LIGAND SUBSTITUTION AND NUCLEOPHILIC REACTIVITY OF TRICARBONYL(1–3:5,6-η-CYCLOOCTADIENYLIUM)IRON CATION AND ITS DERIVATIVES

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Summary

The tricarbonyl(1–3:5,6-η-cyclooctadienylium)iron cation (I) undergoes attack by triphenylphosphine at two different sites, on the organic group or at the metal; the first type of attack leads to a phosphonium ion and the second case to a dicarbonyl(1–3:5,6-η-cyclooctadienylium)triphenylphosphineiron cation. The two products have been isolated and identified by IR spectroscopy. The reaction between cation I and iodide ion can also involve attack on the organic group or the metal, giving rise to tricarbonyl[4–6-η,1-σ-(2-iodocyclooctenyl)]iron and dicarbonyl(1–3:5,6-η-cyclooctadienylium)iodoiron, respectively. Only the latter has been isolated and characterized; for the former indirect evidence is available, involving its reactions with CN^- and PPh_3. The reactions between cation I and the various nucleophiles OMe^-, N_3^-, CN^-, and $AsPh_3$ and those between its iodo derivative and PPh_3 and $AsPh_3$ were also studied.

Introduction

The present paper reports new results, at variance to some extent with those previously reported [1], for reactions involving nucleophilic attack on tricarbonyl(1–3:5,6-η-cyclooctadienylium)iron cation (I) (obtained by hydride abstraction from tricarbonyl(η-cycloocta-1,5-diene)iron) by the species OMe^-, N_3^-, CN^-, I^-, PPh_3, $AsPh_3$. The results are compared with those relating to the reactivity of the tricarbonyl(1–5-η-cyclooctadienylium)iron cation (II) (obtained by abstracting hydride ion from tricarbonyl(η-cycloocta-1,3-diene)iron with nucleophilic reactants) which were the subject of previous publications [2].

Results and discussion

In Scheme 1 are shown the reactions studied between cation I and various nucleophiles.
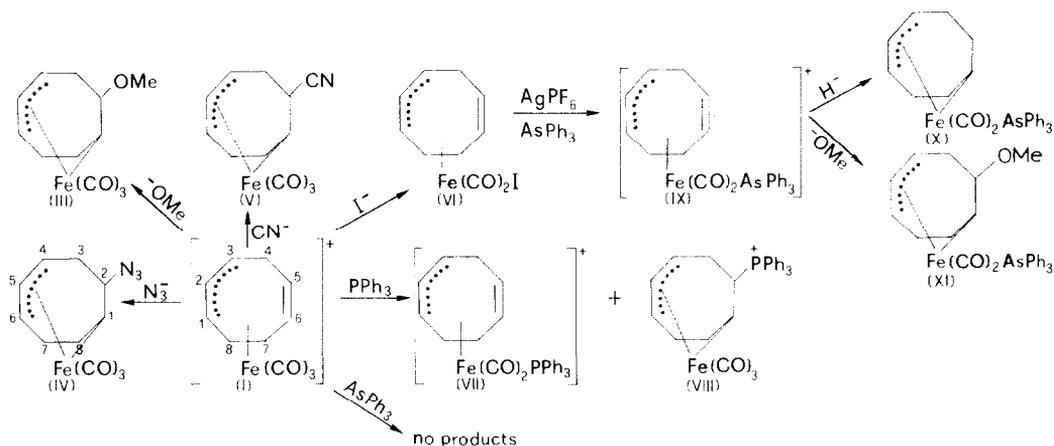
SCHEME 1

Methoxide ion gives tricarbonyl[4–6-η,1-σ-(2-methoxycyclooctenyl)]iron (III), as the sole stable product. Its IR spectrum in dichloromethane shows carbonyl bands at ν 2050, 2030, 1980 cm^{-1} and a band at ν 1080 cm^{-1} ascribable to the methoxy group bound to the organic nucleus in position 2. Its mass spectrum shows the parent peak at $m/e = 278$ and fragmentation with loss of three carbonyls.

