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LIGAND SUBSTITUTION AND NUCLEOPHILIC REACTIVITY OF TRICARBONYL(1-5-η-CYCLOOCTADIENYLIUM)IRON COMPLEXES

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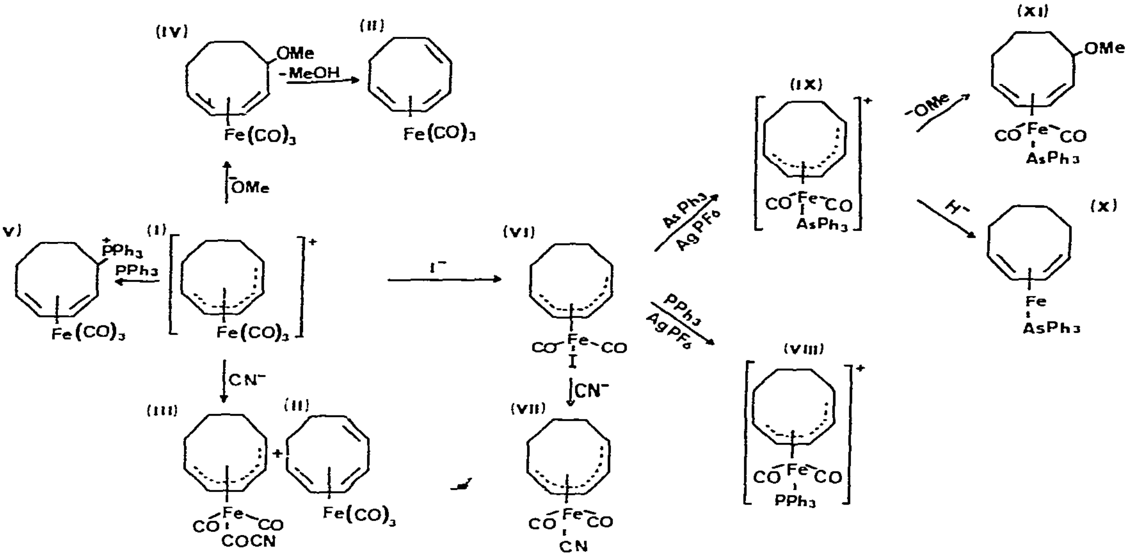
Summary

Nucleophilic attack of CN^- on tricarbonyl(1-5-η-cyclooctadienylium)iron leads to formation of tricarbonyl(cycloocta-1,3,5-triene)iron and dicarbonyl(1-5-η-cyclooctadienyl)carbonitrileiron, and attack of PPh_3 leads to formation of phosphonium ions. Nucleophilic attacks on dicarbonyl(1-5-η-cyclooctadienyl)iodoiron by CN^- gives dicarbonyl(1-5-η-cyclooctadienyl)cyanoiron complex, while that by PPh_3 or $AsPh_3$ gives dicarbonyl(1-5-η-cyclooctadienyl)triphenylphosphineiron hexafluorophosphate or dicarbonyl(1-5-η-cyclooctadienyl)triphenylarsineiron hexafluorophosphate. Treatment of the cationic compound arsine derivative with H^- or OCH_3^- gives the corresponding neutral compounds.

There have been several studies of the synthesis and reactivity of compounds of general formula (diene)$Fe(CO)_3$ [1—14] in which the diene is cyclohexadiene or cycloheptadiene having conjugate double bonds, and of their neutral and cationic derivatives. In these investigations, the emphasis was mainly on the direction of the aromatic character typical of the cyclopentadienyl anion. Fewer studies have dealt with 1,3-cyclooctadiene (1,3-COD) [11—15,21]. We have already reported [21] a scheme for the reaction between the cation (1-5-η-cyclooctadienyl)$Fe(CO)_3^+$ (I), obtained by extraction of hydride ion from (1,3-COD)$Fe(CO)_3$, and the nucleophiles N_3^-, OCH_3^-, and I^-. We have now extended our study to the reaction between the same cation I and the nucleophiles CN^-, PPh_3, and $AsPh_3$, and to that between these nucleophiles and the neutral species dicarbonyl(1-5-η-cyclooctadienyl)iodoiron.

