919. *Transition-metal Complexes of Seven-membered Ring Systems. Part I. The* cyclo*Heptatriene–Metal Complexes and Related Compounds.*

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The preparation and properties of *cyclo*heptatriene-chromium and -molybdenum tricarbonyls are described, together with a number of compounds in which a substituent is present on the 1-position of the *cyclo*heptatriene ring. (Di*cyclo*heptatrienyl)di(molybdenum tricarbonyl) and the (di*cyclo*heptatrienyl ether)di(molybdenum tricarbonyl) complex have been prepared. In these two compounds molybdenum tricarbonyl residues are attached to both of the seven-membered rings present. All attempts to attach the tropylium ion to a transition metal in a " sandwich " type of molecule have resulted only in the isolation of di*cyclo*heptatrienyl. A ditropylium hexachloroplatinate, $(C_7H_7)_2PtCl_6$, has been isolated. Infrared spectra of some of these compounds are reported.

A large number of compounds of the type $AM(CO)_n$, where A is a *cyclo*pentadienyl group or an aromatic hydrocarbon and M is a transition metal, have been prepared by the direct reaction of *cyclo*pentadiene [1] or aromatic hydrocarbons [2,3] respectively with numerous metal carbonyls. It has been suggested [4] that the tropylium cation, having the same number of π-electrons as both the *cyclo*pentadienyl anion and the neutral aromatic nucleus, should be able to form a " sandwich " type of bond to a transition metal. In view of the failure to obtain such compounds from reactions with the tropylium ion, discussed below, it was hoped that the reaction of a metal carbonyl with *cyclo*heptatriene would lead to hydrogen loss of a type similar to that which occurs with *cyclo*pentadiene. The reaction of chromium and molybdenum hexacarbonyls with refluxing *cyclo*heptatriene has produced, however, not tropylium compounds, but the *cyclo*heptatriene-chromium and -molybdenum [5] tricarbonyls, $C_7H_8M(CO)_3$ (M = Cr and Mo), in which the hydrocarbon ligand remains intact, without loss of hydrogen:

$$C_7H_8 + M(CO)_6 \longrightarrow C_7H_8M(CO)_3 + 3CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The *cyclo*heptatriene-metal tricarbonyls form orange-red crystals, which can be sublimed without decomposition, and are soluble in light petroleum, chloroform, benzene, and many other organic solvents. Although in the solid state these compounds may be stored indefinitely, their solutions decompose in air and light, the decomposition being particularly rapid in acetone or alcohol.

In addition to the two simple *cyclo*heptatriene compounds, a number of compounds (I) have been obtained (Table), in which there is a substituent present on the 1-carbon atom of the *cyclo*heptatriene ring, by methods essentially the same as were used for the simple compounds.

In the light of the formation of substituted arene-metal tricarbonyls,[3] it is interesting that in the reaction between 1-phenyl*cyclo*heptatriene and the metal carbonyls the seven-membered ring takes precedence as donor ligand over the six-membered aromatic ring, the phenyl group acting merely as a ring substituent. That the metal is bound to the seven- and not the six-membered ring, is shown by the fact that the compound is red, as are all the other *cyclo*heptatriene metal carbonyls, and has not the yellow colour of the

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[1] Cf. (*a*) Wilkinson, *J. Amer. Chem. Soc.*, 1954, **76**, 209; (*b*) Fischer and Hafner, *Z. Naturforsch.*, 1954, **9**b, 503; (*c*) Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

[2] Natta, Ercoli, and Calderazza, *Chimica e Industria*, 1958, **40**, 287; *Angew. Chem.*, 1958, **70**, 322.

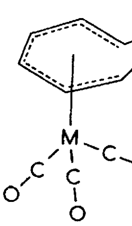
[3] Nicholls and Whitting, *Proc. Chem. Soc.*, 1958, 152.

