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1. *Preparation and Reactions of Some Oxoalkyl-iron Complexes.*

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The oxoalkyl complexes $C_5H_5Fe(CO)_2{\cdot}CH_2{\cdot}CO{\cdot}R$, where $R = H$ or Me, have been prepared and characterised. They are readily and reversibly protonated by hydrogen halides or mineral acids, forming cationic species, $[C_5H_5Fe(CO)_2{\cdot}C_2H_3OR]^+$. The infrared and proton magnetic resonance spectra of the halide salts of the protonated and deuterated complexes have been studied. Structures containing an enol system are suggested for the cations.

We have recently shown that some 1-cyanoalkyl-iron complexes are protonated by acids, forming cations containing a ketenimine system, CHR=C=NH.[1] By analogy with this reaction and also with the protonation of σ-allyl systems, $M{-}CH_2{\cdot}CH{=}CH_2$, forming π-propene cations,[2,3] the oxoalkyl complexes (I; $R = H$ or Me) should undergo protonation and form cations containing an enol system bonded to the metal. The complexes (I; $R = H$ or Me) were prepared in about 10% yield by the reaction of the oxoalkyl chlorides, $ClCH_2{\cdot}CO{\cdot}R$ (where $R = H$ or Me), with the sodium salt, $Na^+[C_5H_5Fe(CO)_2]^-$. The analytical data and infrared and proton magnetic resonance spectra of the complexes

$$\text{(I)}\ C_5H_5Fe(CO)_2{\cdot}CH_2{\cdot}COR \qquad [C_5H_5Fe(CO)_2{\cdot}C_2H_3OR]^+\ X^-\ \text{(II)}$$

(I; $R = H$ or Me) are given in the Tables 1 and 2 respectively and are entirely consistent with the formulation given above and in the chart; this evidence is not further discussed.

Properties of the Oxoalkyl Complexes (I).—The orange-yellow crystalline complexes (I) are moderately stable to atmospheric oxidation. They sublime in a vacuum at ~60° and they are moderately soluble in light petroleum and very soluble in ether. The solutions are stable under nitrogen but decompose after a few minutes in air. The complexes give yellow solutions in water from which they may be recovered with ether. They are also very soluble in mineral acids giving deep yellow solutions. Neutralisation of the acid solutions with calcium carbonate and extraction with ether recovers the neutral complexes (I). Both neutral and acid aqueous solutions give precipitates with suitable large anions. Thus the neutral complexes (I) readily and reversibly form cationic species.

Reaction of Oxoalkyl Complexes with Acids.—Treatment of solutions of the complexes (I) in light petroleum with dry hydrogen chloride or hydrogen bromide affords deep yellow precipitates which are very souble in water. Concentrated aqueous solutions of the salts are strongly acidic and deposit crystals of the neutral complexes within a few minutes. The hydrohalides are also soluble in liquid sulphur dioxide, however some dissociation occurs in the solution and again the neutral complexes (I) can be isolated. The yellow precipitates have the stoicheiometry $C_9H_8O_3FeXR$, where $X = Cl$ or Br and $R = H$ or

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[1] Ariyaratne and Green, *J.*, **1963**, 2976.

[2] Green and Nagy, *J.*, **1963**, 189.

[3] Cousins and Green, *J.*, **1963**, 889.

TABLE 1.

Infrared spectra.[a]

$R\cdot CH_2\cdot CHO$ [b]	$R\cdot CH_2\cdot CO\cdot CH_3$ [b]	$[R\cdot CH_2{=}CH\cdot OH]^+Br^-$ [c]	$[R\cdot CH_2{=}CMeOH]^+Br^-$ [c]
3100w [d]	3110m [d]	3095m [d]	3065m [d]
2980w [e]	2980m [e]	2910sh	2955w
2925w [e]	2935m [e]	2810s	2905w
2800w [f]	2840w [e]	2580s	2835m
2700w		2500s } [g]	2785s
		2350sh	2730s
			2655s
			2570s } [g, h]
			2450s
			2385m
2030vs	2028vs	2060vs	2045vs
1983vs } [i]	1976vs }	2010vs } [i]	1991vs } [i]
1655vs [j]	1658vs [j]		
1435m	1433s	1550s [k]	1515s [k]
1425m	1423s	1433m	1460m
1387w	1350s	1425m	1455m
1365w	1228s	1375s	1430s
1145s	1097w	1280s	1380s
1005m	1057w	1017m [l]	1367s
843sh [l]	1012sh [l]	935m	1245s
832s [l]	942m	890w	1072w
	840sh	875w	1060w
	830s [l]	852m [l]	1030w
		836w	1005w [l]
		826m	962s
		816m	872m
			862m
			825m

