The Reactions of $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5-C_8H_8R'')]^+$ with Halide Ions: Ring opening of η^5-Bicyclo-octadienyl ($R'' = H$), and Methyl Halide Elimination of η^5-Cyclo-octatrienyl ($R'' = N_2R$, where R = aryl) Complexes

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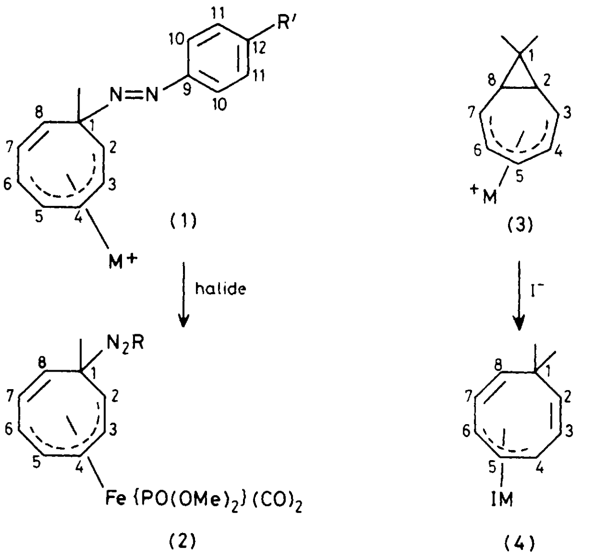
The cyclo-octatrienyl complex $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5-C_8H_8N_2C_6H_4R'-p)]^+$ (1) undergoes methyl halide elimination with halide ions to give the phosphonate $[Fe\{PO(OMe)_2\}(CO)_{2-n}\{P(OMe_3)\}_n(\eta^5-C_8H_8N_2C_6H_4R'-p)]$ (2) ($R' = F$ or NO_2). By contrast, the bicyclo[5.1.0]octadienyl complex $[Fe(CO)_2\{P(OMe)_3\}(\eta^5-C_8H_9)][BF_4]$ (3) undergoes ring opening to give the η^3-cyclo-octatrienyl derivative $[FeI(CO)_2\{P(OMe)_3\}(\eta^3-C_8H_9)]$ (4). The mechanisms of the alkyl halide elimination and ring-opening reactions are discussed.

The ready isolation[1] of arylazocyclo-octatrienyl complexes $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5-C_8H_8N_2C_6H_4R'-p)]X$ (1; $n = 1$ or 2, $R' = F$ or NO_2, $X = BF_4$ or BPh_4), *via* the reaction of $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene) with arenediazonium ions, led us to explore the possible synthesis of disubstituted cyclo-octatrienes by nucleophilic addition. We now report that (1) and halide ions give $[Fe\{PO(OMe)_2\}(CO)_{2-n}\{P(OMe)_3\}_n(\eta^5-C_8H_8N_2C_6H_4R'-p)]$ (2; $n = 0$ or 1, $R' = NO_2$ or F) in a reaction similar to the Michaelis–Arbusov elimination. By contrast, the related bicyclo[5.1.0]octadienyl compound $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5-C_8H_9)][BF_4]$ (3; $n = 0$ or 1) undergoes ring opening with I^- to give $[FeI(CO)_{3-n}\{P(OMe)_3\}_n(\eta^3-C_8H_9)]$ (4; $n = 0$ or 1) (see Scheme 1).



Scheme 1. $M = Fe(CO)_2\{P(OMe)_3\}$, R = aryl, $R' = F$ or NO_2. The atom numbering shown differs from that used in the systematic names for the compounds (see Experimental section)

Results and Discussion

Reaction of $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5-C_8H_8N_2C_6H_4R'-p)]X$ (1; $n = 1$, $R' = NO_2$, $X = BF_4$) with $[PMePh_3]I$ in CH_2Cl_2 gives, after toluene–hexane crystallisation, good yields of $[Fe\{PO(OMe)_2\}(CO)_{2-n}\{P(OMe)_3\}_n(\eta^5-C_8H_8N_2C_6H_4R'-p)]$ (2; $n = 0$, $R' = NO_2$). The *p*-fluoro-analogue (2- $n = 0$, $R' = F$) was similarly prepared from $[Fe(CO)_2\{P(OMe)_3\}(\eta^5-C_8H_8N_2C_6H_4F-p)][PF_6]$ and $[N(PPh_3)_2]Cl$, and low yields of (2; $n = 1$, $R' = F$) were isolated from (1; $n = 2$, $R' = F$, $X = PF_6$) and chloride ions.