Compound I behaves differently in this reaction from the dienyl cation II, for which attack of the methoxy group on a carbonyl first occurs, giving rise initially to an ester group and to migration to the organic ligand in position 5. The latter methoxy derivative is unstable and undergoes facile deprotonation with loss of an MeOH molecule [1,2].

With sodium azide complex I gives, as the sole product, tricarbonyl[4–6-η,1-σ-(2-azidecyclooctenyl)]iron (IV). Its IR spectrum in pentane shows carbonyl bands at ν 2045, 1990 cm^{-1}, and a band at ν 2085 cm^{-1} which can be assigned to the azide group bound to the organic nucleus in position 2. Its mass spectrum shows the parent peak at $m/e = 289$ and fragmentation corresponding to the loss of three carbonyls. Its structure is confirmed by the ^{1}H NMR spectrum, which shows multiplets at τ 4.51 [H(4,6)], 5.1 [H(5)], 5.8 [H(2)], 7–8.9 ppm [H(1,3,7,8)].

Reaction between complex I and NaCN gives compound V, tricarbonyl[4–6-η,1σ-(2-cyanocyclooctenyl)]iron. Its IR spectrum in dichloromethane shows carbonyl bands at ν 2050, 1980 cm^{-1} and a band at ν 2225 cm^{-1} which can be attributed to the cyano group bound to position 2 of the organic group. Its mass spectrum exhibits the parent peak at $m/e = 273$ and fragmentation with loss of three carbonyls. The same compound was previously obtained [3] along with its isomer, the 4-cyano derivative of tricarbonyl(η-cycloocta-1,5-diene)iron, in a ratio of 7/3. Cation I also behaves differently from cation II in reactions with CN$^-$. In the latter case [2] the cyano group attacks a coordinated carbonyl giving a carbonitrile derivative, and migration to the organic ligand does not occur, but instead there is deprotonation via loss of an HCN molecule, so that a cycloocta-1,3,5-triene coordinated to iron(0) is formed.

Reaction between complex I and NaI gives compound VI, dicarbonyl(1–3:5,6-η-cyclooctadienylium)iodoiron. Its IR spectrum in dichloromethane shows carbonyl bands at ν 2020, 1980 cm^{-1}. The mass spectrum shows a parent peak at $m/e = 346$,

and fragmentation with loss of two carbonyls gives peaks at $m/e = 318$ and 290.

Reaction between complex I and triphenylphosphine gives two compounds, which can be separated by chromatography on alumina, these are complex VII, dicarbonyl(1–3:5,6-η-cyclooctadienylium)triphenylphosphineiron cation, and VIII, which is formulated as a phosphonium salt, thus the product mixture in dichloromethane has an IR spectrum with carbonyl bands at ν 2050, 2030, and 1980 cm^{-1}, while compound VII shows carbonyl bands at ν 2030, 1980 cm^{-1} and compound VIII at ν 2050, 1970 cm^{-1}. The higher frequency observed here is reminiscent of the effect observed in analogous compounds involving cations derived from cyclohexa- and cyclohepta-diene and the cation II (see ref. 2).

Reaction between the iodo derivative VI and triphenylarsine in the presence of a stoichiometric amount of AgPF$_6$ gives complex IX, dicarbonyl(1–3:5,6-η-cyclooctadienylium)triphenylarsineiron. Its IR spectrum in dichloromethane shows carbonyl bands at ν 2030, 1980 cm^{-1}. Treatment of IX with NaBH$_4$ leads to X, dicarbonyl(4–6-η,1-σ-cyclooctenediyl)triphenylarsineiron, the IR spectrum in dichloromethane of which shows carbonyl bands at ν 1970, 1920 cm^{-1}. On the other hand, treatment of complex IX in dichloromethane with a stoichiometric amount of NaOMe produces compound XI, dicarbonyl[4–6-η,1-σ-(2-methoxycyclooctenyl)]triphenylarsineiron, which is characterized by carbonyl bands at ν 1980, 1920 cm^{-1} and a band at ν 1080 cm^{-1} due to the methoxy group bound to the organic ligand in position 2.

