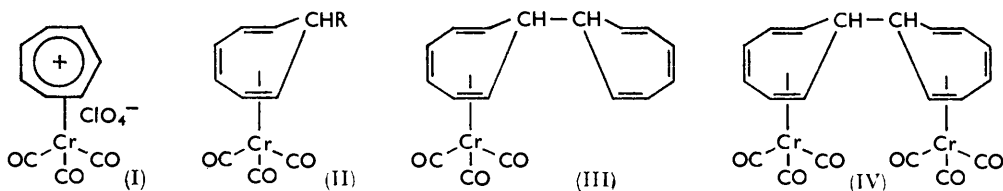


676. *Cycloheptatriene and Tropylium Metal Complexes. Part III.*<sup>1</sup>  
*The "Abnormal" Reaction with Anions.*

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Various anions are shown to cause reductive coupling of tricarbonyltropyliumchromium salts, giving a mixture of hexacarbonylbi(cycloheptadienyl)bischromium and tricarbonylbi(cycloheptadienyl)chromium as the principal products.

IN Part I,<sup>2</sup> the normal reaction of the tricarbonyltropyliumchromium perchlorate (I) with anions was shown to be addition to the ring to produce compounds of the type (II). One of the first such reactions investigated by us was that with cyanide. Although the expected product (II; R = CN) was isolated in small amount, the two main products had compositions corresponding to the mono- (III) and bis-tricarbonylchromium derivative (IV) of



bi(cycloheptatrienyl). The structure of the latter was confirmed by its formation on reduction of the perchlorate (I) with zinc dust, and both products afforded bi(cycloheptatrienyl) on treatment with diethylenetriamine. To test whether the alkalinity of cyanide solutions accounted for the formation of the dimeric products, the perchlorate (I) was treated with sodium hydrogen carbonate. The two bi(cycloheptatrienyl) derivatives (III and IV) were obtained in this way, and also by treating the tropylium compound (I) with sodium acetate, sodamide, phenyl-lithium, or benzamide.

We obtained the same products (III and IV) during an attempted acid hydrolysis of the malonate complex<sup>1</sup> [II; R = CH(CO<sub>2</sub>Et)<sub>2</sub>] and were thus led to treat the tropylium salt (I) with dilute hydrochloric acid. The formation of the bi(cycloheptatrienyl) derivatives (III and IV) under the latter conditions implies that the malonate complex [II; R = CH(CO<sub>2</sub>Et)<sub>2</sub>] is readily cleaved to give back diethyl malonate and the tropylium complex (I), a deduction which has been confirmed by subsequent work.<sup>3</sup> Similar cleavages of related metal-free cycloheptatriene derivatives have been observed and discussed by Conrow.<sup>4</sup>

We cannot propose a detailed mechanism for the coupling of tricarbonyltropyliumchromium salts by various anions to give bi(cycloheptatrienyl) derivatives, but the partial removal of chromium from the product is undoubtedly significant. In general terms it appears probable that attack by the anion on the chromium atom (in I or IV) leads to cleavage of the complex with liberation of a Cr(0) complex which then (like zinc) reduces the tropylium complex (I) to the bi(cycloheptatrienyl) complex (IV) by electron transfer.

Abel *et al.*<sup>5</sup> obtained a complex formulated as (III) by reaction of bi(cycloheptatrienyl) with chromium hexacarbonyl, but reported only the positions of its carbonyl stretching bands in the infrared. Repetition readily led to a crystalline product, but this differed from that (A) described above and is regarded as its stereo- (or possibly a position) isomer (B). No bischromium complex was isolated.

Reaction of the bischromium complex (IV) with triphenylmethyl perchlorate does not

<sup>1</sup> Part II, preceding paper.

<sup>2</sup> Munro and Pauson, *J.*, 1961, 3475.

<sup>3</sup> Pauson and Smith, unpublished observations.