The yellow complexes (2) were characterised by elemental analysis, i.r. spectroscopy (Table 1), and, for ($n = 1$, $R' = F$), by a parent ion in the mass spectrum, $m/e = 448$. The presence of the dimethyl phosphonate ligand was verified by ^{31}P and ^1H n.m.r. spectroscopy. For (2; $n = 0$, $R' = NO_2$) the ^{31}P spectrum shows a single resonance at 21.0 p.p.m. (downfield from H_3PO_4, in $[^2H_6]$acetone) in sharp contrast to iron-co-ordinated $P(OMe)_3$ which commonly absorbs in the range 140—190 p.p.m. The 200-MHz ^1H n.m.r. spectrum (Table 2) shows two phosphonate methyl peaks each split by ^{31}P coupling. The inequivalence of the phosphorus-bound methoxy-groups is due to the asymmetric, substituted η^5-cyclo-octatrienyl ligand the presence of which was determined by $^1H-\{^1H\}$ decoupling experiments despite the near coincidence of peaks due to the free double bond and to the dienyl protons.

The reactions of the bicyclo[5.1.0]octadienyl complexes $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5-C_8H_9)][BF_4]$ (3; $n = 0$ or 1) with halide ions contrast with those of (1). Complex (3; $n = 1$) is readily prepared in good yield from $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-cot})]$ and HBF_4 in diethyl ether; the ^1H n.m.r. spectrum of the orange-yellow complex is very similar to that of the tricarbonyl (3; $n = 0$).[2] On reaction with $[PMePh_3]I$ in CH_2Cl_2 good yields of the black, crystalline cyclo-octatrienyl complex $[FeI(CO)_{3-n}\{P(OMe)_3\}_n(\eta^3-C_8H_9)]$ (4; $n = 1$) are isolated. The identity of the product readily follows from a comparison of the ^1H n.m.r. spectrum (Table 2) with that of (4; $n = 0$).[3] No evidence for phosphonate-complex formation, either during the reaction or on heating to 69 °C in n-hexane, was found. However, reconversion into the η^5-cyclo-octatrienyl salt (3; $n = 1$) was effected, albeit in low yield, on reaction with $[CPh_3][BF_4]$.

It has been suggested previously,[3] on the basis of deuterium-labelling experiments, that the mechanism of the ring-opening reaction between $[Fe(CO)_3(\eta^5-C_8H_9)]^+$ and I^- is as shown in Scheme 2. Although this mechanism may well apply to the reaction between (3; $n = 0$) and pyridine,[3] we believe it to be less likely for that with iodide ion and propose the alternative mechanism shown in Scheme 3. Evidence for initial attack of iodide ion at the metal is provided by a kinetic study of the reaction with $[M(CO)_3(\eta-C_7H_7)]^+$ (M = Mo or W).[4] In addition, the mechanism in Scheme 3 does not require the hydrogen (or iodine) migration implicit in the ring-opening step of Scheme 2.

The reaction of (1) with halide ions is also likely to occur

Table 1. I.r. and analytical data

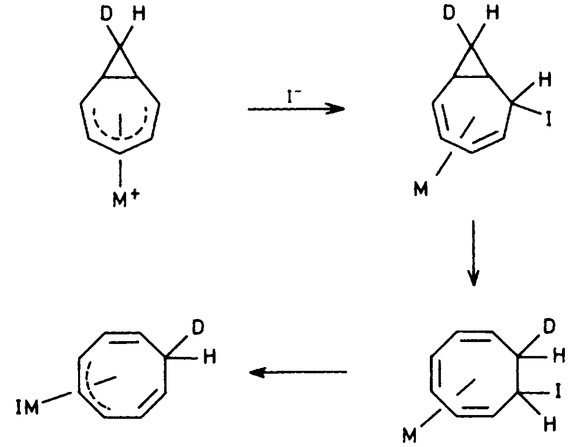
Compound	$\tilde{\nu}$ (CO) [a]/cm^{-1}	Analysis [b]/% C	H	N
$[Fe\{PO(OMe)_2\}(CO)_2(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)]$	2 049, 2 003	45.8 (45.5)	3.8 (3.8)	8.4 (8.8)
$[Fe\{PO(OMe)_2\}(CO)_2(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)]$	2 037, 1 994	46.8 (48.3)	4.0 (4.0)	6.2 (6.3)
$[Fe\{PO(OMe)_2\}(CO)\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)]$	1 976	44.1 (44.2)	5.0 (5.0)	5.1 (5.1)
$[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_9)][BF_4]$	2 053, 2 001	36.2 (36.4)	4.6 (4.2)	—
$[FeI(CO)_2\{P(OMe)_3\}(\eta^3\text{-}C_8H_9)]$	2 021, 1 973	34.0 (33.3)	4.3 (3.9)	—

[a] In CH_2Cl_2. [b] Calculated values are given in parentheses.

