

## Preliminary communication

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### Heptafulvene complexes of tricarbonylchromium

J.A.S. HOWELL, B.F.G. JOHNSON and J. LEWIS\*

*University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)*

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Heptafulvene and its 8-substituted derivatives are reactive materials undergoing oxidation in air and showing a marked tendency to undergo polymerisation under ambient conditions. Recently it has been demonstrated that such compounds may be stabilised as their tricarbonyliron complexes<sup>1,2</sup> and that their reactivity is substantially modified towards electrophilic reagents by the coordinated metal group. The practical synthetic utility of these reactions is limited by the difficulty in removing the iron tricarbonyl grouping without decomposition of the organic product. The ready displacement of the ligand from cycloheptatrienetricarbonylchromium complexes<sup>3</sup> suggests that the related chromium derivatives may have more synthetic potential. To this end, we have prepared a number of heptafulvene complexes of tricarbonylchromium.

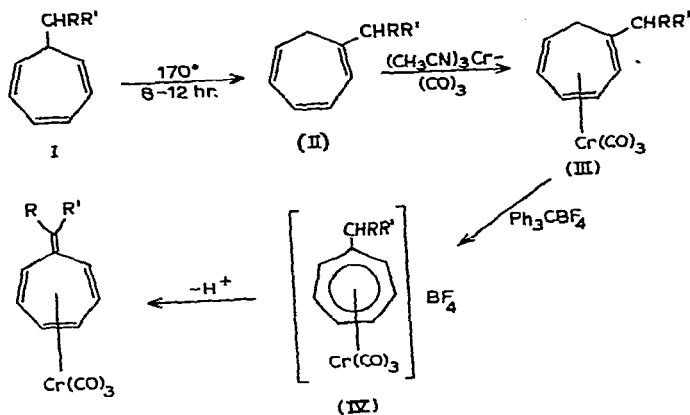
The new heptafulvene complexes were prepared by the route shown in Scheme 1. The precursor ligands (I) were prepared from either tropylium tetrafluoroborate or 7-ethoxycycloheptatriene and the appropriate lithium alkyl or Grignard reagent. Thermal isomerization at 170° for 8–12 hours gave predominantly the 1-isomer (II). Treatment of (II) with tris(acetonitrile)tricarbonylchromium gave predominantly complex (III) as a red oil, which on reaction with Ph<sub>3</sub>CBF<sub>4</sub> yielded the tropylium salt (IV) as an orange-yellow solid. Proton abstraction with 1,8-bis(dimethylamino)naphthalene gave the deep red heptafulvene derivative (V).

Compounds (Va) and (Vb) have been fully characterised by the usual analytical and spectroscopic techniques. The proton NMR spectra are fully consistent with their proposed structure (see below). In complex (Va), the equivalence of the two methyl substituents is clearly demonstrated.

The remaining complexes (Vc), (Vd), and (Ve) have not been isolated as pure compounds. However, mass spectroscopic and infrared measurements clearly indicate that they are produced in the reaction sequence. Further evidence is the reaction of the crude reaction products with dimethylacetylenedicarboxylic ester to produce the azulene derivatives (VI), which have been characterized.

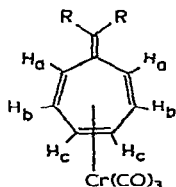
\* Author to whom correspondence should be addressed.

## Scheme 1



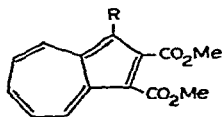
- (Va)  $R = R' = \text{Me}$   
 (Vb)  $R = R' = \text{Ph}$   
 (Vc)  $R = R' = \text{H}$   
 (Vd)  $R = \text{H}, R' = \text{Ph}$   
 (Ve)  $R = \text{H}, R' = \text{Me}$

Unlike tricarbonyliron, which coordinates through a butadiene unit, the tricarbonylchromium is bonded via a triene system, and consequently, the chemistry of the two sets of heptafulvene derivatives is different. Thus, whereas electrophilic addition or substitution occurs on the ring system of the iron complexes, the chromium complexes resemble free heptafulvenes<sup>4</sup>, showing the greater reactivity to electrophiles at the



- Va—Ha, asym. doublet,  $\tau$  5.92, 2H  
 Hb, sym. mult.,  $\tau$  5.36, 2H  
 Hc, sym. mult.  $\tau$  4.22, 2H  
 Me, singlet,  $\tau$  8.44, 6H

- Vb—Ha, Hb, sym. multiplet,  $\tau$  5.60, 4H  
 Hc, sym. mult.  $\tau$  4.24 2H  
 Ph, mult.,  $\tau$  2.86, 10H.



- (VIa)  $R = \text{H}$   
 (VIb)  $R = \text{Ph}$   
 (VIc)  $R = \text{Me}$

exocyclic double bond. Thus protonation of complexes (Va) and (Vb) with  $\text{HPF}_6$  regenerates the tropylium derivative (IV). As anticipated the chromium complexes also function as sources of the heptafulvene, the heptafulvene derivative being readily formed by displacement of the ligand in an appropriate arene solvent, in the presence of a dienophile.

Further work on the synthesis and reactions of these compounds is continuing.

#### ACKNOWLEDGEMENT

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