<sup>4</sup> Conrow, *J. Amer. Chem. Soc.*, 1959, **81**, 5461.

<sup>5</sup> Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.

yield the corresponding cation (or the heptafulvalene complex which might be expected to result from proton elimination). Instead, cleavage to tricarbonyltropyliumchromium perchlorate (I) is observed.

#### EXPERIMENTAL

For general directions see Part I.<sup>2</sup>

*Reaction of Tricarbonyltropyliumchromium Perchlorate with Potassium Cyanide.*—(a) *In aqueous solution.* Solutions of the perchlorate (I) (0.756 g., 0.0023 mole) in water (150 ml.) and potassium cyanide (0.2 g., 0.0031 mole) in water (5 ml.) were mixed and left at room temperature for 10 min. The mixture was then extracted with ether, and the ether layer washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. The residue (0.42 g.) was chromatographed in ligroin-benzene (1 : 1) on alumina (150 g.), with the same solvents as eluent. Four bands were obtained yielding in order of elution: (1) Orange crystals of *tricarbonylbi(cycloheptatrienyl)chromium* (A) (III) (0.163 g., 46%), m. p. 148—149° (from ligroin) (Found: C, 63.9; H, 4.5; O, 14.9.  $\text{C}_{17}\text{H}_{14}\text{CrO}_3$  requires C, 64.1; H, 4.4; O, 15.1%), soluble in the common organic solvents. (2) Deep red needles (86 mg., 17%) of *hexacarbonylbi(cycloheptatrienyl)bischromium* (IV), m. p. 223—225° (decomp.) (from benzene or acetone) alone or mixed with a specimen prepared by reduction of the perchlorate with zinc dust (see below) (Found: C, 52.8; H, 3.3; O, 20.8.  $\text{C}_{20}\text{H}_{14}\text{Cr}_2\text{O}_6$  requires C, 52.9; H, 3.1; O, 21.1%), insoluble in ligroin and chloroform and only slightly soluble in ether and in tetrahydrofuran. (3) Yellow crystals (3.8 mg.) of unidentified structure [the compound forms yellow needles, m. p. 100—101°, from ligroin, is soluble in common organic solvents, and absorbs in the metal carbonyl stretching region of the infrared (KBr disc) at 1986, 1923, and 1892  $\text{cm}^{-1}$  and in the  $\text{C}\equiv\text{N}$  stretching region at 2229  $\text{cm}^{-1}$ ]. (4) Deep red needles of *tricarbonyl-7-cyanocyclohepta-1,3,5-trienechromium* (0.105 g., 18%), m. p. 118—119° (from ligroin-ether) (Found: C, 52.0; H, 3.0; N, 5.7.  $\text{C}_{11}\text{H}_7\text{CrNO}_3$  requires C, 52.2; H, 2.8; N, 5.5%), soluble in benzene, ether, and ethanol, almost insoluble in ligroin or methylene chloride, having  $\nu_{\text{max}}$  in the  $\text{C}\equiv\text{N}$  stretching region at 2229  $\text{cm}^{-1}$  (KBr disc).

(b) *In ethanol.* Tricarbonyltropyliumchromium perchlorate (1 g., 0.0031 mole) and potassium cyanide (0.5 g., 0.0077 mole) were refluxed in ethanol (30 ml.) for 1 hr. After evaporation under reduced pressure, the residue was extracted with ligroin and chromatographed on alumina (50 g.). Elution with ligroin gave tricarbonylbi(cycloheptatrienyl)chromium (A) (III) as orange needles (20 mg., 4.2%), m. p. and mixed m. p. 148—149°. The ligroin-insoluble material was dissolved in benzene and filtered from a mixture of unchange perchlorate and insoluble products (0.1 g.). The benzene-soluble fraction (0.46 g.) was chromatographed on alumina (60 g.) to yield hexacarbonylbi(cycloheptatrienyl)bischromium (IV) (0.28 g., 41.2%), yellow crystals (4 mg.) of the unidentified product, and tricarbonyl-7-cyanocyclohepta-1,3,5-trienechromium (97 mg., 12.8%), identity in each case being established by m. p., mixed m. p., and infrared comparison. In addition, a fifth band was eluted from the chromatogram. This afforded purple needles (3 mg.), which did not melt below 300°, are soluble in ether, acetone, and benzene and show carbonyl absorption at 1980 and 1900  $\text{cm}^{-1}$  (KBr disc) but no  $\text{C}\equiv\text{N}$  absorption.

