STUDIES ON SOME ALKYL AND OLEFIN COMPLEXES OF IRON AND MANGANESE

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It has been shown that the olefin complexes $C_7H_8Mo(CO)_3$[1], $C_6H_8Fe(CO)_3$[2] and $C_5H_6Fe(CO)_2Ph_3P$[3] readily lose a hydride ion when treated with triphenylmethyl salts, affording the cations $[C_7H_7Mo(CO)_3]^+$, $[C_6H_7Fe(CO)_3]^+$ and $[C_5H_5Fe(CO)_2Ph_3P]^+$, respectively. We have noted recently that some alkyl-iron complexes undergo a similar reaction and lose a hydride ion forming ethylenic cations[4]. We also found that, as in the case of the complex $[C_5H_5Fe(CO)_2Ph_3P]^+$[3], this reaction is reversible in that treating the ethylenic cation salts with sodium borohydride reforms alkyl complexes[5]. This work is now presented in greater detail with some analogous studies on manganese complexes.

PREPARATION AND PROPERTIES OF THE METAL-ALKYL COMPLEXES

The preparation of the complexes $C_5H_5Fe(CO)_2R$, (I), where R = Me or Et, by the reaction of the sodium salt $Na^+[C_5H_5Fe(CO)_2]^-$ with suitable alkyl halides has been described[6] and the *n*-propyl and isopropyl complexes (I; R = *n*-Pr or iso-Pr) were prepared similarly in satisfactory yields. Using 2-deutero-2-bromopropane the deuteroisopropyl complex (I; R = $CDMe_2$) was obtained in 70% yield. During the preparation of the alkyl complexes (I; R = *n*-Pr or iso-Pr) there were also formed, in small yields, organometallic complexes which their infrared spectra showed to contain bands assignable to ketonic carbonyl stretches.

The propyl complexes (I; R = *n*-Pr or iso-Pr) are amber oils which are less stable to oxidation by air and thermal decomposition than the ethyl analogue (I; R = Et), and they decompose slowly under nitrogen at room temperature forming *inter alia* ketonic products and the complex $[C_5H_5Fe(CO)_2]_2$. The isopropyl complex is noticeably less stable to thermal decomposition than the *n*-propyl isomer, and decomposes rapidly above 60°.

The purity and formulation of each alkyl complex (I) was confirmed by analysis and the infrared and proton magnetic resonance spectra. The spectra of the new complexes given in Tables 1 and 2 are entirely compatible with the formulations given above.

Pentacarbonylethylmanganese (II), which has been reported[7] but without preparative details, was prepared in good yields by the reaction of sodium pentacarbonylmanganese with ethyl iodide. The pure compound is a straw-yellow, very volatile liquid which is very unstable, both thermally and to atmospheric oxidation. Pure samples decomposed slowly even when kept in the dark, in vacuum and at

—10°. The decomposition products contained the acyl complex $(CO)_5MnCOEt$ and an unidentified red oil.

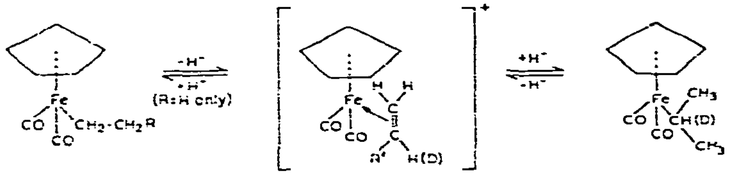
REACTION OF SODIUMCYCLOPENTADIENYLDICARBONYLIRON WITH *tert*-BUTYL CHLORIDE

In an attempt to prepare the complex (I; R = *tert*-Bu) by the reaction of the sodium salt $Na^+[C_5H_5Fe(CO)_2]^-$ with *tert*-butyl chloride a new route to the hydride $C_5H_5Fe(CO)_2H$[8] has been found. During the reaction a gas containing isobutene and hydrogen was evolved and chromatography of the reaction products separated the hydride (I; R = H) in high yield. The complex $[C_5H_5Fe(CO)_2]_2$ was also formed. The hydride (I; R = H) was characterised by analysis and the infrared spectrum, which was obtained at —20°. The reaction may be regarded as a standard elimination reaction, *viz*:

$$Na^+[C_5H_5Fe(CO)_2]^- + H{-}CH_2{-}CMe_2Cl \longrightarrow C_5H_5Fe(CO)_2H + Me_2C{=}CH_2 + NaCl.$$