We should mention in this connection the different behaviour of the dienyl salts I and II, derived from (1,5-COD)Fe(CO)$_3$ and (1,3-COD)Fe(CO)$_3$, respectively, in reactions with triphenylphosphine. With complex I, phosphine attacks the cation both at the organic group with formation of a phosphonium salt (VIII) and at the metal, giving the dicarbonyl compound (VII); on the other hand, with cation II only a phosphonium salt is formed [2].

A possibility of two types of attack, as observed here for complex I, is proposed for the reaction between complex I and I$^-$, as in the sequence shown in Scheme 2.
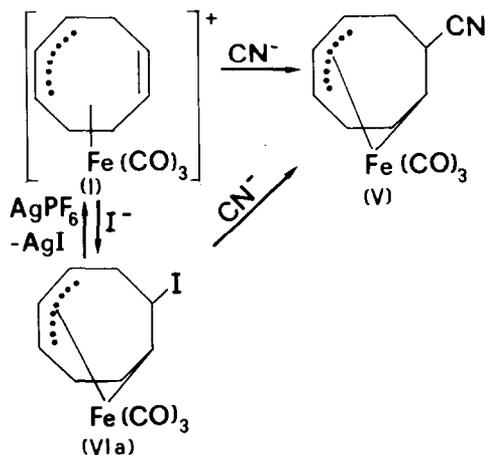
SCHEME 2

Upon treatment of compound I with NaI, compound VIa is formed, having an IR spectrum with carbonyl bands at ν 2020, 1980 cm^{-1}. This iodo derivative was further treated with NaCN in a 1/1.5 concentration ratio, giving rise to a compound which (from its IR and mass spectrum) can be identified as compound V, which can also be obtained by direct attack of CN$^-$ upon complex I (see Scheme 1). On the other hand, treatment of VIa in dichloromethane with a stoichiometric quantity of solid AgPF$_6$ allows the isolation of a compound characterized by an IR spectrum with carbonyl bands at ν 2100, 2050 cm^{-1}, i.e. the same as those of the starting cation 1 species. This cation upon treatment with NaBH$_4$ gives rise to the well known isomeric mixture [3], and upon treatment with NaCN reforms complex V. On the basis of these results we suggest that in the case of iodide ion attack also, two modes of attack are possible, as shown in Scheme 3, even though (in contrast with the case
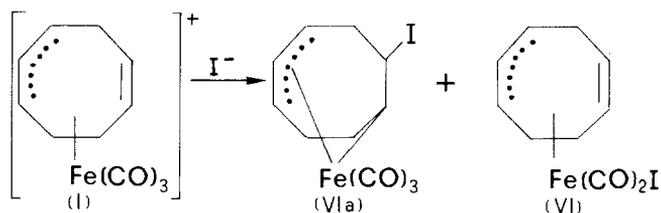
SCHEME 3

of triphenylphosphine) only one of the expected reaction products dicarbonyl(1–3:5,6-η-cyclooctadienylium)iodoiron, (VI) was actually isolated. The other product would be tricarbonyl[4–6-η,1-σ-(2-iodocyclooctenyl)]iron (VIa).

Scheme 4 shows the reactions which are believed to take place between the iodo
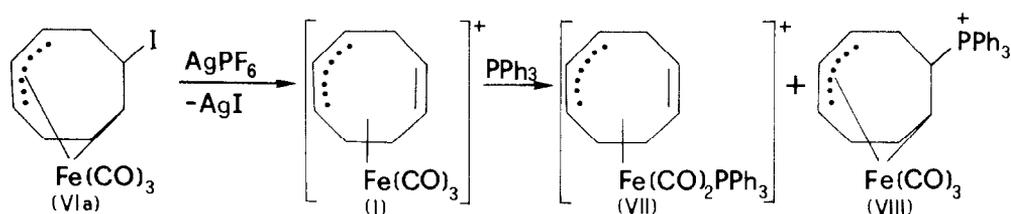
SCHEME 4

derivative VIa and PPh$_3$. Treatment of VIa with AgPF$_6$ gives the cation I, which undergoes phosphine attack by both modes, giving compounds VII and VIII, which were isolated and analysed as indicated above.