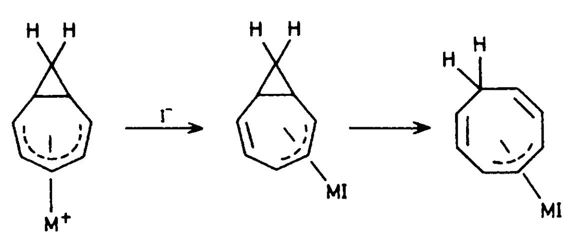
Table 2. Proton n.m.r. data [a]

Compound	^1H (δ) [b]
(2) $[Fe\{PO(OMe)_2\}(CO)_2(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)]$ [c,d]	3.62 [6 H, dd, J(PH) 11, $PO(OMe)_2$], 4.33 (2 H, m, H^2, H^8) 4.59 (1 H, m, H^6), 5.25 (2 H, m, H^5, H^7), 5.56 (1 H, m, H^3), 6.24 (1 H, s, H^1), 6.45 (1 H, t, H^4), 7.02 [2 H, d, $J(H^{11}H^{10})$ 9, H^{11}], 8.15 [2 H, d, $J(H^{10}H^{11})$ 9, H^{10}]
(3) $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_9)][BF_4]$ [c]	1.40 (2 H, m, H^1, $H^{1'}$), 2.55 (2 H, m, H^2, H^8), 3.80 [9 H, d, J(PH) 11, $P(OMe)_3$], 5.40 (4 H, m, H^3, H^4, H^6, H^7), 7.85 (1 H, m, H^5)
(4) $[FeI(CO)_2\{P(OMe)_3\}(\eta^3\text{-}C_8H_9)]$ [d,e]	2.56 (1 H, m, H^1), 3.05 (1 H, m, $H^{1'}$), 3.84 [9 H, d, J(PH) 11, $P(OMe)_3$], 5.00 (1 H, m, H^5), 5.10 (2 H, m, H^4, H^6), 5.60 (2 H, m, H^2, H^8), 6.18 (2 H, m, H^3, H^7)

[a] Numbering as in Scheme 1, 100-MHz spectrum unless stated otherwise. [b] Downfield from $SiMe_4$, J values in Hz. [c] In $CDCl_3$. [d] 200-MHz spectrum. [e] In $[^2H_6]$acetone.



Scheme 2. $M = Fe(CO)_3$



Scheme 3. $M = Fe(CO)_{3-n}\{P(OMe)_3\}_n$, $n = 0$ or 1

via initial metal attack, to give $[FeI(CO)_2\{P(OMe)_3\}(\eta^3\text{-}C_8H_8N_2C_6H_4R'\text{-}p)]$ related to (4); loss of methyl halide then yields (2) in a reaction reminiscent of Michaelis–Arbusov elimination.[5]

The question then remains, why does (1) but not (3) undergo alkyl halide elimination? The carbonyl spectrum of $[FeI(CO)_2\{P(OMe)_3\}(\eta^3\text{-allyl})]$ [$\tilde{\nu}$(CO)(cyclohexane) = 2 026 and 1 983 cm^{-1}] is[6] virtually identical to that of (4) (Table 1) showing the two species to differ only by the allyl substituents. The structure of (4) is, therefore, likely to be similar to that of $[FeI(CO)_2(PPh_3)(\eta^3\text{-allyl})]$ *X*-ray studies[7] on which revealed a distorted capped-octahedral geometry for the metal atom, with the iodide and phosphine ligands in mutually *trans* positions. Steric factors are, therefore, unlikely to control the formation of (2) rather than an analogue of (4).