HYDRIDE ION ABSTRACTION

The iron complexes (I; R = Et, *n*-Pr or iso-Pr, but not Me) react readily with triphenylmethyl perchlorate or tetrafluoroborate in tetrahydrofuran affording ethylenic cations in high yields. These cations may be readily isolated as yellow crystalline salts of suitable anions such as perchlorate, hexachloroplatinate or hexafluorophosphate. The cations formed were identified by analysis and by their infrared and, in some cases, proton magnetic resonance spectra as the previously reported complexes $[C_5H_5Fe(CO)_2 \cdot CH_2{=}CHR']^+$ (III; where R′ = H or Me)[9]. As shown in the chart, the complex (I; R = Et) gives the cation (III; R′ = H) and the complexes (I; R = *n*-Pr or iso-Pr) give the cation (III; R′ = Me). Hydride abstraction from the deuteroisopropyl complex (I; R = $CDMe_2$) affords the 2-deuteropropene cation (III; R′ = Me) in high yields. The spectrum of this cation is given below.



I III I

(R = R′ = H, Me)

Treatment of the complexes $C_5H_5Fe(CO)_2CH_2CH_2CN$[10] and $C_5H_5Fe(CO)_2CF_2CF_2H$[11] with triphenylmethyl salts in tetrahydrofuran gave no reaction, and the complexes were recovered unchanged after 3 h. Also, the methyl derivative (I; R = Me) did not show any immediate reaction with triphenylmethylperchlorate under similar conditions and after 10 h only a small amount of a cation, identified as the aquo cation $[C_5H_5Fe(CO)_2H_2O]^+$, could be isolated.

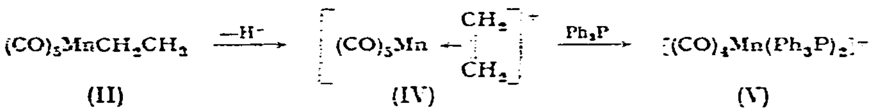
Treatment of pentacarbonylethylmanganese with triphenylmethylperchlorate in tetrahydrofuran or benzene resulted mainly in the decomposition of the ethyl complex (II). However the reaction of pure triphenylmethyl tetrafluoroborate with the pure ethylpentacarbonylmanganese in the absence of a solvent gave small yields of a crystalline salt, and a little ethylene was evolved. Analysis, conductivity measurements and the infrared spectrum identify the salt as pentacarbonylethylenemanganese tetrafluoroborate, $[(CO)_5Mn\cdot CH_2{=}CH_2]^+BF_4^-$, (IV). The physical properties and infrared spectrum of the complex (IV) closely resemble those of the propene analogue $[(CO)_5MnCH_2{=}CHCH_3]^+ClO_4^-$[11]. The ethylene cation (IV) has also been prepared by the reaction of ethylene with pentacarbonylmanganese chloride[12]. Further evidence for the formulation of this complex comes from a study of its reaction with triphenylphosphine (see below).

HYDRIDE ADDITION

The ethylenic cation salts (III) react readily with sodium borohydride in tetrahydrofuran. The products of the reaction depend on the nature of the anion. Reaction of the cation (III) chlorides under the above conditions affords mainly the complex $[C_5H_5Fe(CO)_2]_2$. The cation (III) perchlorates or tetrafluoroborates, however, give petrol-soluble yellow-brown oils which may be readily isolated. Comparison of the infrared spectra of the purified samples so obtained with those of the fully characterised alkyl complexes (I) show that the cation (III; R′ = H) reforms the ethyl complex (I; R = Et), and the cation (III; R′ = Me) gives the alkyl complex (I; R = iso-Pr). The reactions are shown in the chart. No evidence for the presence of the *n*-propyl isomer (I; P = *n*-Pr) was found in the reduction products from the cation (III; R′ = Me), although there are distinct differences in the infrared spectra of the two isomers. The reduction of the cation (III; R′ = Me) perchlorate was also carried out in the presence of a large excess of 1-hexene and also with a rapid stream of butadiene passing through the reaction mixture. In both cases the only alkyl product isolated was the isopropyl complex (I; R = iso-Pr).

REACTION OF PENTACARBONYLETHYLENEMANGANESE PERCHLORATE WITH TRIPHENYLPHOSPHINE

Treatment of the ethylene complex (IV) with triphenylphosphine affords evolution of a gas, identified as a mixture of carbon monoxide and ethylene, and a solid residue from which a pale yellow crystalline salt may be readily isolated. Analysis, conductivity measurements and the infrared spectrum show that the complex must be formulated as a tetracarbonylbistriphenylphosphinemanganese complex $[(CO)_4Mn(Ph_3P)_2]^+BF_4^-$, (V). The reactions of the manganese complexes are thus:



$$(CO)_5MnCH_2CH_3 \xrightarrow{-H^-} \left[(CO)_5Mn \leftarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}\right]^+ \xrightarrow{Ph_3P} [(CO)_4Mn(Ph_3P)_2]^+$$

(II) (IV) (V)

The cation (V) has also been prepared by the analogous reaction of the propene cation $[(CO)_5Mn\cdot CH_2{=}CHCH_3]^+$ with triphenylphosphine[11]. Detailed studies, considering the presence of isomers of the complex (V), will be presented in a later work.