[a] $R = C_5H_5Fe(CO)_2$. [b] Measured in solutions in CS_2 and CCl_4. [c] Measured as mulls in Nujol and hexachlorobutadiene. [d] C–H stretch of C_5H_5. [e] C–H stretch of alkanes. [f] C–H stretch of –CHO. [g] O–H stretch. [h] O–D stretches at 2103s, 1963s, 1938s. [i] C≡O stretch. [j] $\rangle$C=O stretch of CHO. [k] Co-ordinated C=C stretch. [l] π-C_5H_5 frequencies.

TABLE 2.

Proton magnetic resonance data.

Compound [a]	Band (τ) [b]	Rel. intensity [e]	Multiplicity	Sepn. of components (c./sec.) [c]	Assignment
$R\cdot CH_2\cdot CHO$ in CS_2	0·70	1	3	app. $J(H,CH_2)$ 8·0	CHO
	5·20	5	1	—	π-C_5H_5
	8·40	2	2	app. $J(CH_2,H)$ 5·3	CH_2
$R\cdot CH_2\cdot COMe$ in CCl_4	5·10	5	1	—	π-C_5H_5
	7·98	3 } 5	1	—	CH_3
	8·30	2			CH_2
$[R\cdot CH_2{=}CH\cdot OH]^+Br^-$ in liq. SO_2	1·43	1	1	—	OH
	1·83	1	3	app. $J(H,CH_2)$ 8·0	=CH·O·
	4·62	5	1	—	π-C_5H_5
	7·15	2	2	app. $J(CH_2,H)$ 8·0	$H_2C{=}$
$[R\cdot CH_2{=}CMe\cdot OH]^+Br^-$ in liq. SO_2 [d] ...	0·12	1	1	—	OH
	4·65	5	1	—	π-C_5H_5
	7·35	2 } 5	1	—	CH_2
	7·52	3	1	—	CH_3
$R\cdot CH_2\cdot COMe$ in CF_3COOH	4·75	5	1	—	π-C_5H_5
	7·38	2 } 5	1	—	CH_2
	7·55	3	1	—	CH_3
$[R\cdot CH_2{=}CMe\cdot OD]^+Br^-$ in liq. SO_2 ...	0·70	0·4	1	—	OH impurity
	4·68	5	1	—	π-C_5H_5·
	7·35	2 } 5	1	—	CH_2
	7·52	3	1	—	CH_3

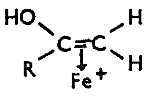
[a] $R = \pi$-$C_5H_5Fe(CO)_2^-$. [b] Relative to $SiMe_4$ ($\tau = 10$) as internal standard. [c] Where multiplicity occurs which may be understood as first-order spin-spin couplings the splittings are recorded as the apparent coupling constants (app. *J*). [d] The spectrum of the chloride salt is very similar. [e] Estimated to whole numbers, rel. π-$C_5H_5 = 5$.

Me. Attempts to determine the conductivity of the salts in nitrobenzene were unsuccessful because of dissociation of the complexes in solution. However, the infrared spectra of the chlorides and the bromides are essentially similar to those of the silicotungstate precipitates obtained from acid aqueous solutions of the complexes (I); and the aqueous solutions of the halogeno-complexes give precipitates immediately with silver nitrate solution indicating that they are salts. By analogy with the protonation of the 1-cyanoalkyl[1] and σ-allyl complexes of iron[2] it is reasonable to postulate that the complexes are 1 : 1 electrolytes and may be formulated as (II; R = H or Me; X = Cl or Br).

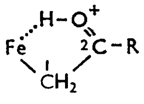
Spectral Studies.—The infrared and proton magnetic resonance spectra of the complexes (II) are given in Tables 1 and 2, respectively, together with tentative assignments. Both types of spectra show the characteristic bands due to a π-cyclopentadienyl group. The infrared spectra of complexes (II) show two bands assignable to terminal carbonyl frequencies, which are 25 cm.$^{-1}$ higher than those of the neutral complexes. Similarly, in the proton magnetic resonance spectra of the complexes (II) the band arising from the cyclopentadienyl protons occurs about 0·5 τ lower than in the neutral complexes (I). These shifts are consistent with a higher oxidation state of the metal.[2] The proton magnetic resonance spectra of the complexes (II) do not show bands assignable to a hydrogen attached to the iron, and the spectra may be assigned as shown in Table 2. The band at ~1·0 τ assigned to the enol hydrogen occurs in the region associated with normal hydroxyl protons and is at higher frequencies than the bands assigned to the enol hydrogen in compounds such as β-diketones.[4] In the latter case, however, the occurrence of these bands at very low fields (~ —5·0 τ) is attributed to strong intramolecular hydrogen bonding of the enol hydrogen which would not be expected to occur for the enol hydrogen atoms of the complexes (II). The position of the band due to the enol hydrogen varies slightly with both concentration and nature of the cation. A similar effect of variation of position of band with concentration has been noted for other hydroxylic protons in phenols and alcohols.[4] The spectrum of the complex (I; R = Me) in trifluoroacetic acid is identical with that of the complex bromide (II; R = Me) except that the band assignable to the enol hydrogen atom is absent. This absence may be due to the exchange of the enol hydrogen atom in this solution.[4]