Repetition of this experiment with longer reaction times resulted in lower yields of tricarbonyl-7-cyanocyclohepta-1,3,5-trienechromium.

*Other Reactions of the Perchlorate (I) yielding the Bi(cycloheptatrienyl) Derivatives (III and IV).*—Reactions with the reagents listed in the Table were carried out similarly to that with

Reagent	Solvent	Reaction time <sup>a</sup> (hr.)	Products			
			(III)		(IV)	
			mg.	%	mg.	%
$\text{NaHCO}_3$ (excess)	Water	0.25	98	21	278	41
$\text{NaOAc}$ (0.003 mole)	Methanol	1 <sup>b</sup>	130	29	280 <sup>d</sup>	41
$\text{NaNH}_2$ (0.006 mole)	Tetrahydrofuran	16	47	10	363	54
$\text{PhLi}$ (0.005 mole)	Ether	16	57	12	233	33
$\text{Ph}\cdot\text{CO}\cdot\text{NH}_2$ (0.003 mole)	Water	6 <sup>c</sup>	110	23	305	45
$\text{HCl}$ (excess, 2N)	Water	1 <sup>b</sup>	74	15	332	49

<sup>a</sup> At room temperature, unless otherwise indicated. Under reflux. <sup>c</sup> At 80°. <sup>d</sup> Filtered off directly from the cooled mixture.

cyanide (above). The quantities are based on 1 g. (0.003 mole) of the perchlorate (I) in each case.

A third, unidentified substance (2.8 mg.), m. p. 124—129° (from ligroin), preceded the others

on chromatography of the product from the bicarbonate reaction. It showed metal-carbonyl absorption at 2000, 1934, and 1905  $\text{cm}^{-1}$  (in  $\text{CCl}_4$ ).

*Reduction of Tricarbonyltropyliumchromium Perchlorate (I) by Zinc Dust.*—The perchlorate (0.75 g., 0.0023 mole) in tetrahydrofuran (30 ml.) was shaken with zinc dust (0.4 g.) at room temperature for 36 hr. The solvent was evaporated *in vacuo* and the residue extracted with benzene and chromatographed on alumina (55 g.). Elution with benzene gave hexacarbonylbi(cycloheptatrienyl)bischromium (IV) (0.3 g., 58%), which recrystallised from acetone as deep red needles, m. p. 223—225° (decomp.) (Found: C, 52.7; H, 3.3; O, 20.9. Calc. for  $\text{C}_{20}\text{H}_{14}\text{Cr}_2\text{O}_6$ : C, 52.9; H, 3.1; O, 21.1%), slightly soluble in ether and tetrahydrofuran and almost insoluble in ligroin.

*Reaction of Bi(cycloheptatrienyl) with Chromium Hexacarbonyl.*—Bi(cycloheptatrienyl)<sup>6</sup> (3.32 g., 0.018 mole) and chromium hexacarbonyl (8 g., 0.036 mole) were refluxed in ligroin (b. p. 100—120°, 50 ml.) for 24 hr. Filtration followed by evaporation *in vacuo* yielded a red gum, which was chromatographed on alumina (250 g.). Elution with ligroin afforded unchanged bi(cycloheptatrienyl) (0.81 g.), m. p. 69—70°, and a red gum (0.57 g.), which was rechromatographed on alumina and then partly crystallised from ligroin as red needles of *tricarbonylbi(cycloheptatrienyl)chromium (B) (III)* (53 mg.), m. p. 124—125° (Found: C, 64.2; H, 5.2.  $\text{C}_{17}\text{H}_{14}\text{CrO}_3$  requires C, 64.1; H, 4.4%). Only uncrystallisable gums were obtained from the mother-liquors. The last compound is soluble in all common organic solvents and shows strong absorption at 1980, 1931 and 1873  $\text{cm}^{-1}$  in the metal-carbonyl stretching frequency region. A trace of a second red band was eluted with light petroleum-benzene (1:1), but was obtained in too low a yield for characterisation.