INFRARED SPECTRA

The spectra of some of the alkyl complexes (I) and some of the ethylenic complexes (III) have already been reported and discussed. Therefore, although the spectra of these complexes were measured in this work for the purposes of direct comparison with the products from hydride abstraction or addition, only the spectra of new complexes are presented here; they are given in Table 1 down to 650 cm^{-1}. The spectra of all the complexes (I) and (III) show bands characteristic of a π-C_5H_5–metal grouping, including a sharp single C—H stretch at 3100 cm^{-1}. The spectra of all the

TABLE 1

INFRARED SPECTRA[a]

$M—CH_2CH_2CH_3$[b]	$M—CH(CH_3)_2$[b]	$M—CD(CH_3)_2$[b]	$[M\text{-}CH_2{=}CDCH_3]BF_4$[c]	$(CO)_5MnEt$[b]	$[(CO)_5Mn\text{-}CH_2{=}CH_2]BF_4$[c]
3105 w[d]	3105 w[d]	3120 w[d]	3105 m[d,e]	2930 s[f]	3150 m[e]
2950 s[f]	2960 s[f]	2960 s[f]		2860 s[f]	3040 w[e]
2920 s[f]	2930 s[f]	2900 sh[f]			3005 w[e]
2900 m[f]	2900 sh[f]	2850 s[f]			2980 w[e]
2860 m[f]	2845 s[f]				
2820 m[f]		2165 m[b]			
				2107 s[g,n]	2166 s[g]
2013 vs[g]	2012 vs[g]	2012 bs[g]	2089 vs[g]	2071 vs[g,n]	2075 vs[g]
1953 vs[g]	1953 vs[g]	1951 vs[g]	2055 vs[g]	1993 vs[g,n]	
1464 sh[j]	1463 s[j]	1455 s[j]	1517 w[h]	1463 m[j]	1450 m
1455 m[j]	1436 m[j]	1438 m[j]	1457 m	1376 m[j]	1288 m
1436 m[j]	1421 m[i]	1421 m[i]	1431 m[i]	1200 w	1161 vs[m]
1421 m[i]	1382 m[j]	1380 m[j]	1393 m	1188 sh	
1300 w[j]	1366 s[j]	1364 s[j]	1367 m	1170 sh	
1363 w[j]	1315 w	1166 m	1285 m	1073 m	
1267 w	1260 vw	1135 m	1053 vs[m]	1617 m	
1141 s[k]	1191 m	1090 s[k]	908 sh	970 m	
1114 w	1175 m	1061 sh	878 s	930 w	
1057 m	1116 s[k]	1015m[i]	723 w	968 w	
1015 m[i]	1090 sh	998 m[i]		865 w	
1001 m[i]	1060 w	918 w			
977 w	1040 w	840 sh[i]			
916 w	1017 m[i]	824 s[i]			
886 m	1000 m[i]	737 m			
840 s[i]	960 w				
825 s[i]	920 w				
794 m	965 sh				
	842 s[i]				
	825 s[i]				

[a] $M=C_5H_5Fe(CO)_2$.
[b] Measured as thin films of the pure oil.
[c] Measured in Nujol and hexachlorobutadiene.
[d] C—H stretch of π-C_5H_5.
[e] Olefinic C—H stretch.
[f] C—H stretch of alkanes.
[g] $C{\equiv}O$ stretch.
[h] Coordinated $C{=}C$ stretch.
[i] π-C_5H_5 frequencies.
[j] C—H deformation.
[k] Band possibly characteristic of metal–alkyls[8].
[l] C—D stretch.
[m] BF_4^-.
[n] 2107 s, A_1 mode, 2071 and 1993 vs, E and A_1 modes[13].

compounds show bands which may be assigned to the stretching frequencies of terminal carbonyl groups. A strong band at about 1110 cm^{-1}, which may be characteristic of metal–alkyl systems[6], is present in the spectra of the propyl complexes (I; R = *n*-Pr or iso-Pr).

All the spectra are consistent with the proposed formulations, and assignments are given in the Table 1.