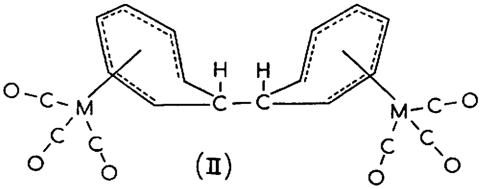
[4] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[5] Abel, Bennett, and Wilkinson, *Proc. Chem. Soc.*, 1958, 152.

arene-metal carbonyls.[3] Further, whereas the latter have only two carbonyl stretching modes, the *cyclo*heptatriene derivatives have three.

A limited time of reaction between di*cyclo*heptatrienyl and molybdenum carbonyl formed the monomolybdenum tricarbonyl complex, in which a molybdenum tricarbonyl residue is attached to one ring only. A longer reaction time has produced the bis(molybdenum tricarbonyl) complex (II), in which both rings are attached to molybdenum tricarbonyl residues In a similar manner it has been possible to isolate the compound (di*cyclo*heptatrienyl ether)di(molybdenum tricarbonyl). These binuclear compounds are much less soluble in organic solvents than are the mononuclear ones. The compounds prepared and some of their properties are given in the Table).


(I)


(II)

Attempts to obtain compounds with the tropylium cation bound to a transition metal have been unsuccessful. Interaction of tropylium bromide and sodium manganese carbonyl in tetrahydrofuran resulted in the quantitative formation of di*cyclo*heptatrienyl and manganese carbonyl:

$$2NaMn(CO)_5 + 2C_7H_7Br \longrightarrow C_{14}H_{14} + 2NaBr + Mn_2(CO)_{10} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Similarly, di*cyclo*heptatrienyl is formed in the reaction between potassium iron carbonyl hydride or mercury iron carbonyl with tropylium bromide. Addition of tropylium bromide to ethanolic solutions of hexachloroplatinic acid gave an immediate brown precipitate of empirical formula $(C_7H_7)_2PtCl_6$, insoluble in water, ethanol, chloroform, and benzene; this product was undoubtedly ditropylium hexachloroplatinate.

Infrared spectra in the carbonyl region of the hydrocarbon metal compounds.

Compound	M. p.	C–O stretches, cm.$^{-1}$
$Cr(CO)_3$–*cyclo*heptatriene	128—130° (dec.)	1991, 1921, 1893
$Mo(CO)_3$–*cyclo*heptatriene	100	2000, 1929, 1895
$Cr(CO)_3$–di*cyclo*heptatrienyl †	—	1990, 1927, 1895
$Mo(CO)_3$–di*cyclo*heptatrienyl	*	1998, 1929, 1898
$Cr(CO)_3$–methyl*cyclo*heptatriene	72—73	1990, 1921, 1893
$Mo(CO)_3$–methyl*cyclo*heptatriene	*	2001, 1929, 1896
$Cr(CO)_3$–phenyl*cyclo*heptatriene †	—	1989, 1921, 1890
$Mo(CO)_3$–phenyl*cyclo*heptatriene	*	2000, 1926, 1897
$[Mo(CO)_3]_2$–di*cyclo*heptatrienyl	*	1991, 1928, 1889
$[Mo(CO)_3]_2$–di*cyclo*heptatrienyl ether	*	1993, 1928, 1889

* Decompose above 150° without melting. † Insufficient for analysis.

Attempts to carry out substitution in the aromatic ring by methods successfully applied to ferrocene [6] (*e.g.*, Friedel–Crafts reactions, sulphonation, etc.) failed, owing to fission of the metal–ring bond and complete decomposition of the molecule. Attempts to replace the three remaining carbonyl groups by other ligands also failed. However, with a number of ligands (trialkyl- or triaryl-phosphines; amines; arsines), the reaction has produced a series of compounds $L_3Mo(CO)_3$, *e.g.*, $(Ph_3As)_3Mo(CO)_3$, in which it may reasonably be assumed that the carbon monoxide groups are *cis* to each other: these will be discussed in a later paper.

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[6] Rausch, Vogel, and Rosenburg, *J. Chem. Educ.*, 1957, **34**, 268.

