Electrophilic Substitution Reactions of Cycloheptatrienetricarbonyliron

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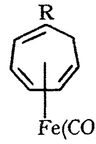
Summary The reactivity of cycloheptatrieneirontricarbonyl towards electrophilic reagents and the variation in the reactivity of the carbonium ions produced from that of the cyclo-octatetraene series are reported.

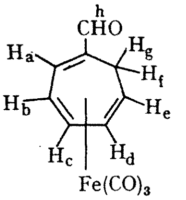
PREVIOUSLY we have shown that the reactivity of cyclo-octatetraene towards electrophilic reagents is considerably modified on co-ordination to a tricarbonyliron unit.[1] Johnson and his co-workers[2] have also reported that the reactivity of a seven-membered heterocyclic ring system *viz. N*-ethoxycarbonylazepine is modified towards electrophilic attack on co-ordination to the tricarbonyliron unit.

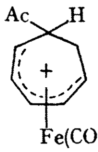
Reaction of cycloheptatrienetricarbonyliron (**1**) with Me_2NCHO–$POCl_3$ gives the aldehyde complex $C_{11}H_8O_4$ Fe (**2**) as a yellow volatile solid (sublimes 70°/0·01 mm. Hg). Elemental analysis is satisfactory, and the molecular weight was confirmed by the mass spectrum. On reaction with 2,4-dinitrophenylhydrazine, the expected hydrazone was obtained. The i.r. spectrum (CCl_4) shows bands at 2044, 2004, and 1999 cm.$^{-1}$ (co-ordinated carbonyl groups) and at 1684 and 1644 cm.$^{-1}$ (aldehyde carbonyl and un-co-ordinated double bond, respectively). The n.m.r. spectrum (100 MHz in CS_2; Me_4Si internal standard; 30°) shows a singlet at τ 0·98, a doublet at τ 3·20, multiplets at τ 4·5 and 6·45, a triplet at τ 6·82, and an AB-quartet with one side coupled, centred at 7·57, of relative intensities 1 : 1 : 2 : 1 : 1 : 2, assigned to H_h,H_a,H_c + H_d,H_e,H_b and H_t + H_g in (**2**).

Cycloheptatrienetricarbonyliron reacts under typical Friedel–Crafts conditions to give the ketone complex $C_{12}H_{10}O_4Fe$ (**3**) as a yellow oil which forms a 2,4-dinitrophenylhydrazone derivative. In addition the intermediate acyl salt $C_{12}H_{11}O_4FePF_6$ (**9**) may also be isolated from the reaction as the hexafluorophosphate salt. This acyl salt (**9**) is readily converted into the ketone complex (**3**) by reaction with sodium methoxide in methanol. The ketone complex (**3**) is reduced to the alcohol $C_{12}H_{12}O_4Fe$ (**5**) which is also produced by reaction of the aldehyde complex (**2**) with methylmagnesium iodide. On passing through a silica column the alcohol (**5**) is dehydrated to give vinylcycloheptatrieneirontricarbonyl $C_{12}H_{10}O_3Fe$ (**6**).

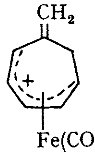


(**1**) R=H
(**2**) R=CHO
(**3**) R=Ac
(**4**) R=CH_2OH
(**5**) R=MeCHOH (**6**) R=CH:CH_2

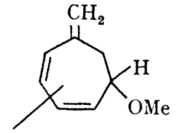




PF_6^- (**9**)



(**7**) PF_6^-
(**8**) BF_4^-



(**10**)

The aldehyde complex (**2**) may be reduced to the alcohol complex $C_{11}H_{10}O_4Fe$ (**4**) with sodium borohydride in ethanol. Treatment of this alcohol with hexafluorophosphoric acid or triphenylmethyltetrafluoroborate gave the salts $C_{11}H_9O_3$-$FePF_6$ (**7**) and $C_{11}H_9O_3FeBF_4$ (**8**). In the i.r. spectra of these salts, high-frequency bands are observed, consistent with the charge associated with the metal. An additional band at 1625 cm^{-1} is assigned to the stretching vibration of the exocyclic double bond. The n.m.r. spectrum and the results of double irradiation experiments are consistent with the structure suggested for this cation (**7**) or (**8**).

In marked contrast to the behaviour of the related salts obtained in the cyclo-octatetraeneirontricarbonyl series, nucleophilic attack occurs with methoxide ion, to give substitution in the seven-membered ring with retention of the exocyclic methylene group *i.e.* complex $C_{12}H_{12}O_4Fe$ (**10**). This behaviour is related to that of other dienyl systems (see ref. 3) and is consistent with the formulation of the salt as a dienyl adduct of the structure (**7**) or (**8**). This difference in behaviour between the salts derived from the cyclo-octatetraene and cycloheptatriene systems may be related to the relative strain induced in the two ring systems in forming a dienyl grouping.

We are currently studying the corresponding reactions of benzocyclo-octatetraene- and cyclo-octatriene-iron tricarbonyl adducts towards electrophilic attack in order to obtain further information about these systems.

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