PROTON MAGNETIC RESONANCE SPECTRA

Only the spectra which have not been previously reported are given in this work, although for purposes of characterisation the spectra of all the compounds discussed above were measured. The spectra of the complexes are given in Table 2, together with some assignments. It may be noted that the spectrum of the 2-deuteropropene cation (III; R′ = Me) supports the assignments previously given for the analogous propene and 1-butene cations $[C_5H_5Fe(CO)_2CH_2{=}CHCH_2R'']^+$, where R″ = H or Me[9]. In the assignment of the spectra of the latter complexes it was assumed that $J(3,4)$ was small and that the doublets at ~ 6.5 τ and ~ 6.0 τ were due to spin-spin

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA

Compound	*Band pos* *(τ)*[a]	*Rel. intensity*[b]	*Multiplicity*[d]	*Sepn. of components*[c] *(c/sec)*	*Assignment*
$C_5H_5Fe(CO)_2Et$	8.59	5	Complex band (12)	—	Et
as pure liq.	5.40	5	1	—	C_5H_5
$Mn(CO)_5Et$	8.69	—	Complex band (6)	—	Et
as pure liq.					
$C_5H_5Fe(CO)_2$-*n*-Pr	8.72	7	Complex band (6)	—	*n*-Pr
as pure liq.	5.41	5	1	—	C_5H_5
$C_5H_5Fe(CO_2)$-iso-Pr	8.68	6	2	App. $J(CH_3, H)$ = 6.5	Me_2 split by tertiary CH
as pure liq.					
	7.35	1	Complex band (9)	App. $J(H, CH_3)$ = 6.1	Tertiary CH split by Me_2
	5.42	5	1	—	C_5H_5
$C_5H_5Fe(CO)_2CDMe_2$	8.67	6	1[e]	—	Me_2
as pure liq.	5.41	5	1	—	C_5H_5
Me_2CDBr	8.35	—	3	App. $J(CH_3, D)$ = 1	Me_2 split by CD
as pure liq.					
Me_2CDOH	8.86	6	3	App. $J(CH_3, D)$ = 0.9	Me_2 split by CD
as pure liq.					
$[C_5H_5Fe(CO)_2CH_2{=}CDCH_2]^+BF_4^-$ in liq. SO_2	8.16	3	1[e]	—	CH_3
	6.53	1	1[e]	—	H^3
	6.66	1	1[e]	—	H^4
	4.40	5	1	—	C_5H_5

[a] Relative to $SiMe_4$ (τ = 10) as internal standard.

[b] Estimated to whole numbers by method of counting squares, rel. to $C_5H_5 = 5$.

[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] Number of components are given in the brackets.

[e] Band slightly broad due to unresolved multiplicity arising from coupling with the adjacent deuterium.

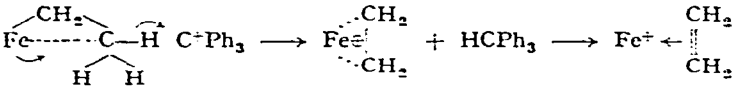
coupling with the (2) hydrogen. The spectrum of the 2-deuteropropene cation (III; R = Me) shows that there are two single bands at 6.53 τ and 6.06 τ and that therefore the (4) and (3) hydrogens are in a different environment. The bands due to these hydrogens are rather broad due to their coupling with the deuterium at position (2).

DISCUSSION

The above work and similar studies on related alkyl complexes of molybdenum[14] and tungsten[11] show that some metal–alkyl complexes readily lose a hydride ion on treatment with suitable triphenylmethyl salts. The hydride ion from the deuteroisopropyl complex (I; $R = CDMe_2$) clearly comes from a carbon atom *beta* to the metal, and it seems reasonable that this should be the case in the other reactions. That pentacarbonylethylmanganese (II) also undergoes hydride abstraction indicates that a cyclopentadienyl group is not necessary for the reaction, and therefore the loss of a hydride ion from the β-carbon of suitable transition metal–alkyl complexes may well be a general reaction.

MECHANISM OF HYDRIDE ABSTRACTION

Since the alkyl complexes (I) do not react readily with mineral acids to evolve hydrogen, a mechanism involving the equilibrium $M{-}CH_2CH_3 \leftrightharpoons M^{+}CH_2{=}CH_2 + H^{-}$ does not seem reasonable. We propose a bimolecular mechanism for the reaction, such as:



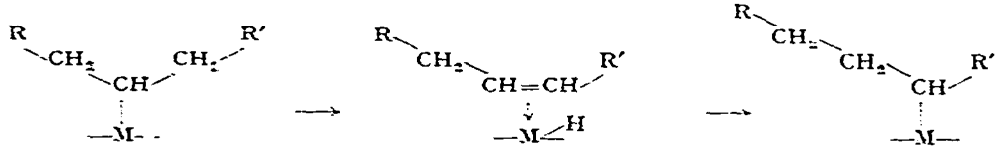
This mechanism shows that the electron-deficient carbonium ion together with the metal atom effect the removal of the hydride ion and the stabilization of the resulting carbonium ion intermediate by formation of a bond with the metal. The complexes $C_5H_5Fe(CO)_2R'$, where $R' = CH_2CH_2CN$ or CF_2CF_2H, do not lose a hydride ion when treated with triphenylmethyl salts which can be understood since hydrogens on the 2-carbon in these complexes would be expected to be reluctant to leave as hydride ions. It is to be noted that the above mechanism is similar in the final stages to that proposed for the mechanisms of protonation of metal complexes containing the groups $M{-}CH_2CH{=}CH_2$[9], $Fe{-}CH_2CN$[10], and $Fe{-}CH_2CHO$[15] in that they all postulate the formation of an intermediate carbonium ion species which is stabilised by bonding to the metal. It is possible that suitable metal complexes which may be regarded as electron deficient may act as both the hydride acceptor and stabilise the carbonium ion intermediate. For example, the 16-electron platinum hydride complex $(Et_3P)_2PtHCl$ undergoes a reversible addition of ethylene, forming the ethyl complex $(Et_3P)_2PtClEt$[16]. The reaction may proceed by the loss of a hydrogen from the β-carbon of the ethyl group to the platinum[16], forming an unstable 18-electron ethylene hydride intermediate $[(Et_3P)_2PtClH{\cdot}CH_2{=}CH_2]$, which could then readily lose the ethylene.

MECHANISM OF REDUCTION OF THE ETHYLENIC CATIONS

The reduction of suitable salts of ethylenic cations of iron, molybdenum[14] and tungsten[11] with sodium borohydride affords metal–alkyl complexes in moderate yields. For the iron-ethylenic complex (III; R′ = Me), an external mechanism, involving the prior formation of the hydride $C_5H_5Fe(CO)_2H$ and expulsion of the olefin followed by the addition of the Fe–H across the olefinic double bond, may be discarded since the only σ-alkyl product of the reduction, when carried out in the presence of alternative olefins such as 1-hexene and butadiene, is the σ-isopropyl complex (I; R = iso-Pr). For an internal mechanism of addition of a hydride ion to the ethylenic ligand there are two plausible alternatives. The hydride ion may either first attack the metal, followed by hydrogen transfer to the ethylenic ligand or attack the ethylenic ligand directly. The latter mechanism would be the reverse of that proposed for the hydride abstraction reaction. Both mechanisms can satisfactorily account for the formation of the isopropyl isomer (I; R = iso-Pr) from the propene cation and they are discussed in detail elsewhere[17].

ISOMERISATION OF ALKYL GROUPS ATTACHED TO TRANSITION METALS

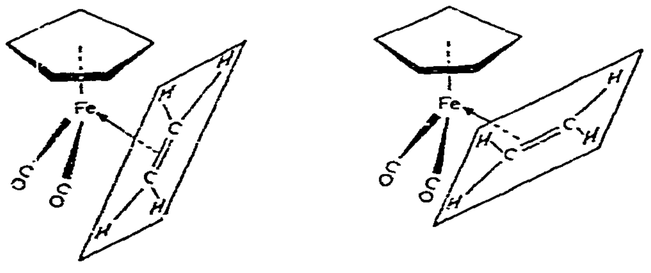
As shown in the chart above, the isomerisation of *n*-propyl to isopropyl may be understood as a simple, two-step hydride removal and addition process. This reaction may be regarded as a model system for the double-bond isomerisation of chemisorbed olefins in that, if the hydrogen is reversibly added and abstracted by the metal, as suggested above for the platinum complex, then a scheme for the isomerisation may be written as follows:



A similar external mechanism has been previously suggested[13].

CONFIGURATION OF DICARBONYLETHYLENECYCLOPENTADIENYLIRON CATIONS

For the cation (III; R′ = H) two orientations for the ethylene group relative to the metal may be considered and they are shown in Fig. 1. In the configurations A and B



A B

Fig. 1. Two orientations of the ethylene group relative to iron in the dicarbonylethylenecyclopentadienyliron cation.

the ethylene groups are in a plane facing the iron but differ in that the C–C axis of the ethylene group is either in the plane of the metal-ring axis (A) or perpendicular to it (B).

A molecular orbital description of the bonding in the complex $C_5H_5Mn(CO)_3$ has been discussed by several authors[19,20,21] and their conclusions are summarised in Table 3.

