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Preliminary communication

HYDRIDE-TRANSFER REACTIONS OF [(h^5-CYCLOHEXADIENYL)-(h^5-CYCLOPENTADIENYL)IRON] ALKYLIUM IONS

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Summary

In CF_3CO_2H solution, (h^5-cyclohexadienyl)(h^5-cyclopentadienyl)iron derivatives containing an $R^1R^2C(OH)$ substituent attached either to the cyclopentadienyl ring or to C(1) of the cyclohexadienyl ligand are converted into (h^6-arene)(h^5-cyclopentadienyl)iron cations by hydroxyl loss and hydride migration.

Stabilisation of carbenium ions by an organometallic residue is a well-documented phenomenon [1]. The best known and most thoroughly studied of such systems are the metallocenylcarbenium ions [2] but other organometallic groupings have been found to function in a similar although usually less effective manner, e.g. cymantrene [3], benchrotrene [4], tricarbonylcyclobutadieneiron [5], and nonacarbonylmethinyltricobalt [6]. We now report some preliminary results obtained in an investigation of the properties of carbenium ions incorporating an (h^5-cyclohexadienyl)(h^5-cyclopentadienyl)-iron system adjacent to the electron-deficient centre.

The required alcohol precursors (IIa, IIb) were prepared by hydride reduction ($NaBH_4$/1,2-dimethoxyethane) of the corresponding salts Ia and Ib, which were obtained as described previously [7] from acetyl- and benzoyl-ferrocene respectively by ligand exchange with benzene in the presence of Al_2Cl_6. The readily available ester IIIa [8] proved a convenient starting material for the synthesis of the alcohols IIIb and IIIc, which were obtained by treatment of the ester in ether with $LiAlH_4$ and MeLi respectively. In the former reaction, the conditions must be carefully controlled to avoid the formation of the fully reduced product IIId which results when the ester is treated with an excess of $LiAlH_4$ in ether at room temperature.

The alcohols IIa, IIb, IIIb and IIIc, which are much less stable than their ferrocenyl analogues in solution or in the absence of solvent, were fully

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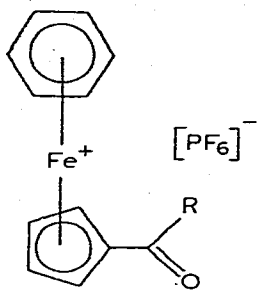
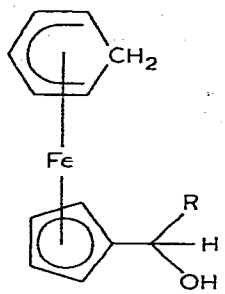
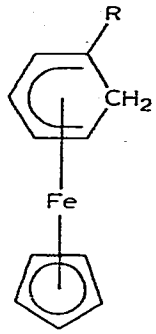


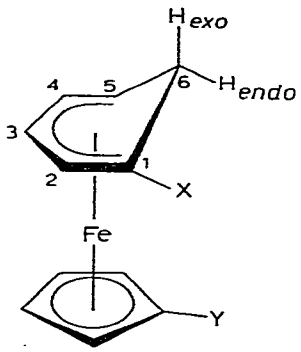
(Ia) R = Me
(Ib) R = Ph



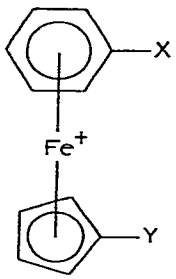
(IIa) R = Me
(IIb) R = Ph



(IIIa) R = CO_2Me
(IIIb) R = CH_2OH
(IIIc) R = CMe_2OH
(IIId) R = Me



(IVa) X = H, Y = $\overset{+}{C}HMe$
(IVb) X = H, Y = $\overset{+}{C}HPh$
(IVc) X = $\overset{+}{C}H_2$, Y = H
(IVd) X = $\overset{+}{C}Me_2$, Y = H



(Va) X = H, Y = CH_2Me
(Vb) X = H, Y = CH_2Ph
(Vc) X = Me, Y = H
(Vd) X = $CHMe_2$, Y = H

characterised by spectroscopic methods (IR, ^{1}H NMR, mass). The IR spectra (CCl_4 solutions) each contained an intramolecularly Fe-bonded hydroxyl-stretching absorption around 3500 cm^{-1}, as found also for the structurally related (1-hydroxyalkyl)ferrocenes [10]. The ^{1}H NMR spectra* were particularly characteristic and it is noteworthy that in the case of the tertiary