Structure of the Compounds.—Nuclear magnetic resonance studies,[7, 8] and measurements of vibrational spectra,[9] of *cyclo*heptatriene suggest that the six olefinic carbon atoms in the molecule are almost planar, and that the six π-electrons present form a delocalized system which to some extent " by-passes " the methylene group to give a quasi-aromatic system. The bonding of the *cyclo*heptatriene nucleus to the metal atoms must be due to the overlap of the *d*-orbitals of the metal with the delocalized π-electron density of the ring. A similar type of bonding has also been proposed for butadieneiron tricarbonyl.[10] In both the latter and the present type of complex the metal atom can formally be considered as having attained an inert-gas structure. Although, as in the well-known *cyclo*pentadienyl- and arene-metal complexes,[11] the electronic structure is more complicated than this simple view suggests, it is not to be assumed that all of the six π-electrons have abandoned the ring for the metal atom.

The *cyclo*pentadienyl- and arene-metal compounds of similar formula, *e.g.*, $C_5H_5Mn(CO)_3$ and $C_6H_6Cr(CO)_3$, irrespective of the presence of substituents on the ring and the total symmetry of the molecules, show only two strong C–O stretching modes, in keeping with the local symmetry of the carbon monoxide groups. There is now evidence for free rotation of the *cyclo*pentadienyl and arene rings about the metal–ring axis from various physical measurements on di(π-*cyclo*pentadienyl) and diarene compounds (see ref. 11), and the infrared data of the carbonyls are also consistent with this view. In the *cyclo*heptatriene derivatives, however, three strong C–O stretching modes are always observed (see Table). In view of the incomplete delocalization of the π-electron system, free rotation about the metal–ring axis is perhaps not to be expected, and the *cyclo*heptatriene-metal carbonyls thus have the ring fixed with respect to the carbon monoxide groups, giving a lower symmetry to the molecules than in the *cyclo*pentadienyl and arene analogues. One carbon monoxide group could lie along the plane of symmetry of the ring, and the other two at an angle to it; whatever the exact disposition, three infrared-active carbonyl modes would result. The *cyclo*heptatriene-metal compounds are thus formulated as (I), where the disposition of the carbonyl groups relative to the ring is merely symbolic.

EXPERIMENTAL

Microanalyses are by the Microanalytical Laboratory of Imperial College. Infrared spectra were recorded on a Model 21 Perkin–Elmer double-beam spectrometer with sodium chloride optics. Phenyl*cyclo*heptatriene,[12] tropylium bromide,[13] di*cyclo*heptatrienyl ether,[12] and di*cyclo*heptatrienyl [13] were prepared by methods described previously. Whilst the existence of methyl*cyclo*heptatriene has been noted,[14] preparative details and characterization have not previously been recorded.

1-*Methyl*cyclo*heptatriene.*—Finely powdered tropylium bromide (4·0 g.) was gradually added to a solution of methylmagnesium iodide (from 0·8 g. of magnesium and 4·7 g. of methyl iodide) in ether (75 c.c.). After rapid stirring for 1 hr. at 20° the mixture was refluxed for 0·5 hr., then excess of the Grignard reagent was decomposed by water (40 c.c.). Removal of solvent from the ether layer at 20°/50 mm. and subsequent distillation gave 1-*methyl*cyclo*heptatriene* (1·04 g.), b. p. 50°/35 mm., n_D^{20} 1·5050 (Found: C, 89·7; H, 9·7. C_8H_{10} requires C, 90·6; H, 9·4%).

Preparation of the Hydrocarbon–Metal Complexes.—The preparation of the compounds was similar in all cases. The metal carbonyl was heated under reflux in nitrogen with the pure hydrocarbon, or with a solution of the hydrocarbon in light petroleum (b. p. 100—120°). Reaction times for reaction of *cyclo*heptatriene varied from 7 hr. with molybdenum carbonyl

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[7] Corey, Burke, and Remers, *J. Amer. Chem. Soc.*, 1955, **77**, 4941.

[8] Doering, Laber, Vonderwahl, Chamberlain, and Williams, *ibid.*, 1956, **78**, 5448.