TABLE 3

π-C_5H_5	*non bonding*	Mn—(CO)$_3$	
$(a_1 + s + d_{z^2} - p_z)^2$	$(s - d_{z^2})^2$	$(a_1 + s + d_{z^2} + p_z)^2$	σa_1
$\left\{\begin{matrix} e_{1x} + d_{xz} - p_x \\ e_{1y} + d_{yz} - p_y \end{matrix}\right\}^4$	$(d_{xy})^2$ $(d_{x^2-y^2})^2$	$\left\{\begin{matrix} e_x + d_{xz} + p_x \\ e_y + d_{yz} + p_y \end{matrix}\right\}^4$	σe

As shown in Table 3, the three sp_{CO} lone pairs, which transform under the local C_{3v} symmetry as $A_1 + E$ form molecular orbitals called σa_1 and σe. However it is clear that in metal carbonyl complexes a considerable contribution to the bonding is made by the anti-bonding orbitals of the carbon monoxide (π^*) which are not considered in the above treatment. These π^* orbitals transform under C_{3v} symmetry as $A_1 + A_2 + 2E$, and hence the σa_1 and σe orbitals will both have some π^* character. Since the π^* orbitals are unfilled and are located on the ligands, this delocalisation of the σa_1 and σe orbitals represents the familiar back-bonding property of π-acceptor ligands. For the ethylene cation (III; R' = H) the ethylene may be regarded as a carbon monoxide with only one π^* orbital. Using this simplification it can be readily shown that for the configuration *A* the $\pi^*_{C_2H_4}$ orbitals can mix with both the σa_1 and σe orbitals whereas for configuration *B*, the $\pi^*_{C_2H_4}$ may only mix with the σe orbital. Therefore, if the mixing of the π^* orbitals with the σe orbital is similar for both configurations then the extra bonding which can arise in configuration *A* would be expected to stabilise it relative to configuration *B*.

It may be noted that from Table 3 it can be shown that the 2-carbon of an alkyl group in the complexes (I; R = Me) is near regions of high electron density, namely the non-bonding electron in the *xy* and *yz* planes. The presence of this suitably localised electron density may account for the facile loss of a hydride ion from the 2-carbons in these complexes and for the ready stabilization of the postulated carbonium ion intermediates.

EXPERIMENTAL

Microanalyses were done in the Microanalytical Laboratory, Lensfield Road, Cambridge. All preparations, reactions and purification procedures were carried out under nitrogen or in a vacuum. Light petroleum is AnalaR material, b.p. 30–40°.

Dicarbonylalkylcyclopentadienyliron complexes

The method of Piper and Wilkinson[6] was adapted to a slightly different procedure which is described in detail elsewhere[9]. The *n*-propyl complex (I; R = *n*-Pr) was prepared using an excess (10 %) of *n*-propyl iodide and the product was purified by chromatography and distillation as described for dicarbonyl-σ-allylcyclopentadienyliron[9]. Yield 47 %. [Found: C, 54.94; H, 5.37; mol.wt. (cryoscopic in dioxane),

236. $C_{10}H_{12}FeO_2$ calcd.: C, 54.6; H, 5.46%; mol.wt, 220]. Other products from the reaction which were separated by chromatography were the complex $[C_5H_5Fe(CO)_2]_2$ and small amount of an iron complex whose infrared spectrum showed bands assignable to ketonic and terminal carbonyl frequencies. The isopropyl complex (I; R = iso-Pr) was prepared using isopropyl iodide or bromide. A study of the reaction showed that using the isopropyl bromide and keeping the reaction mixture at —70° gave yields of ~ 70%. (Found: C, 54.36; H, 5.35. $C_{10}H_{12}FeO_2$ calcd.: C, 54.6; H, 5.46%). The deuteroisopropyl complex (I; R = $CDMe_2$) was prepared using 2-deutero-2-bromopropane in the manner indicated above. Yield 72%. The 2-deutero-2-bromopropane was prepared as previously described[22]. The purity was verified from the infrared and proton magnetic resonance spectrum and by vapour pressure measurements.

The propyl complexes (I; R = *n*-Pr or iso-Pr) are amber oils which are readily oxidised when exposed to air. The pure compounds decompose on prolonged standing even at —10° and when kept in the dark under nitrogen. They are thermally unstable and decompose readily at temperatures > 60°. The isopropyl derivative is noticeably more unstable than the *n*-propyl analogue. Infrared spectra showed that there were always bands assignable to ketonic carbonyl in the decomposition products. The alkyl complexes (I) were always repurified before use.