Cation II, when treated with NaI, yields a single carbonyl substitution product, viz. a dicarbonyl derivative having iodine coordinated to the metal, in which position it can be replaced by the cyano group by reaction with CN$^-$ [2].

It is possible to rationalize the behaviour of complex I with nucleophiles I$^-$ and PPh$_3$ allowing for the existence of the equilibria shown for I$^-$ in Scheme 5 and for PPh$_3$ in Scheme 6. The positions of such equilibria will depend upon the particular nucleophile and the stability of the substitution product. Thus, for instance, in the reaction between a iodo derivative and CN$^-$ the equilibrium lies over to the right, and so VIa is the species which undergoes replacement of iodide with cyanide and is
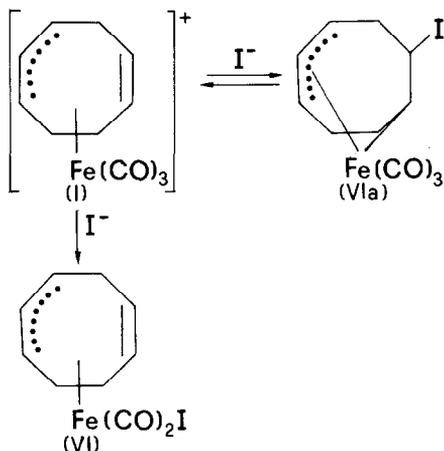
SCHEME 5
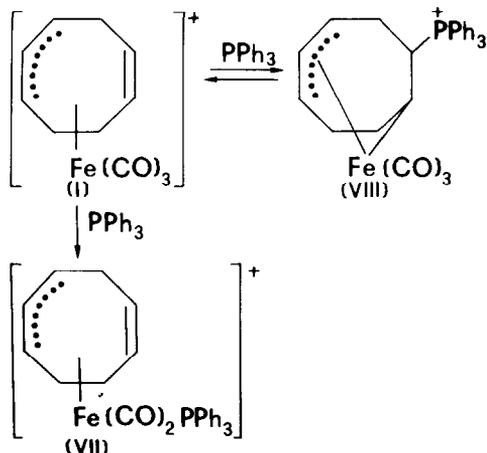
SCHEME 6

transformed into V, the same product as is obtained in higher yield in the direct reaction between salt I and NaCN. However, the product which was isolated and identified by means of elemental analysis and mass spectrometry is, in fact, VI. Similarly, in the reaction between the iodo derivative and $AgPF_6$ the reacting species is VIa, which is converted into cation I, a species involved in two equilibria with triphenylphosphine, and so VII and VIII are formed, the latter in larger amount.

Since introducing arsine in place of phosphine inhibits the direct reaction to give the dienyl salt I (see Scheme 1), an equilibrium strongly shifted to the left can be envisaged; so that a single reaction product, the dicarbonylarsine derivative IX, is formed only by the route indicated in Scheme 1.

In general a comparison between cation I, derived from 1,5-COD, a diene with non conjugated double bonds coordinated to iron(0) in which the organic ligand is coordinated through the bond system 1–3:5,6-η, and cation II, derived from 1,3-COD, a diene with conjugated double bonds, coordinated to iron(0) in which the

organic ligand is coordinated through the system containing five delocalized electrons, η-1–5, shows that the former, the cation investigated here, offers the possibility of two types of attack though attack on the organic ligand is favoured since it gives rise to stable substitution products.

Cation II, on the other hand, is preferentially attacked by the nucleophile at the metal or at a coordinated carbonyl, and only afterwards that migration into the organic ligand occurs, but with formation of unstable substitution products. This behaviour may be related to the greater aromaticity of the organic entity in II, which would cause a localization of the positive charge of the cation on the metal or on a carbonyl coordinated to the metal, with these two sites being preferred for nucleophilic attack.