The infrared spectra of complexes (II) differ markedly from those of compounds (I) in that they do not show bands assignable to ketonic carbonyl groups, and new broad bands appear in the region 2400—2800 cm.$^{-1}$. The intensity of the latter bands is reduced in the spectrum of the partially deuterated complex (II; R = Me) bromide and new bands appear in the region 1900—2100 cm.$^{-1}$ which are partially hidden by the terminal carbonyl stretching frequencies. The bands in the region 2400—2800 cm.$^{-1}$ are assigned to O–H stretches and therefore on protonation of the complexes (I) a proton is attached to the oxygen of the ketonic carbonyl. The spectra also show bands in the region 1500—1550 cm.$^{-1}$ which are assigned to co-ordinated C=C stretches.[2]

Discussion.—From the above evidence, structures (A) or (B) can be considered for the protonated oxoalkyl systems in the cations (II). The absence, from the proton magnetic spectrum of the cation (II; R = H), of bands assignable to *cis–trans* coupling of the carbon-1 hydrogen atoms with the carbon-2 hydrogen atom favours structure (B). It is, however, possible that the close presence of the metal to the enol system, as shown in the structure (A), may prevent occurrence of coupling. The distribution of the positive charge to the metal, as discussed above, is more easily understood in terms of structure (A),



(A)



(B)

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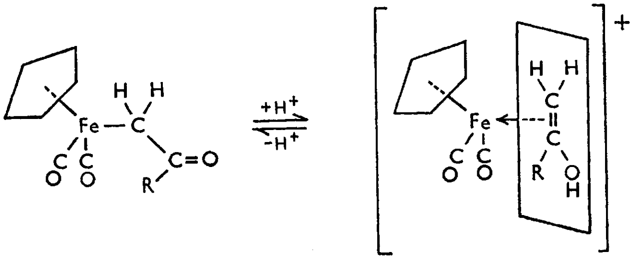
[4] Pople, Schneider, and Bernstein, " High-resolution Nuclear Magnetic Resonance," McGraw-Hill Inc., New York, 1959.

although it is possible that, as shown for structure (B), there is some interaction of the hydroxyl hydrogen with the metal. In some protonated acylferrocenes[5] the hydroxyl hydrogen is strongly hydrogen-bonded internally and the stretching frequency is lowered to the region 2200—2400 cm.$^{-1}$. The hydroxyl hydrogen atom in the cations (II) similarly shows hydrogen bonding but to a lesser extent than the protonated ferrocenes, the stretching frequency being broad and intense and occurring in the region 2400—2800 cm.$^{-1}$. This hydrogen bonding may arise also from intermolecular interactions. The anomalous absence of the methyl-group absorptions from the spectrum of the cation (II; R = Me) is consistent with similar absences from spectra of π-propene–metal complexes.[2] Finally, there are no bands which can be assigned to C–H stretches arising from the methylene group in structure (B) and there is only one band in the region 2900—3200 cm.$^{-1}$ assignable to C–H stretching frequencies, as observed for some π-cyclopenta-dienyl–olefin–iron complexes.[2,3] The latter observations favour structure (A).

The complexes (II) are diamagnetic, as shown by the sharpness of the lines in their proton magnetic resonance spectra. Therefore, in accord with the inert-gas formalism, and the salts being assumed to be 1 : 1 electrolytes, by analogy with the protonated products obtained from the metal–σ-allyl and iron–σ-1-cyanoalkyl complexes, it is suggested that the structure of the cations (II) is as shown. In these structures, the enol forms of acetone and acetaldehyde are stabilised by bonding to the iron. The mechanism for the protonation, may be considered analogous to that put forward for the protonation of the iron–σ-1-cyanoalkyl complexes.[1] The close similarity in the reactions of the systems, $\mathrm{M{\cdot}CH_2{\cdot}CH{=}CH_2}$, $\mathrm{Fe{-}CH_2R{\cdot}CN}$, and $\mathrm{Fe{-}CH_2{\cdot}COR}$ with acids suggests that suitable metal complexes containing an $\mathrm{M{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}}$ system will react forming a $\mathrm{M{-}\overset{|}{\underset{|}{C}}{-}\overset{|\,+}{\underset{|}{C}}{-}}$ intermediate system which would be stabilised by the metal.