Ethylpentacarbonylmanganese

Sodiumpentacarbonylmanganese was prepared by stirring decacarbonyldimanganese (5.0 g) in pure, dry tetrahydrofuran with excess sodium amalgam (3%) for 2 h. The residual amalgam was separated from the solution which was washed twice with pure mercury to remove traces of amalgam. Ethyl iodide (20 g) was slowly added to the solution of the sodium salt $Na^+Mn(CO)_5^-$, with stirring. After 3 h all volatile products were removed under vacuum at 50° and collected. The resulting distillate was then partitioned between water (300 ml) and light petroleum (100 ml). The light petroleum layer was separated and washed twice with water (2 × 50 ml) to remove tetrahydrofuran and dried ($MgSO_4$). The light petroleum was removed carefully in vacuum and the residual pale yellow oil was finally purified by fractional distillation under vacuum. Attempts to further purify the yellow oil so obtained by chromatography resulted in the immediate decomposition of the product on the alumina column. Yield ~ 40%. [Found: C, 35.11; H, 2.2; mol.wt. (cryoscopic in dioxane), 223. $C_7H_5MnO_5$ calcd.: C, 37.5; H, 2.23%; mol.wt., 225]. The compound is a pale yellow oil, m.p. ~ —30°. It is similar in thermal stability to the isopropyl complex (I; R = iso-Pr) and moderate yields of the acyl complex $(CO)_5MnCOEt$[23] can be isolated from the decomposition products by sublimation.

Reaction of sodiumdicarbonylcyclopentadienyliron with tert-butyl chloride

A solution of the sodium salt $Na^+C_5H_5Fe(CO)_2^-$, prepared from tetracarbonyldicyclopentadienyldiiron (5 g)[9], in tetrahydrofuran was added dropwise to a vigorously stirred solution of *tert*-butyl chloride (10 g) in tetrahydrofuran (100 ml). After stirring the mixture for 16 h the solvent was removed *in vacuo* and the residue was chromatographed and distilled in the manner used for the alkyl compounds (I). The pure product was a yellow oil, dec. 20°. (Found: C, 47.2; H, 5.28. $C_7H_6FeO_2$ calcd.: C, 47.2; H, 3.37%).

The oil (1 g) decomposed vigorously at 40° evolving a noncondensible gas, identified by combustion analysis as hydrogen, and the residue was characterised as the pure complex $[C_5H_5Fe(CO)_2]_2$. The above reaction was repeated using the more involatile solvent 1,2-dimethoxyethane. The gases evolved during the reaction were collected, separated by fractional distillation and identified as isobutene and hydrogen by analysis, molecular weight determination, and the infrared spectrum.

Reaction of $C_5H_5Fe(CO)_2R$, *where* R = Et, *n*-Pr *and* iso-Pr, *with triphenylmethyl salts*

A typical reaction is described. Pure dicarbonyl(ethyl)cyclopentadienyliron (1.0 g) in tetrahydrofuran was treated with a stoichiometric amount of triphenylmethyl perchlorate in tetrahydrofuran. After 30 min the solvent was removed and the crude product was dissolved in a small amount of acetone (30 ml) and a few drops of water were added to hydrolyse any unreacted triphenylmethyl perchlorate. Then ether was added to the solution slowly precipitating yellow crystals which were washed twice by decantation with ether. Finally the crystals were recrystallized from acetone–ether, or liquid sulphur dioxide–ether. Triphenylmethyl fluoroborate may also be used for hydride abstraction, in the above manner, even though it is only slightly soluble in tetrahydrofuran. The reaction mixture in this case was stirred vigorously for 30 min.

The propyl complexes (I; R = *n*-Pr or iso-Pr) give yellow crystalline perchlorates and fluoroborates. The fluoroborates are advantageous in being nonexplosive, but crystallize less readily.

The complex (I; R = Et) affords the complex $[C_5H_5Fe(CO)_2 \cdot C_2H_4]^+ClO_4^-$. (Found: C, 35.8; H, 2.79; CO, 2.08 moles. $C_9H_9ClFeO_6$ calcd.: C, 35.5; H, 2.95%; CO, 2.00 moles).

The propyl complexes afford the propene cation $[C_5H_5Fe(CO)_2 \cdot C_3H_6]ClO_4$. (Found: C, 37.21; H, 2.98. $C_{10}H_{11}ClFeO_6$ calcd.: C, 37.8; H, 3.15%). The salts were further identified by their infrared and proton magnetic resonance spectra. The deuteroisopropyl complex (I; R = CDMe$_2$) similarly affords the 2-deuteropropene cation (III; R′ = Me) fluoroborate in high yields. (Found: C, 39.19; H and D, 3.72. $C_{10}H_{10}BF_4Fe$ calcd.: C, 39.1; H, 3.93%). Yield 86%.