The electron-withdrawing substituent $N_2C_6H_4NO_2\text{-}p$ stabilises the η^5-cyclo-octatrienyl structure for (1) over the bicyclo[5.1.0]octadienyl ring system for (3). It is possible then that a similar stabilisation of η^5- over η^3-bonding for (2) facilitates alkyl halide elimination.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Where appropriate, reactions were monitored by i.r. spectroscopy; unless stated the complexes are air-stable in the solid state dissolving in polar solvents such as CH_2Cl_2 and acetone to give moderately air-sensitive solutions. The complexes $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-cot})]$[8] and $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5\text{-}C_8H_8N_2C_6H_4R'\text{-}p)]X$[1] ($n = 1$ or 2, $R' = F$ or NO_2, $X = BF_4$ or BPh_4) were prepared by published methods. Infrared spectra were recorded on a Perkin-Elmer PE 457 spectrophotometer and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were obtained on Varian Associates HA 100 or JEOL PS100 or FX200 spectrometers, and calibrated against $SiMe_4$ as internal reference. Phosphorus-31 n.m.r. spectra were recorded on a JEOL FX90Q instrument and calibrated against H_3PO_4 as external reference. Mass spectra were measured on an A.E.I. MS902 instrument. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Dicarbonyl(dimethyl phosphonato)(1—5-η-8-p-*nitrophenylazocyclo-octatrienyl)iron*, $[\mathrm{Fe\{PO(OMe)_2\}(CO)_2(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}}p)]$.—To a solution of $[\mathrm{Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}}p)][\mathrm{BF_4}]$ (0.158 g, 0.26 mmol) in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$) was added $[\mathrm{PMePh_3}]\mathrm{I}$ (0.10 g, 0.25 mmol). After 18 h the orange solution was evaporated to dryness under vacuum and the residue extracted with toluene (50 $\mathrm{cm^3}$). Addition of hexane gave a yellow precipitate which was recrystallised from benzene–heptane to give the complex as a bright yellow *powder*, yield 0.07 g (58%). It is soluble in benzene giving air-stable yellow solutions.

A similar procedure gave $[\mathrm{Fe\{PO(OMe)_2\}(CO)_2(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}}p)]$ from $[\mathrm{Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}}p)][\mathrm{PF_6}]$ and $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ in $\mathrm{CH_2Cl_2}$. Under these conditions the reaction was complete in 30 min at 20 °C, yield 52%.

Carbonyl(dimethyl phosphonato)(1—5-η-8-p-*fluorophenylazocyclo-octatrienyl)(trimethyl phosphite)iron*, $[\mathrm{Fe\{PO(OMe)_2\}(CO)\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}}p)]$.—To a brown solution of $[\mathrm{Fe(CO)\{P(OMe)_3\}_2(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}}p)][\mathrm{PF_6}]$ (0.36 g, 0.51 mmol) in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$) was added $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}\cdot 0.5\mathrm{CH_2Cl_2}$ (0.322 g, 0.53 mmol), giving an immediate red colour. After refluxing for 3 d the solution had darkened slightly. The solvent was then removed under vacuum and the dark red residue extracted into diethyl ether (100 $\mathrm{cm^3}$). Addition of hexane gave an orange precipitate which was then dissolved in a minimum of $\mathrm{CH_2Cl_2}$ and chromatographed on an alumina–hexane column. Elution with diethyl ether, then acetone, gave four bands, yellow, yellow, purple, and yellow, respectively, all uncharacterised. Elution with methanol–acetone (1 : 3) gave the major product as an orange band. After removal of the solvent under vacuum the orange product was recrystallised from diethyl ether–hexane to give the complex as a yellow *solid*, yield 0.01 g (5%).

(2—6-η-*Bicyclo*[5.1.0]*octadienyl) dicarbonyl (trimethyl phosphite)iron Tetrafluoroborate*, $[\mathrm{Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_9)}][\mathrm{BF_4}]$.—To a solution of $[\mathrm{Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-cot})}]$ (0.243 g, 0.715 mmol) in diethyl ether (60 $\mathrm{cm^3}$) was added a solution of 40% $\mathrm{HBF_4}$ (aqueous) (0.5 $\mathrm{cm^3}$, 4.0 mmol). After 1 h the liquors were decanted, leaving the complex as a yellow-orange *powder*, yield 0.198 g (65%). It is soluble in polar solvents giving yellow air-stable solutions.

Dicarbonyl(1—3-η-*cyclo-octatrienyl)iodo(trimethyl phosphite)iron*, $[\mathrm{FeI(CO)_2\{P(OMe)_3\}(\eta^3\text{-}C_8H_9)}]$.—To a yellow solution of $[\mathrm{Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_9)}][\mathrm{BF_4}]$ (0.198 g, 0.46 mmol) in $\mathrm{CH_2Cl_2}$ (60 $\mathrm{cm^3}$) was added $[\mathrm{PMePh_3}]\mathrm{I}$ (0.189 g, 0.47 mmol). After 10 min the red solution was evaporated to dryness and the residue extracted with toluene (50 $\mathrm{cm^3}$). Evaporation to dryness and recrystallisation from hexane (40 $\mathrm{cm^3}$) at −78 °C gave black crystals of the *product*, yield 0.116 g (54%). The complex is moderately soluble in hexane.

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