Experimental

Tricarbonyl(1–3:5,6-η-cyclooctadienylium)iron tetrafluoroborate was prepared by published procedures [3]. IR spectra were recorded on Perkin–Elmer 397 infrared spectrophotometer. NMR spectra were recorded on Perkin–Elmer R12B spectrometer. Mass spectra were recorded on a Finnigan-Mate 112S spectrometer.

All starting materials and solvents were purified before use. All reactions were carried out under dinitrogen. Typical experiments are given below.

(a) Tricarbonyl[4–6-η,1-σ-(2-methoxycyclooctenyl)]iron (III)

A mixture of dichloromethane solutions of complex I (300 mg, 0.9 mmol in 30 cm^3) and NaOCH$_3$ (60 mg, 1.11 mmol in 5 cm^3) was stirred for one hour, then filtered, and the solvent was removed under vacuum. The residue was extracted with pentane (2 × 20 cm^3). The extracts were filtered through a short column of deactivated alumina and evaporated to give a yellow-green oil. The oil was sublimed (0°C, 0.005 mmHg, −30°C cold finger) to yield complex III (83 mg) as yellow crystals. (Found: C, 51.43; H, 4.99. C$_{12}$H$_{14}$FeO$_4$ calcd.: C, 51.82; H, 5.04%). The complex was characterized by its IR and mass spectra.

(b) Tricarbonyl[4–6-η,1-σ-(2-azidecyclooctenyl)]iron (IV)

A solution of complex I (230 mg, 0.69 mmol) in acetone (25 cm^3) was treated with solid NaN$_3$ (100 mg, 1.5 mmol). The mixture was stirred for 40 min, then filtered, and the filtrate was evaporated under vacuum to give an oil which, on chromatography on alumina with pentane as eluant, yielded IV as the sole product (as a yellowish solid (56 mg). (Found: C, 45.92; H, 3.73; N, 14.40. C$_{11}$H$_{11}$N$_3$FeO$_3$ calcd.: C, 45.70; H, 3.81; N, 14.54%). The complex was characterized by its NMR, IR, and mass spectra.

(c) Tricarbonyl[4–6-η,1-σ-(2-cyanocyclooctenyl)]iron (V)

A mixture of aqueous solutions of complex I (150 mg, 0.45 mmol) and of NaCN (22 mg, 0.45 mmol) was stirred for 15 min. The mixture was extracted with diethyl ether (3 × 10 cm^3) and the extracts were dried over magnesium sulphate. The white solid obtained after evaporation of diethyl ether was recrystallized from dichloromethane to yield V (25.2 mg) as white crystals, soluble in dichloromethane, acetone and diethyl ether. (Found: C, 52.15; H, 3.98; N, 5.20. C$_{12}$H$_{22}$FeNO$_3$ calcd.: C, 52.55; H, 4.05; N, 5.0%). The complex was characterized by its IR and mass spectra.

(d) Dicarbonyl(1–3:5,6-η-cyclooctadienylium)iodoiron (VI)

Sodium iodide (75 mg, 0.5 mmol) was added to a solution of complex I (150 mg, 0.45 mmol) in acetone (20 cm^3). After removal of the solvent under vacuum, benzene was added. The purple solution was filtered through alumina. After removal of the solvent under vacuum, the residue was washed with small quantities of ligroin to give brown crystals (77 mg). TLC (on silica, with chloroform as eluant) showed the presence of two compounds, but by chromatography on a silica column only compound VI was isolated. (Found: C, 34.46; H, 3.38; O, 9.49. $C_{10}H_{11}FeO_2I$ calcd.: C, 34.70; H, 3.18; O, 9.25%). The complex was characterized by its IR and mass spectra.