Reaction of pentacarbonylethylmanganese with triphenylmethyl salts

Pure pentacarbonylethylmanganese (1 g) was distilled *in vacuo* on to an excess of finely powdered triphenylmethyl tetrafluoroborate. A reaction took place at room temperature and a small amount of gas, identified as ethylene by the infrared spectrum, was evolved. After 30 min the mixture was extracted with liquid SO_2 (30 ml) and the solution was filtered. Anhydrous ether (30 ml) was slowly added to the filtrate, and the white solid precipitated was separated by decantation and washed twice with ether. The solid was finally recrystallized four times from ether–liquid sulphur dioxide. Yield ~ 10%. (Found: C, 27.35; H, 1.20; Mn, 17.9; CO, 5.04 moles. $C_7H_4BF_4MnO$ calcd.: C, 27.1; H, 1.29; Mn, 17.75%; CO, 5.00 moles.) The pure salt dissolves readily in water and acetone with rapid evolution of ethylene. Conductivity measurements on a 1.06×10^{-3} *M* solution of the pure salt in nitrobenzene gave $\Lambda = 25.6$. The nitrobenzene solution showed decomposition products after about 10 min. Treatment of pentacarbonylethylmanganese with triphenylmethyl perchlorate in tetrahydrofuran, as described above for the complexes (I), resulted in vigorous reaction and the formation of a black, insoluble precipitate. No evidence for the formation of a manganese carbonyl cation was found.

Reaction of the ethylenic cation salts with sodium borohydride

A typical reaction is described. A suspension of dicarbonylethylenecyclopentadienyliron perchlorate (0.5 g) in tetrahydrofuran (50 ml) was treated, in small portions, with a 10% excess of sodium borohydride. The mixture was stirred for 30 min and the colour changed from pale yellow to orange-red. The solvent was removed in vacuum and the residue was extracted with light petroleum (3 × 25 ml). The solution was filtered, the filtrate was evaporated to a small volume and chromatographed on an alumina column in light petroleum, eluting with 1:1 light petroleum–ether mixture. The first yellow band was collected, the solvent was removed in vacuum giving a yellow oil which was distilled at $45°/10^{-3}$. The π-ethylene cation (III; $R' = H$) gave the ethyl complex (I; $R = Et$) in good yield. The cation (III; $R' = Me$) gave the isopropyl complex (I; $R =$ iso-Pr). No *n*-propyl isomer was found in the reaction products from the reduction of the π-propene cation (III; $R' = Me$). The products were identified by comparison of their infrared spectra with those of seperately prepared, fully characterised samples. In all cases, another product of the reaction was the binuclear complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ which was separated from the alkyl complexes during chromatography.

Reaction of pentacarbonylethylenemanganesetetrafluoroborate with sodium borohydride, in the above manner, resulted in the formation of decacarbonyldimanganese in moderate yields. The reduction, in the above manner, of the π-propene cation (III; $R' = Me$) chloride gave mainly the complex $[C_5H_5Fe(CO)_2]_2$. No σ-alkyl complexes can be isolated from the reaction products. The reduction of the π-propene cation (III; $R' = Me$) was carried out as described above but also in the presence of 1-hexene (5 ml) or with a rapid stream of butadiene passing through the solution. Separation and purification of the products as before gave the isopropyl complex (I; $R =$ iso-Pr) as the only metal–alkyl product.

Reaction of pentacarbonylethylenemanganesetetrafluoroborate with triphenylphosphine

Pentacarbonylethylenemanganesetetrafluoroborate (0.1 g) was mixed with excess finely ground triphenylphosphine (1.0 g) and warmed under vacuum, to 80°. Reaction occurred with evolution of a gas which was shown to be a (1:1.3) mixture of carbon monoxide and ethylene by infrared spectral measurements and combustion analysis. The residual solid was extracted with acetone and filtered. Addition of ether to the filtrate precipitated pale yellow crystals which were washed with ether and finally recrystallised from acetone/ether and dried. Yield 57%. (Found: C, 62.04; H, 3.72, $C_{40}H_{30}BF_4MnO_4P_2$ calcd.: C, 61.6; H, 3.85%.) The compound is stable in air and soluble in acetone, tetrahydrofuran and chloroform.

High-resolution nuclear magnetic resonance spectra

Measurements were made on a Perkin–Elmer spectrometer at 40 Mc/sec. The conditions of measurement are given in Table 2.

Infrared spectra

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

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SUMMARY

A hydride ion may be abstracted from the alkyl complexes $C_5H_5Fe(CO)_2R$, where $R = Et$, *n*-Pr or iso-Pr, and $(CO)_5MnEt$, using triphenylmethyl salts. The ethylenic cations $[C_5H_5Fe(CO)_2 \cdot CH_2{=}CHR']^+$, where $R' = H$ or Me, and $[(CO)_5Mn \cdot CH_2{=}CH_2]^+$ are formed.

Studies using the deuteroisopropyl complex $C_5H_5Fe(CO)_2CDMe_2$ show that the hydride ion is lost from a carbon atom *beta* to the metal. The reaction is shown to be reversible in that reduction of the ethylenic cations with sodium borohydride affords alkyl complexes. The mechanism of the reduction has been studied and is discussed. The isomerization of an Fe–*n*-propyl system to an Fe–isopropyl system is demonstrated.

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