*^{1}H NMR spectra ($CDCl_3$ solutions; Me_4Si internal reference). IIa: τ (ppm) 3.93 (tt; H(3)), 5.38 (q; C<u>H</u>OH), 5.6—6.05 (m; C_5H_4 and H(2,4)), 7.4—8.1 (m; H(1,5,6$_{endo}$) and OH), 8.53 (d; Me), and 8.60 (d; H(6$_{exo}$)).
IIb: τ (ppm) 2.6—3.0 (m; Ph), 4.00 (tt; H(3)), 4.65 (s; C<u>H</u>OH), 5.65—6.15 (m; C_5H_4 and H(2,4)), 7.30(br) (s; OH; D_2O-exchanged), 7.5—8.15 (m; H(1,5,6$_{endo}$)), and 8.61 (d; H(6$_{exo}$)).
IIIb: τ (ppm) 4.05 (td; H(3)), 5.83 (s; C_5H_5), 5.6—5.95 (m; H(2,4)), 6.16, 6.52 (2d; C<u>H</u>$_2$OH), 7.7—8.1 (m; H(5,6$_{endo}$) and OH), and 8.75 (d; H(6$_{exo}$)).
IIIc: τ (ppm) 3.94 (td; H(3)), 5.73 (s; C_5H_5), 5.5—5.8 (m; H(2,4)), 7.4—8.1 (m; H(5,6$_{endo}$) and OH), 8.72 (d; H(6$_{exo}$)), and 8.68, 8.88 (2s; Me_2).

alcohol IIIc, the geminal Me groups of the CMe_2OH substituent, which is attached to a dissymmetric residue, are magnetically non-equivalent and give rise to two singlets. Likewise, the $C\underline{H}_2OH$ protons of the alcohol IIIb are diastereotopic.

By analogy with the behaviour of ferrocenylalkanols, which afford stable carbenium ions in acidic solutions [2b] (i.e. $FcCR_2OH \rightarrow Fc\overset{+}{C}R_2$; R = H, alkyl, aryl, etc.), generation of the cations IVa—IVd by acid treatment of the alcohols IIa, IIb, IIIb and IIIc was anticipated. However, the ^1H NMR spectra of these alcohols in CF_3CO_2H were incompatible with structures of the type IV and showed clearly that (h^6-arene)(h^5-cyclopentadienyl)iron cations (V) had been formed as the major products* in each case; i.e. IIa → Va, IIb → Vb, IIIb → Vc, and IIIc → Vd. These cations could be isolated from these solutions as $[PF_6]^-$ salts which were identical with those obtained independently and unambiguously by ligand-exchange reactions of ferrocene or 1,1′-dialkylferrocenes with appropriate arenes in the presence of Al_2Cl_6/Al [11]; i.e. Va from 1,1′-diethylferrocene/benzene, Vb from 1,1′-dibenzylferrocene/benzene, Vc from ferrocene/toluene, and Vd from ferrocene/cumene.

Although intermolecular processes have not been excluded, the most likely mechanism for the formation of the cations Va—Vd involves acid-promoted dehydroxylation of the alcohol precursors followed by intramolecular hydride transfer from C(6) of the cyclohexadienyl ligand to the formal C^+-centre of the resulting intermediate carbenium ions IVa—IVd**. Related intermolecular hydride-transfer reactions occur readily on treatment of neutral (h^5-cyclohexadienyl)metal complexes with Ph_3C^+ [12] (e.g. IV → V; X = Y = H, alkyl, etc.) and the reported [13] formation of the tricarbonyl(1-methylcyclohexadienyl)iron cation on acid treatment of tricarbonyl[1-(hydroxymethyl)cyclohexa-1,3-diene]iron may involve a similar mechanism. In the present reactions, the operation of intramolecular processes would require stereoselective transfer of $H(6_{endo})$ from the CH_2 group of the cations IVa and IVb while migration of either $H(6_{exo})$ or $H(6_{endo})$ appears feasible in the case of the cations IVc and IVd. We plan to investigate this aspect using selectively D-labelled precursors.

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*Resonances due to unidentified minor products were present in the spectra of these solutions.
**It is conceivable that the conjugate acids ($R\overset{+}{O}H_2$) of the alcohols undergo concerted dehydration and hydride transfer.

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