(e) Reaction of complex I with triphenylphosphine

Triphenylphosphine (185 mg, 0.7 mmol) was added to a dichloromethane solution of complex I (230 mg, 0.69 mmol in 30 cm^3). The colour turned from yellow to yellow-green. On addition of diethyl ether a bulky yellow precipitate formed, and this was redissolved in dichloromethane. TLC on alumina showed the presence of two components, as did chromatography on a deactivated alumina column. The first fraction was eluted with chloroform and the second with acetone. The chloroform solution was evaporated to give the compound dicarbonyl(1–3:5,6-η-cyclooc-tadienylium)triphenylphosphineiron tetrafluoroborate (VII). The acetone solution was evaporated to give the 2-phosphonium ion of tricarbonyl(4–6-η,1-σ-cyclo-octenyl)iron (VIII). Both compounds were characterized by their IR spectra.

(f) Reaction of complex I with triphenylarsine

Complex I did not react with triphenylarsine even when a large excess of the latter was used along with long reaction times and high temperatures.

(g) Dicarbonyl(1–3:5,6-η-cyclooctadienylium)triphenylarsineiron hexafluorophosphate (IX)

To a dichloromethane solution of complex VI (200 mg, 0.58 mmol) and an excess of triphenylarsine (306 mg, 1 mmol in 20 cm^3) was added the stoichiometric amount of AgPF$_6$. After 1 h the mixture was filtered and diethyl ether was added to the yellow-orange solution to give a pale yellow precipitate. TLC analysis showed this to be a single species (IX, 53 mg). (Found: C, 49.95; H, 3.94. $C_{28}H_{26}FeAsPF_6$ calcd.: C, 50.17; H, 3.88%). The complex was characterized by its IR spectrum.

(h) Dicarbonyl(4–6-η,1-σ-cyclooctenediyl)triphenylarsineiron (X)

To a solution of complex IX (250 mg, 0.37 mmol) in 4/1 acetone/water mixture was added the stoichiometric amount of solid NaBH$_4$. After 5 min the mixture was extracted with diethyl ether (3 × 10 cm^3), and the extracts were dried over mag-nesium sulphate. The solvent was removed under vacuum to give complex X as red crystals (81 mg). (Found: C, 63.24; H, 4.99. $C_{28}H_{27}FeO_2As$ calcd.: C, 63.91; H, 5.13%). The complex was characterized by its IR spectrum.

(i) Dicarbonyl[4–6-η,1-σ-(2-methoxycyclooctenyl)]triphenylarsineiron (XI)

To a dichloromethane solution of complex IX (250 mg, 0.37 mmol in 20 cm^3) was added solid NaOCH$_3$ (20 mg, 0.37 mmol). The mixture was stirred for 6 h, then filtered, and the solvent was removed under vacuum. The residue was extracted with

pentane (3×10 cm^3). The yellow-green extracts were evaporated. The residue was recrystallized from dichloromethane to give compound XI as yellow crystals (53 mg). (Found: C, 61.98; H, 5.21; O, 8.71. $C_{29}H_{30}FeO_3As$ calcd.: C, 62.50; H, 5.39; O, 8.62%). The complex was characterized by its IR spectrum.

(j) Reaction of complex I with I$^-$ and CN$^-$

The product of the reaction between complex I and NaI obtained as described in section d, and formulated as VIa in Scheme 2, was dissolved in acetone (20 cm^3) and treated with an excess of NaCN (about 1/1.5). The colour changed from purple to yellow. The mixture was stirred for 90 min. The solvent was removed under vacuum and dichloromethane was added. The solution was chromatographed on alumina with dichloromethane as eluant. The solvent was removed under vacuum to yield compound V as white crystals. The complex was characterized by elemental analysis and by its IR and mass spectra.

(k) Reaction of complex VIa with AgPF$_6$ · tricarbonyl(1–3:5,6-η-cycloocta-dienylium)iron hexafluorophosphate (I)

A dichloromethane solution of complex VIa (200 mg, in 40 cm^3) was treated with an approximately stoichiometric amount of solid AgPF$_6$. The colour turned from purple to yellow and AgI was precipitated. The mixture was filtered and the filtrate was evaporated to give complex I as a yellow solid. The complex was characterized by elemental analysis and by its IR spectrum.

References

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