It would therefore seem that metal–organo-systems show a rather different chemistry from the normal organic analogues. Further studies on metal-σ-organic complexes are in progress.

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory, Cambridge. Preparation, reactions, and purifications were carried out under nitrogen or in a vacuum. Light petroleum was " AnalaR " material, of b. p. 30—40°.

Dicarbonylcyclopentadienyloxoalkyliron Complexes.—A typical reaction is described. A solution of the sodium salt $\mathrm{Na^+[C_5H_5Fe(CO)_2]^-}$ in tetrahydrofuran was prepared from tetracarbonyldicyclopentadienyldi-iron (10 g.) as previously described.[2] This solution was slowly added to a stirred and cooled (solid carbon dioxide–acetone bath) solution of chloroacetone (20 ml.) in ether (100 ml.). After the addition (30 min.), the mixture was allowed to warm to room temperature and was stirred for 1 hr. The solvents and excess of chloroacetone were removed under reduced pressure and the residue was extracted with 1 : 1 ether–light petroleum mixture (3 × 100 ml.). The extract was concentrated under a reduced pressure and chromatographed on an alumina column made up in light petroleum. Elution with 1 : 1 light petroleum–ether separated, first, a red band, which was collected and shown to contain the binuclear

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[5] Rubalcava and Thomson, *Spectrochim. Acta*, 1962, **18**, 449.

complex $[C_5H_5Fe(CO)_2]_2$, and, secondly, an orange band. The eluate containing the second band was collected, the solvent was removed under reduced pressure, and the semi-solid residue was recrystallised twice from ether–light petroleum mixture giving deep orange-yellow crystals of the *complex*, which finally sublimed *in vacuo* at 60° (yield *ca.* 10%) [Found: C, 51·4; H, 4·5; Fe, 23·8%; *M* (cryoscopic in dioxan), 241. $C_{10}H_{10}FeO_3$ requires C, 51·3; H, 4·3; Fe, 23·9%; *M*, 234]. The *formylmethyl complex* (I; R = H) was prepared in similar yields by the above method, dry chloroacetaldehyde being used in ether [Found: C, 48·9; H, 3·8; Fe, 25·6%; *M* (isopiestic in dichloromethane), 212. $C_9H_8FeO_3$ requires C, 49·1; H, 3·7; Fe, 25·4%; *M*, 220].

Reaction of the Complexes (I) with Hydrogen Halides.—A typical reaction is described. Pure dicarbonylcyclopentadienylformylmethyliron (0·3 g.) in light petroleum (150 ml.) was treated with dry hydrogen bromide. The bright yellow precipitate was washed several times with light petroleum by decantation and dried in a vacuum. The yield was >95%. The salt was analysed without further purification [Found: C, 35·6; H, 2·8; Br, 27·1; Fe, 18·4%. $C_9H_9BrFeO_3$ requires C, 35·9; H, 3·0; Br, 26·6; Fe, 18·6%]. The acetonyl complex (I; R = Me) was similarly treated with hydrogen chloride and hydrogen bromide giving yellow salts [Found: C, 45·0; H, 4·2; Cl, 13·0; Fe, 20·4%. $C_{10}H_{11}ClFeO_3$ requires C, 44·4; H, 4·1; Cl, 13·1; Fe, 20·6%. Found: C, 38·1; H, 3·1; Br, 24·9; Fe, 17·8%. $C_{10}H_{11}BrFeO_3$ requires C, 38·1; H, 3·5; Br, 25·4; Fe, 17·7%]. The partially deuterated bromide salt from the 2-oxopropyl complex was also prepared in the above manner. Approximately 60% deuterium bromide was prepared from phosphorous pentabromide and deuterium oxide. The spectra of these salts were determined.

Infrared Spectra.—Measurements were made with a Perkin-Elmer model 21 spectrometer. The data and conditions of measurement are given in Table 1.

High Resolution Proton Magnetic Resonance Spectra.—Measurements were made on a Perkin-Elmer spectrometer at 40 Mc./sec. The data and conditions of measurement are given in Table 2.

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