*Reactions of Bi(cycloheptatrienyl) Complexes with Diethylenetriamine.*—Each of the three bi(cycloheptatrienyl) complexes [III (A), III (B), and IV] 100 mg.) was heated with diethylenetriamine (5 ml.) at 100° for 30 min. After addition of water (50 ml.) the mixtures were extracted with ether. In each case, evaporation of the ether layer afforded bi(cycloheptatrienyl), m. p. and mixed m. p. 69—70°, and filtration of the aqueous layer afforded tricarbonyldiethylenetriaminechromium,<sup>7</sup> both in 70—80% yield. The chromium complex darkened above 220° but did not melt below 300°, and proved insoluble in all common organic solvents (Found: C, 35.3; H, 5.6. Calc. for  $\text{C}_7\text{H}_{13}\text{CrN}_3\text{O}_3$ : C, 35.2; H, 5.4%).

*Reaction of Hexacarbonylbi(cycloheptatrienyl)bischromium with Triphenylmethyl Perchlorate.*—Triphenylmethyl perchlorate (0.342 g., 0.001 mole) in methylene chloride (10 ml.) was added to hexacarbonylbi(cycloheptatrienyl)bischromium (IV) (0.454 g., 0.001 mole) in the same solvent (50 ml.). Tricarbonyltropyliumchromium perchlorate (I) (0.24 g.) was precipitated and was characterised by reduction with sodium borohydride and with zinc dust to tricarbonylcycloheptatrienechromium (II; R = H) and hexacarbonylbi(cycloheptatrienyl)bischromium (IV) respectively, the identities being confirmed by mixed m. p.s and infrared comparisons. The tri-iodide was also prepared and crystallised from acetone as brown needles, decomp. >150° (Found: C, 19.8; H, 1.1. Calc. for  $\text{C}_{10}\text{H}_7\text{CrI}_3\text{O}_3$ : C, 19.7; H, 1.2%), having the correct infrared spectrum.

*Acid Hydrolysis of Tricarbonyl-7-[1,1-di(ethoxycarbonyl)ethyl]cycloheptatrienechromium [II; R = CMe(CO<sub>2</sub>Et)<sub>2</sub>].*—The methylmalonyl complex<sup>2</sup> (0.25 g., 0.00063 mole) was heated with 20% hydrochloric acid (3 ml.) for 1 hr. at 100°. The mixture was poured into water (20 ml.) and extracted with ether (2 × 250 ml.). Evaporation of the washed and dried ( $\text{Na}_2\text{SO}_4$ ) ether extract gave red crystals (157 mg.), which were triturated with ligroin and chromatographed on neutralised alumina (30 g.), to give two bands. Elution with ligroin yielded tricarbonylbi(cycloheptatrienyl)chromium (A) (III) (3.1 mg.) as orange needles, m. p. and mixed m. p. 148—149°. Elution with benzene gave starting material (29 mg.), m. p. 91—92°. The ligroin-insoluble material was chromatographed in benzene on alumina (45 g.), giving a single red band. Elution with benzene yielded hexacarbonylbi(cycloheptatrienyl)bischromium (51 mg., 36%), identified by m. p., mixed m. p., and infrared comparison.

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<sup>6</sup> Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203.

<sup>7</sup> Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.