[9] R. C. Lord, personal communication; M. V. Evans, Ph.D. Thesis, Massachusetts Institute of Technology.

[10] Hallam and Pauson, *J.*, 1958, 642.

[11] Cf. Liehr and Ballhausen, *Acta Chem. Scand.*, 1957, **11**, 207.

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

[13] *Idem, ibid.*, 1957, **79**, 352.

[14] Doering and Krauch, *Angew. Chem.*, 1956, **68**, 661.

to 15 hr. with chromium carbonyl. After this time the hydrocarbon and solvent were removed in a vacuum, and excess of the carbonyl sublimed from the residue at 40°/0·05 mm. The residues were extracted with light petroleum, and the solutions filtered and cooled to −60°. The *products* recrystallized from light petroleum (see Table).

R in R–M(CO)$_3$	M in R·M(CO)$_3$	Found (%)				Required (%)			
		C	H	M	O	C	H	M	O
*cyclo*Heptatriene	Mo	44·2	3·1	34·9	17·6	44·1	3·0	35·3	17·6
,,	Cr	52·8	3·6	—	21·2	52·6	3·5	—	21·0
Methyl*cyclo*heptatriene	Mo	46·0	4·1	—	16·8	46·2	3·5	—	16·8
,,	Cr	53·3	4·7	—	—	54·6	4·1	—	—
Phenyl*cyclo*heptatriene	Mo	55·1	3·9	—	15·3	55·2	3·5	—	13·8
,,	Cr *	—	—	—	—	—	—	—	—
Di*cyclo*heptatrienyl	Mo	56·5	4·2	—	13·6	56·4	3·9	—	13·3
,,	Cr *	—	—	—	—	—	—	—	—

* Insufficient crystals were obtained for analysis, but carbonyl modes in infrared spectra were recorded.

The infrared spectrum of $C_7H_8Mo(CO)_3$, in addition to the very strong carbonyl peaks, shows absorption at 3020m, 2938m, 2861s, 2821s, 1462vs, 1440vs, 1402s, 1358s, 1313vs, 940s, and 920m cm.$^{-1}$.

Prolonged Interaction of Di*cyclo*heptatrienyl *and Molybdenum Hexacarbonyl.*—The hydrocarbon (0·19 g.) and carbonyl (0·56 g.) were refluxed for 36 hr. in light petroleum (b. p. 100—120°; 50 c.c.). The solvent was removed at 20°/0·5 mm. and excess of molybdenum carbonyl and di*cyclo*heptatrienyl were sublimed at 60°/0·1 mm. from the residue. The remaining solid was washed with light petroleum to remove the (di*cyclo*heptatrienyl)molybdenum tricarbonyl formed in the reaction; the light brown residue (0·3 g.) was extracted with hot chloroform (3 × 25 c.c.). Concentration of the combined extracts and cooling to −20° gave (*di*cyclo*heptatrienyl*)*di*(*molybdenum tricarbonyl*) (0·03 g.) (Found: C, 43·5; H, 3·1; O, 17·7; Mo, 35·5%; *M*, 517. $C_{20}H_{14}O_6Mo_2$ requires C, 44·3; H, 2·6; O, 17·7; Mo, 35·5%; *M*, 542) as small red crystals.

Interaction of Molybdenum Hexacarbonyl and Di*cyclo*heptatrienyl *Ether.*—The ether (0·79 g.) and the carbonyl (2·1 g.) were refluxed for 15 hr. in light petroleum (b. p. 100—120°; 50 c.c.). After removal of solvent at 20°/0·5 mm. and sublimation of unchanged molybdenum hexacarbonyl at 75°/0·1 mm., the residue was washed with light petroleum (4 × 20 c.c.) and then extracted with hot chloroform (3 × 25 c.c.). Evaporation of the combined chloroform extracts to about 20 c.c., followed by cooling to −20°, gave (*di*cyclo*heptatrienyl ether*)*di*(*molybdenum tricarbonyl*) (0·06 g.) (Found: C, 44·3; H, 2·4; O, 20·4; Mo, 34·2%; *M*, 535. $C_{20}H_{14}O_7Mo_2$ requires C, 42·9; H, 2·5; O, 20·1; Mo, 34·4%; *M*, 558).