The reactions observed are shown in Scheme 1. The reaction between I and KCN gives two products which were separated by column chromatography.



SCHEME 1

The IR spectrum of compound II, tricarbonyl(cycloocta-1,3,5-triene)iron, in CH_2Cl_2 shows two carbonyl bands at ν = 2040 and 1970 cm^{-1} and a band at ν = 1645 cm^{-1}. Its mass spectrum shows a parent peak at m/e 246 and a fragmentation pattern corresponding to sequential loss of three carbonyls. For this compound there were two possible structures: (bicyclo[4.2.0]octa-2,4-diene)Fe$(CO)_3$ and (cyclo-octa-1,3,5-triene)Fe$(CO)_3$. We consider that it is the triene complex, II, because of the presence of the 1645 cm^{-1} band in the IR spectrum, which Manuel and Stone [22] attribute to the carbon—carbon double bond not coordinated to the metal. Further support for this assignment comes from the report that the cation I readily undergoes deprotonation with bases to yield the cycloocta-1,3,5-triene complex, with no evidence for the regeneration of bicyclooctadiene complex [23].

The IR spectrum of compound III (1-5-η-cyclooctadienyl)carbonitrileiron presents in CH_2Cl_2 shows carbonyl bands at ν = 2040, 1970 cm^{-1}, a ketone band at ν = 1730 cm^{-1}, which we attribute to the COCN group coordinated to iron, and a band at ν = 2230 cm^{-1} arising from the cyano group connected by a σ bond to the carbonyl carbon. The mass spectrum shows a parent peak at m/e 246, and a fragmentation pattern involving loss of three carbonyls. The behaviour is identical to that observed for compound II.

When the reaction between I and KCN was carried on for a longer time, the yield of II (triene complex) increased. This seems to indicate that the triene complex II is formed via a deprotonation induced by the base CN$^-$ during the migration of the cyano group from the carbonyl to the organic entity with loss of one HCN molecule. Such a reaction occurs instantaneously in the mass spectrometer during the vaporization of the product. This mass behaviour is analogous to that exhibited by the product obtained from the reaction of I and Na-OCH_3 in methanol. Product IV, tricarbonyl(η-5-methoxycycloocta-1,3-diene)iron, which was discussed previously [21], gives an IR spectrum (in cyclohexane) with carbonyl bands at $\nu = 2040, 1970\ cm^{-1}$ and a band at $\nu = 1080\ cm^{-1}$, which we attribute to the methoxide bound to the organic nucleus in position 5. Its mass spectrum shows the parent peak at m/e 246 and fragmentation with loss of three carbonyls. In this case a methanol molecule is lost during evaporation as a result of deprotonation by the strong base methoxide ion.

Addition of triphenylphosphine to a solution of I yields compound V which in CH_2Cl_2 gives an IR spectrum with carbonyl bands at $\nu = 2062, 1980\ cm^{-1}$. For this compound, which was characterized only by its IR spectrum, we propose the structure shown as V in Scheme 1, in agreement with the results reported by Lewis et al. [9] for the reaction between phosphine and cations (cyclohexadienyl)- and (cycloheptadienyl)$Fe(CO)_3^+$. We also observed attack of PPh_3 upon the organic nucleus with formation of a phosphonium ion V, as evidenced by the comparison of carbonyl bands higher than those observed in compounds where the phosphine is coordinated to iron [9,11] (this work).

Compound I does not react with triphenylarsine event when a large excess of the latter is used along with long reaction times and high temperatures.

From the reaction between salt I and KI we obtained dicarbonyl(1-5-η-cyclooctadienyl)iodoiron (VI). Its IR spectrum in CH_2Cl_2 shows carbonyl bands at $\nu = 2030, 1990\ cm^{-1}$. The mass spectrum shows a parent peak at m/e 346 and a fragment arising from loss of two carbonyls. Product I thus behaves very similarly to the corresponding cyclohexa- and cyclohepta-derivatives described by Pauson et al. [6].

