solvents.

Reaction of Phenylcycloheptatriene with Chromium Hexacarbonyl.—Phenylcycloheptatriene [9] (4 g., 0·02 mole) was heated with chromium hexacarbonyl (5 g., 0·023 mole) in diethylene glycol dimethyl ether (15 ml.) at 120° for 6 hr. The solvent was then removed *in vacuo* and the residue chromatographed on alumina with ligroin as solvent. This eluted a first orange band from which a red uncrystallisable gum (24 mg.) was obtained. The second scarlet band afforded a deep red gum (0·51 g.). This solidified partly to a red solid, m. p. 60—72°, on trituration with a mixture of ligroin and ether. Recrystallisation from the same solvent mixture raised the melting range to 71—77° (0·42 g., 6·05%), but a product possessing a sharp m. p. could not be obtained in this way. The product is probably a mixture of several isomers of *tricarbonylphenylcycloheptatrienechromium* (Found: C, 63·5; H, 4·3. $C_{16}H_{12}CrO_3$ requires C, 63·2; H, 4·0%). The third yellow band afforded a yellow gum (0·12 g.) which failed to crystallise from a number of solvents and did not sublime. The presence of tricarbonylcycloheptatrienylbenzenechromium in this fraction is indicated by the strong absorption at 1962 and 1889 cm.$^{-1}$ (CCl_4 solution) in the metal–carbonyl stretching frequency region.

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[9] Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203.