Interaction of Potassium Iron Carbonyl Hydride and Tropylium Bromide.—Potassium iron carbonyl hydride was produced by the rapid stirring of iron pentacarbonyl (6·0 g.) with potassium hydroxide (5·2 g.) in water (50 c.c.) under an atmosphere of nitrogen. To this solution was added tropylium bromide (5·2 g.), and stirring was continued for 4 hr. After complete removal of solvent at 40°/0·1 mm., the crude solid product was sublimed at 70°/0·1 mm. Chromatography of the light green sublimate in light petroleum yielded di*cyclo*heptatrienyl (0·1 g.), m. p. 61°. The green colour of the sublimate was shown (infrared spectrum) to be due to a small amount of iron dodecacarbonyl which was destroyed during the chromatography.

Interaction of Sodium Manganese Carbonyl and Tropylium Bromide.—The carbonyl (2·24 g., 1 mol.) in tetrahydrofuran (75 c.c.) was added to finely powdered 15% sodium amalgam (5 g.) and the whole was stirred for 4 hr. After filtration in a dry nitrogen atmosphere, the resulting dark green solution was added to tropylium bromide (2·0 g., 2 mol.) in tetrahydrofuran (50 c.c.) and the mixture stirred for 2 hr. After removal of solvent at 25°/0·2 mm., the solid residue was sublimed at 70°/0·1 mm., to give white and yellow crystals. Chromatography in light petroleum on alumina gave manganese carbonyl (1·93 g., 86%) and di*cyclo*heptatrienyl (0·89 g., 82%), m. p. 60° (Found: C, 92·0; H, 8·2%; *M*, 176. Calc for $C_{14}H_{14}$: C, 92·3; H, 7·7%; *M*, 182). The organic product was found to be identical with that obtained by Doering and Knox's method.[13]

Interaction of Mercury Iron Carbonyl and Tropylium Bromide.—The carbonyl (2·15 g.) and the bromide (0·8 g.) were refluxed for 3 hr. in tetrahydrofuran (75 c.c.) under nitrogen. The solvent was removed at 25°/0·5 mm., and the residue extracted with light petroleum (4 × 30 c.c.). Concentration of the combined extracts gave di*cyclo*heptatrienyl (0·25 g., 59%), m. p. 59—61°.

Preparation of Ditropylium Hexachloroplatinate.—A solution of tropylium bromide (2 g.) in aqueous ethanol (50 c.c.) was added at 20° to an aqueous-ethanolic solution (50 c.c.) of hexachloroplatinic acid (from 4 g. of platinum tetrachloride). The precipitate, which was formed immediately, was filtered off and washed with alcohol and then ether. Removal of solvent at 20°/0·2 mm. left pure *ditropylium hexachloroplatinate* (2·5 g., 75%) (Found: C, 28·7; H, 2·4; Cl, 36·0; Pt, 32·9. $C_{14}H_{14}Cl_6Pt$ requires C, 28·5; H, 2·4; Cl, 36·1; Pt, 33·1%), as a light brown microcrystalline powder.

Catalytic Hydrogenations.—These were carried out with hydrogen and Adams platinum catalyst in ethyl acetate. *cyclo*Heptatriene absorbed 3 mols. of hydrogen in 15 min. The *cyclo*heptatriene-chromium and -molybdenum tricarbonyls, however, were recovered (88 and 90% respectively) after similar treatment for 3 hr.

We thank the Department of Scientific and Industrial Research (R. B.) and the Ethyl Corporation (E. W. A. and M. A. B.) for financial support. Gifts of molybdenum hexacarbonyl (Climax Molybdenum Company), chromium hexacarbonyl (Ethyl Corporation), and *cyclo*heptatriene (Shell Petroleum Company Ltd.) are gratefully acknowledged.

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[*Received, July 28th*, 1958.]