Treating compound VI with KCN gave dicarbonyl(1-5-η-cyclooctadienyl)-cyanoiron (VII), the IR spectrum (film) of which shows carbonyl bands at $\nu = 2040, 2000\ cm^{-1}$ and a cyano group band at $\nu = 2110\ cm^{-1}$, in line with the π character of the bond of the cyano group coordinated to the iron. Reaction of compound VI with $AgPF_6$ followed by addition of triphenylphosphine or triphenylarisine gives rise to compound VIII of IX. The IR spectrum (in CH_2Cl_2) of VIII shows carbonyl bands at $\nu = 2040, 1970\ cm^{-1}$, and that of IX at $\nu = 2040, 2000\ cm^{-1}$.

Treating compound IX with $NaBH_4$ gave the neutral compound X. Its IR spectrum in cyclohexane shows carbonyl bands at $\nu = 1970, 1910\ cm^{-1}$, and the mass spectrum includes a peak for the parent ion at m/e 526 and a fragmentation pattern consistent with (m/e) $P - (CO + H_2) = 496$; $P - 2\ CO = 470$; $P - (2\ CO + H_2) = 466$; $FeAsPh_3 = 362$; $AsPh_3 = 306$. Treatment of IX with $NaOCH_3$ gave compound XI, which has an IR spectrum in cyclohexane with carbonyl bands at $\nu = 1970, 1910\ cm^{-1}$ and a band at $\nu = 1080\ cm^{-1}$ which is attributed to methoxide ion.

We conclude that the reaction of compound I with CN^- gives results differing from those suggested previously. Lewis et al. showed that the reaction between (1-5-η-cyclooctadienylium)$Fe(CO)_3^+$ and H^- give (1,3-COD)$Fe(CO)_3$ as the sole neutral product, and suggested that the reaction between the dienylic salt I and CN^- gave the 2-cyanodienyl derivative, by analogy with what was observed for similar compounds containing Co^I, Rh^I, and Ir^I [23].

In our experiments, the reaction between I and CN^- shows behaviour similar to that observed for reaction with OCH_3^- [21]; the preferential site for attack of the CN^- is a coordinated carbonyl resulting in a carbonitrile derivative which, unlike the product containing the $COOCH_3$ group formed from methoxide, is stable enough to be isolated. However, after longer times and in solution the dicarbonyl(1-5-η-cyclooctadienyl)carbonitrileiron is eventually transformed into tricarbonyl(cycloocta-1,3,5-triene)iron, while the methoxy derivative gives rise to to tricarbonyl(η-5-methoxycycloocta-1,3-diene)iron, in the same way as was observed for the reactions of analogous compounds of ruthenium such as (dienyl)Ru(CO)$_3^+$ [24].

A different pattern is observed in the reaction between the dienylic salt I and phosphine, for which the site of attack is the organic nucleus, with consequent formation of a phosphonium salt, and in the reaction between compound I and I$^-$ ions, where the site of attack is iron and substitution of an CO group results [21].

On the other hand, the reactions between iodo derivative VI and CN$^-$, PPh$_3$, AsPh$_3$, are very similar to those observed for the analogous compounds containing cyclohexadiene and cycloheptadiene rings.

As far as the neutral compounds IV, X and XI, obtained by direct attack of nucleophiles OCH$_3^-$ and H$^-$ on the organic moiety of the corresponding cationic compounds, are concerned, they were assigned the cycloocta-1,3-diene structure in agreement with the proposal [11] that the sole site for nucleophilic attack is position 5 of the organic nucleus, since in 1,3-cyclooctadiene there is no possibility of attack at position 2 via an organic moiety coordinated through the system 3-5-η, 1 σ, a possibility which exists for the cationic derivatives of cyclohexadiene and cycloheptadiene.

We are at present (a) gathering further mass spectral and NMR data in order to confirm the proposed phosphonium salt structure V, (b) attempting reduction of the cationic compound VIII; (c) studying the mass spectrum of the methoxy derivative XI to ascertain whether in this case, as in the case of the other neutral compounds (III and IV), a peak corresponding to the mass of the triene complex is also present.

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